Abstract Book

CMD-24

24th General Conference of the Condensed Matter Division of the European Physical Society

held jointly with

ECOSS-29
29th European
Conference
on Surface Science

CMMP-12
Condensed Matter
and Materials Physics
Conference

ECSCD-11
11th European Conference
on Surface Crystallography
and Dynamics

3–5 September 2012
Edinburgh International Conference Centre,
Edinburgh, Scotland, UK

www.cmd-24.org

IOP Institute of Physics   EPS

FORTHCOMING INSTITUTE CONFERENCES
AUGUST 2012 – JULY 2014

2012

10–11 September
Magnetic Tight Binding
Institute of Physics, London, UK
Organised by the IOP Computational Physics Group

20–21 September
A Celebration of the 50th Anniversary of the Diode Laser
University of Warwick, Coventry, UK
Organised by the IOP Quantum Electronics and Photonics and Semiconductor Physics Groups

8 - 9 November 2012
Complex Molecules at Surfaces II (CMAS-2)
Institute of Physics, London, UK
Organised by the IOP Thin Film and Surfaces Group

26–27 November
Biomolecular Thermodynamics
Institute of Physics, London, UK
Organised by the IOP Biological Physics Group

17–18 December
Topical Research Meetings on Physics: Quantum technologies: taking concepts through to implementations
Institute of Physics, London, UK

2013

16 - 18 January
AFPAC 2013 - 12th Anglo-French Physical Acoustics Conference
Villa Clythia, Fréjus, France
Organised by the IOP Physical Acoustics Group

17–18 January
Ferroelectrics UK 2013
University of Sheffield, Sheffield, UK
Organised by the IOP Materials and Characterisation Group

6–8 March
Adiabatic Quantum Computation 2013
Institute of Physics, London, UK
Organised by the IOP Quantum Optics, Quantum Information, Quantum Control Group

25–28 March
The 40th IOP Annual Conference on Plasma Physics
University of York, York, UK
Organised by the IOP Plasma Physics Group

25–28 March
Interdisciplinary Surface Science Conference (ISSC-19)
East Midlands Conference Centre, Nottingham, UK
Organised by the IOP Thin Films and Surfaces Group

7–10 April
IOP Nuclear Physics Group Conference 2013
University of York, York, UK
Organised by the IOP Nuclear Physics Group

10–12 April
Dielectrics 2013
University of Reading, Reading, UK
Organised by the IOP Dielectrics Group

24–25 June
Physics of Emergent Behaviour: from Molecules to Individuals
The Grand Hotel, Brighton, UK
Organised by the IOP Biological Physics Group

8–12 July
International Conference on Neutron Scattering (ICNS2013)
Edinburgh International Conference Centre, Edinburgh, UK

3–6 September
Electron Microscopy and Analysis Group Conference 2013 (EMAG)
University of York, York, UK
Organised by the IOP Electron Microscopy and Analysis Group

4–6 September
PR'13: International Conference on Photorefractive Effects, Materials and Devices
The Winchester Hotel, Winchester, UK
Organised by the IOP Optical Group and the IOP Quantum Electronics and Photonics Group

9–11 September
Physical Aspects of Polymer Science
University of Sheffield, Sheffield, UK
Organised by the IOP Polymer Physics Group

16–18 September
Sensors & their Applications XVII
Rixos Libertas, Dubrovnik, Croatia
Organised by the IOP Instrument Science and Technology Group

16–19 September
EuroDisplay 2013 (33rd International Display Research Conference)
Imperial College London, London, UK
Organised by the IOP Optical Group and Society for Information Display

18–20 November
High-speed imaging for dynamic testing of materials and structures – 21st DYMAT Technical Meeting
Institute of Physics, London, UK
Organised jointly by the IOP Applied Physics and Technology Division and DYMAT Association

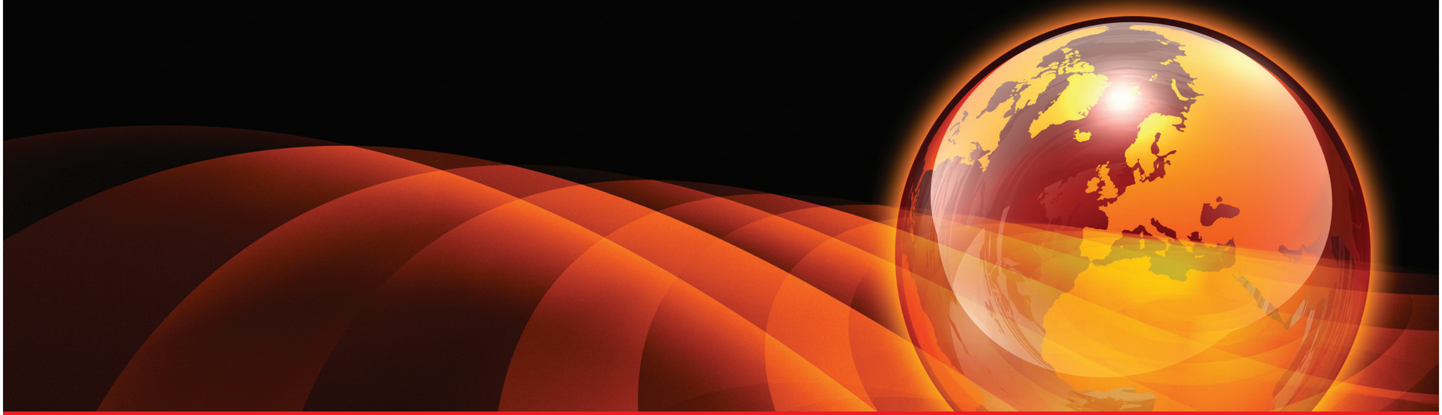
2014

21–25 July
ICSOS'11: 11th International Conference on the Structure of Surfaces
University of Warwick, Coventry, UK
Organised by the IOP Thin Films and Surfaces Group

See **www.iop.org/conferences** for a full list of IOP one-day meetings.

The conferences department provides a professional event-management service to the IOP Groups and Divisions and supports bids to bring international physics events to the UK.

Institute of Physics,
76 Portland Place, London W1B 1NT, UK
Tel +44 (0)20 7470 4800
E-mail **conferences@iop.org**
Web **www.iop.org/conferences**



IOP Institute of Physics

Contents page

Dear Delegates

On behalf of the organising committees of CMD-24, ECOSS-29, ECSCD-11, and CMMP-12 we welcome you to Edinburgh, Scotland's capital city, a UNESCO World Heritage Site and home to the world's oldest and largest festival of the arts. Welcome too to what is the largest physics conference to be held in the UK in 2012. While on the surface our conference may appear less important than other events that have filled the UK calendar this year, the Diamond Jubilee, the London Olympics and Para-Olympics and the Edinburgh Festival itself, it is important to us that you are here and enjoy the scientific programme that the organising committees have assembled for you. Enjoy too, the hospitality of the Scots!

In view of the ever increasing problem of fitting international conferences into the busy summer season without major clashes a decision was made by the EPS about three years ago to try a new format whereby a number of related European conferences would be held at the same place at the same time. This year's event combines the 24th Conference of the EPS Condensed Matter Division (CMD-24), the 29th European Conference on Surface Science (ECOSS-29), the 11th European Conference on Surface Crystallography and Dynamics (ECSCD-11), and the 2012 UK Condensed Matter and Materials Physics Conference (CMMP-12). We hope that the combination will be even more attractive than each individual conference to both delegates, who can attend sessions in several related areas, and exhibitors, who reach a bigger audience. In addition the organising committees have made every effort to combine sessions whenever possible and create platforms for interaction between surface scientists and condensed matter physicists in emerging fields which could benefit from more collaboration.

At this point we would like to thank all members of the scientific and local organising committees for their input and commitment and all sponsors and exhibitors for their financial support without which the conference would not have been possible. A special "thank you" goes also to the IoP conference team for their professional management of this event.

Of course, it is you, the delegates, who ultimately will make this conference a success. We thank you for coming in such large numbers and invite you to make ample use of the space for discussing both novel and established topics of condensed matter physics and surface science. We look forward to a lively conference, where high-quality science will be presented and ideas for exciting new work will be developed.

We hope you enjoy the event in all its aspects, formal and informal and look forward to meeting you in person over a drink at one of the social events or in one of the many nearby pubs.

Again, a warm welcome to Edinburgh!

Georg Held, Martin McCoustra, Eoin O'Reilly, Karsten Reuter, Peter Weightman

Sunday 2 September

18:00	**Whisky welcome reception and registration** *Cromdale Hall*
20:00	**Close**

Monday 3 September

08:00	**Registration and refreshments** *Strathblane Hall and Cromdale Hall*								
09:00	**Welcome** *Pentland Suite*								
09:20	**(plenary) Polymer photovoltaics – sophisticated nanostructures that make themselves** R Jones, The University of Sheffield, UK *Pentland Suite*								
10:20	**Organic Layers and Polymers 1** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 3** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 1** *Fintry Auditorium* *Level 3*	**Magnetism 1** *Carrick Suite* *Level 1*	**Low Temperature Physics 1** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 1** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 1** *Tinto* *Level 0*	**Nanostructures 1** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 1** *Kilsyth* *Level 0*
11:20	**Refreshment break** *Cromdale Hall*								
11:40	**Organic Layers and Polymers 1 (continued)** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 3 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 1 (continued)** *Fintry Auditorium* *Level 3*	**Magnetism 1 (continued)** *Carrick Suite* *Level 1*	**Low Temperature Physics 1 (continued)** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 1 (continued)** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 1 (continued)** *Tinto* *Level 0*	**Nanostructures 1 (continued)** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 1 (continued)** *Kilsyth* *Level 0*
13:20	**Lunchtime break and exhibition** *Cromdale Hall*								
13:20	**Product based talks** *Lomand Suite*								
14:20	**Organic Layers and Polymers 2** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 4** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 2** *Fintry Auditorium* *Level 3*	**Magnetism 2** *Carrick Suite* *Level 1*	**Low Temperature Physics 2** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 2** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 2** *Tinto* *Level 0*	**Nanostructures 2** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 2** *Kilsyth* *Level 0*
16:00	**Refreshment break** *Cromdale Hall*								
16:20	**Organic Layers and Polymers 2 (continued)** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 4 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 2 (continued)** *Fintry Auditorium* *Level 3*	**Magnetism 2 (continued)** *Carrick Suite* *Level 1*	**Low Temperature Physics 2 (continued)** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 2 (continued)** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 2 (continued)** *Tinto* *Level 0*	**Nanostructures 2 (continued)** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 2 (continued)** *Kilsyth* *Level 0*
18:00	**Poster session A (CMD/CMMP)** *Cromdale Hall*								
20:00	**Close**								

Tuesday 4 September

08:00	**Registration and refreshments** *Strathblane Hall and Cromdale Hall*								
09:00	**(plenary) Epitaxial cobalt-oxide films – The importance of surface crystallography** K Heinz, University Erlangen-Nuremberg, Germany *Pentland Suite*								
10:00	**Organic Layers and Polymers 3** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 1** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 3** *Fintry Auditorium* *Level 3*	**Magnetism 3** *Carrick Suite* *Level 1*	**Metals, Alloys and their Surfaces 1** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 3** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 3** *Tinto* *Level 0*	**Nanostructures 3** *Moorfoot* *Level 0*	**Surface Dynamics 1** *Kilsyth* *Level 0*
11.20	**Refreshment break** *Cromdale Hall*								
11:40	**Organic Layers and Polymers 3 (continued)** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 1 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 3 (continued)** *Fintry Auditorium* *Level 3*	**Magnetism 3 (continued)** *Carrick Suite* *Level 1*	**Metals, Alloys and their Surfaces 1 (continued)** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 3 (continued)** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 3 (continued)** *Tinto* *Level 0*	**Nanostructures 3 (continued)** *Moorfoot* *Level 0*	**Surface Dynamics 1 (continued)** *Kilsyth* *Level 0*
13:20	**Lunchtime break and exhibition** *Cromdale Hall*								
14:40	**Organic Layers and Polymers 4** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 2** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 4** *Fintry Auditorium* *Level 3*	**Magnetism 4** *Carrick Suite* *Level 1*	**Metals, Alloys and their Surfaces 2** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 4** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 4** *Tinto* *Level 0*	**Nanostructures 4** *Moorfoot* *Level 0*	**Surface Dynamics 2** *Kilsyth* *Level 0*
16:20	**Refreshment break** *Cromdale Hall*								
16:40	**Organic Layers and Polymers 4 (continued)** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 2 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 4 (continued)** *Fintry Auditorium* *Level 3*	**Magnetism 4 (continued)** *Carrick Suite* *Level 1*	**Metals, Alloys and their Surfaces 2 (continued)** *Harris Suite* *Level 1*	**Electronic Structure and Topological Insulators 4 (continued)** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 4 (continued)** *Tinto* *Level 0*	**Nanostructures 4 (continued)** *Moorfoot* *Level 0*	**Surface Dynamics 2 (continued)** *Kilsyth* *Level 0*
18:20	**Poster session B (CMD/CMMP)** *Cromdale Hall*								
20:00	**Dinner ECOSS/ECSCD (pre-booked only)** *Dynamic Earth*								

Wednesday 5 September

08:00	**Registration and refreshments** *Strathblane Hall and Cromdale Hall*								
09:00	**(plenary) Controlling atomic- and molecular-scale electrochemical reactions at designated positions** M Aono, International Center for Materials Nanoarchitectonics, Japan *Pentland Suite*								
10:00	**Organic Layers and Polymers 8** *Sidlaw Auditorium* *Level 3*	**Theory and Modelling 1** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 5** *Fintry Auditorium* *Level 3*	**Magnetism 5** *Carrick Suite* *Level 1*	**Neutron Diffraction 1** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 1** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 5** *Tinto* *Level 0*	**ECOSS Student Prize Session** *Moorfoot* *Level 0*	**ECOSS Student Prize Session** *Kilsyth* *Level 0*
11.20	**Refreshment break** *Cromdale Hall*								
11:40	**Organic Layers and Polymers 8 (continued)** *Sidlaw Auditorium* *Level 3*	**Theory and Modelling 1 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 5 (continued)** *Fintry Auditorium* *Level 3*	**Magnetism 5 (continued)** *Carrick Suite* *Level 1*	**Neutron Diffraction 1 (continued)** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 1 (continued)** *Ochil Suite* *Level 1*	**Semiconductors and their Surfaces 5 (continued)** *Tinto* *Level 0*	**ECOSS Student Prize Session (continued)** *Moorfoot* *Level 0*	**ECOSS Student Prize Session (continued)** *Kilsyth* *Level 0*
13:20	**Lunchtime break and exhibition** *Cromdale Hall*								
14:20	**(plenary) Research in the energy industry** E Williams, BP, UK *Pentland Suite*								
15:20	**(plenary) Berry phases and curvatures in computational electronic structure theory** D Vanderbilt, Rutgers University, USA *Pentland Suite*								
16:20	**Refreshment break** *Cromdale Hall*								
16:40	**EPS Europhysics prize and lecture** *Pentland Suite*								
17:40	**Mott lecture** **Towards understanding high-temperature superconductivity** A S Alexandrov, Loughborough University, UK *Pentland Suite*								
18:20	**Poster session C (ECOSS/ECSCD)** *Cromdale Hall*								
20:00	**Close**								

Thursday 6 September

08:00	**Registration and refreshments** *Strathblane Hall and Cromdale Hall*								
09:00	**(plenary) Transient electronic structure and ultrafast dynamics of solids** M Wolf, Fritz-Haber-Institute of the Max-Planck-Society, Germany *Pentland Suite*								
10:00	**Organic Layers and Polymers 6** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 6** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 6** *Fintry Auditorium* *Level 3*	**Magnetism 6** *Carrick Suite* *Level 1*	**Low Temperature Physics 3** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 2** *Ochil Suite* *Level 1*	**Surface Structure 1** *Tinto* *Level 0*	**Theory and Modelling 2** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 3** *Kilsyth* *Level 0*
11:20	**Refreshment break** *Cromdale Hall*								
11:40	**Organic Layers and Polymers 6 (continued)** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 6 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 6 (continued)** *Fintry Auditorium* *Level 3*	**Magnetism 6 (continued)** *Carrick Suite* *Level 1*	**Low Temperature Physics 3 (continued)** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 2 (continued)** *Ochil Suite* *Level 1*	**Surface Structure 1 (continued)** *Tinto* *Level 0*	**Theory and Modelling 2 (continued)** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 3 (continued)** *Kilsyth* *Level 0*
13:20	**Lunchtime break** *Cromdale Hall*								
14:40	**Organic Layers and Polymers 7** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 5** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 7** *Fintry Auditorium* *Level 3*	**Neutron Diffraction 2** *Carrick Suite* *Level 1*	**Low Temperature Physics 4** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 3** *Ochil Suite* *Level 1*	**Surface Structure 2** *Tinto* *Level 0*	**Nanostructures 5** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 4** *Kilsyth* *Level 0*
16:20	**Refreshment break** *Cromdale Hall*								
16:40	**Organic Layers and Polymers 7 (continued)** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 5 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 7 (continued)** *Fintry Auditorium* *Level 3*	**Neutron Diffraction 2 (continued)** *Carrick Suite* *Level 1*	**Low Temperature Physics 4 (continued)** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 3 (continued)** *Ochil Suite* *Level 1*	**Surface Structure 2 (continued)** *Tinto* *Level 0*	**Nanostructures 5 (continued)** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 4 (continued)** *Kilsyth* *Level 0*
18:40	**Poster session D (ECOSS/ECSCD)** *Cromdale Hall*								
20:00	**Dinner CMD/CMMP (pre-booked only)** *Dynamic Earth*								

Friday 7 September

08:00	**Registration and refreshments** *Strathblane Hall and Cromdale Hall*								
09:00	**(plenary) Semiconductor nanowires for optoelectronic and energy applications** L Samuelson, Lund University, Sweden *Pentland Suite*								
10:00	**Organic Layers and Polymers 5** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 7** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 8** *Fintry Auditorium* *Level 3*	**Organic Layers and Polymers 9** *Carrick Suite* *Level 1*	**Low Temperature Physics 5** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 4** *Ochil Suite* *Level 1*	**Surface Dynamics 3** *Tinto* *Level 0*	**Theory and Modelling 3** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 5** *Kilsyth* *Level 0*
11.20	**Refreshment break** *Cromdale Hall*								
11:40	**Organic Layers and Polymers 5 (continued)** *Sidlaw Auditorium* *Level 3*	**Carbon, Graphene 7 (continued)** *Pentland Auditorium* *Level 3*	**Reactions on Surfaces 8 (continued)** *Fintry Auditorium* *Level 3*	**Organic Layers and Polymers 9 (continued)** *Carrick Suite* *Level 1*	**Low Temperature Physics 5 (continued)** *Harris Suite* *Level 1*	**Liquids and Liquid Interfaces 4 (continued)** *Ochil Suite* *Level 1*	**Surface Dynamics 3 (continued)** *Tinto* *Level 0*	**Theory and Modelling 3 (continued)** *Moorfoot* *Level 0*	**Oxides and Oxide Surfaces 5 (continued)** *Kilsyth* *Level 0*
13:00	**(plenary) The quantum plasticity of helium crystals** S Balibar, Ecole Normale Supérieure Paris, France *Pentland Suite*								
14:00	**Close**								

Poster programme

Poster session A and B (CMD/CMMP)
Monday 3 September and Tuesday 4 September

Carbon including nanotubes, graphene, diamonds

P1.001 Graphene islands on Ni(111) surface: a first principle investigation
M Peressi, University of Trieste, Italy

P1.002 Quantum oscillations due to structural disorder in graphite
B Camargo, Universidade Estadual de Campinas, Brazil

P1.003 Molecular rotation and the formation of C_{60} polymers under high pressure
B Sundqvist, Umea University, Sweden

P1.004 Detailed studies of Si-graphene/SiC(0001)
C Virojanadara, Linkoping University, Sweden

P1.005 Improved interfacial bonding of multi-walled carbon nanotubes by plasma treatment
J Du Plessis, RMIT University, Australia

P1.006 Scalable, UHV-based growth of high-quality monolayer graphene
D van Baarle, Leiden University, The Netherlands

P1.007 Sensitive detection of multivalent ions via DNA bridge
T Ignatova, Lehigh University, USA

P1.008 Signature of hot electrons in the quantum corrections to the conductivity of graphene
S Hornett, University of Exeter, UK

P1.009 Intercalation of transition metals into stacked benzene rings: A model study of the intercalation of transition metals into bi-layered graphene
I-S Youn, Pohang University of Science and Technology, South Korea

P1.010 Second harmonic generation from vertically aligned CNTs on alumina films
S Okawara, Yokohama National University, Japan

P1.011 The effect of different scattering mechanisms on the 1/f resistance noise in graphene
D Horsell, University of Exeter, UK

P1.012 Effects of toluene doping on electrical conduction in graphene
D Horsell, University of Exeter, UK

P1.013 Spin decoherence by magnetic-like defects in graphene
D Horsell, University of Exeter, UK

Electrochemistry at the atomic molecular scale

P1.014 Peculiarities of obtaining of ZnCdS nanolayers by electochemical deposition for solar cells
M Jafarov, Baku State University, Azerbaijan

P1.015 In-situ SXRD measurement of PtZn electrochemical alloying
J Drnec, ESRF, France

Energy conversion: heat dissapation, photovoltaics, etc.

P1.016 Microstructural and optical properties of Cu-Ni deposits for flat solar collector panels
Ł Skowroński, University of Technology and Life Sciences, Poland

P1.017 Nanopillared SnS thin layers for solar cells and secondary batteries
E Outkina, Belarusian State University of Informatics and Radioelectronics, Belarus

P1.018 Experimental QSSPC curves modelling to study the phosphorus diffusion gettering in HEM multicrystalline Silicon passivated by Iodine-methanol solution
N Khelifati, Silicon Technology Developement Unit, Algeria

Liquids

P1.019 Crystallization and glass transition in a supercooled ionic liquid
M Ribeiro, Universidade de São Paulo, Brazil

P1.020 Magneto-structural properties of lithium-phosphate glasses doped with iron ions
C Andronache, Technical University of Cluj-Napoca, Romania

P1.021 Dynamic scaling for supercooled liquids
F Akira, University of Tokyo, Japan

P1.022 How liquid is a liquid metal?
F Demmel, The Science and Technology Faculties Council (STFC), UK

P1.023 Osmosis in a minimal model system: a molecular dynamics simulation study
T Lion, The University of Edinburgh, UK

P1.024 Observation of crossover from ballistic to diffusion regime for excimer molecules in superfluid ^{4}He
D Zmeev, Lancaster University, UK

P1.025 Computation of the structural properties of liquid metals
R A Raheem, Federal University of Technology, Nigeria

P1.026 Capillary rise in rectangular microchannels with patterned walls
H Javed, Nottingham Trent University, UK

P1.027 The superfluid helium-3 AB interface probed by quartz tuning forks
R Haley, Lancaster University, UK

P1.028 Anomalous damping of a low frequency vibrating wire in superfluid helium-3-B due to vortex shielding
R Schanen, Lancaster University, UK

Low temperature/superconductivity

P1.029 Integrated superconducting NbSi nanowire devices for a quantum phase-slip current standard
J Fenton, University College London, UK

P1.030 Device to measure current-voltage curves in thin-films superconductors down to microsecond range: First applications to $Y_1Ba_2Cu_3O_{7-d}$ Microbridges
F Vidal, Universidade de Santiago de Compostela, Spain

P1.031 Phase diffusion in intrinsic Josephson junctions
P Warburton, University College London, UK

P1.032 Stencil lithography for top-down fabrication of sub-20nm superconducting nanowires
N G N Constantino, University College London, UK

P1.033 Fabrication of chromium oxide resistors and their use in a quantum phase-slip circuit
C R Nash, University College London, UK

P1.034 Simultaneous measurements of the thermal conductivity and response to torsional oscillation of solid ^{4}He
M Brazhnikov, The University of Manchester, UK

P1.035 Study of excimer molecules in superfluid ^{4}He at T
D Zmeev, Lancaster University, UK

P1.036 A new compact rotating dilution refrigerator
M Fear, The University of Manchester, UK

P1.037 Detectors of quantum turbulence with the use of charged vortex rings
F Pakpour, The University of Manchester, UK

P1.038 Observation of vortex ring emission within vortex tangles in superfluid ^{4}He at low temperatures
P Walmsley, The University of Manchester, UK

P1.039 Diamond like carbon (DLC) thin film for industrial application
M Khalid, National Institute of Vacuum Science and Technology (NINVAST), Pakistan

P1.040 2D Fermi liquid collective excitations at high energy and wave-vector: neutron measurements on a liquid ^{3}He monolayer
H Godfrin, CNRS et Université Joseph Fourier, France

P1.041 Spin lattice relaxation at very low temperatures
J Owers-Bradley, University of Nottingham, UK

P1.042 Angle-dependent measurements at low temperature and high magnetic fields with in-situ double rotator
G Coustou, Attocube Systems, Germany

P1.043 Studies of dielectric loss and noise in superconducting resonators
J Burnett, Royal Holloway University of London/National Physical Laboratory (NPL), UK

P1.044 Mobile small bipolarons on a three-dimensional cubic lattice
A Davenport, The Open University, UK

P1.045 Nanoscale Superconducting Quantum Interference Devices for Millikelvin Magnetometry
L Hao, National Physical Laboratory, UK

P1.046 Superconducting microbolometer for the measurement of energy deposited by proton and ion beams
L Hao, National Physical Laboratory, UK

P1.047 Design and measurements of quartz tuning fork arrays for quantum turbulence studies in superfluid Helium-3
E Guise, Lancaster University, UK

P1.048 Thermal conductivity measurements of $Dy_2Ti_2O_7$(Spin Ice) and $Y_2Ti_2O_7$ in the temperature ranges 15mK to 20K
M Človečko, Lancaster University, UK

P1.049 Hydrodynamic properties of a low frequency resonator in normal and superfluid Helium 4
M Poole, Lancaster University, UK

P1.050 Double-oscillator observation of 'Supersolid' effects in solid Helium
B Cowan, Royal Holloway University of London, UK

P1.051 A scalable architecture for solid-state quantum metamaterials
R Wilson, Loughborough University, UK

Magnetism/spintronics/inter-metalic phases

P1.052 Synthesis and magnetic properties of bulk ferrites spinels $Ni_{0.5}Zn_{0.5}Fe_2O_4$: experimental an ab-initio study
R Masrour, Cady Ayyed University, Morocco

P1.053 Structure and magnetism of FePt nanoparticles generated with a gas aggregation source and embedded in a solid matrix
S D'Addato, Università di Modena e Reggio Emilia, Italy

P1.054 Electronic, optical and magnetic properties of Mn doped BN semiconductor
B Abdelaziz, University of Mostaganem, Algeria

P1.055 Crystal structure and magnetic ordering in ultrathin manganese pnictides films: an ab initio study
M Otrokov, Tomsk State University, Russia

P1.056 Study of microstructure and magnetic of electrodeposited CoFeCu in self-assembled mesoporous silicon
G Fortas, Silicon Technology Developpement Unit, Algeria

P1.057 A Hall junction element for memory and logic applications
S Zhang, University of Oxford, UK

P1.058 Field dependence of microwave frequency absorption in antiferromagnet/ferromagnet exchange coupled multilayers
F Trindade, University of Glasgow, UK

P1.059 Low frequency spin dynamics in unsaturated YIG films: correlation of spin dynamics with magnetic domain structures
F Trindade, University of Glasgow, UK

P1.060 Critical properties of a two-dimensional site-diluted Ising model
U Fulco, Universidade Federal do Rio Grande do Norte (UFRN), Brazil

P1.061 Transmission band gaps in generalized Fibonacci magnonic crystals
P W Mauriz, Instituto Federal de Educação Ciência e Tecnologia, Brazil

P1.062 Ab-initio and tight-binding calculations of magnetic anisotropy phenomena in CoPt
J Zemen, The University of Nottingham, UK

P1.063 Quantitative estimation of the contribution of the metallic Co nanoparticles magnetization to the total magnetization in In_2O_3
M Alshammari, King Abdulaziz City for Scince and Technology, Saudi Arabia

Magnetism at the atomic and molecular scale

P1.064 Domain walls nucleation of super paramagnetic Cobalt nano-wire on Pt(111) by Magnetic Molecular Dynamics simulations
D Beaujouan, Combustion Engineering Association (CEA), UK

P1.065 Magnetic stability of rare earth atoms and clusters on metallic surfaces
T Miyamachi, Karlsruher Institut für Technologie (KIT), Germany

P1.066 Local magnetism control with surface states confinement and electric fields
O Brovko, Max Planck Institute of Microstructure Physics, Germany

P1.067 AC magnetic susceptibility measurements at high pressure in uranium intermetallics
C O'Neill, The University of Edinburgh, UK

Nanostructures

P1.068 Strain in free standing core-shell nanocrystals
F Rajadell, Universitat Jaume I, Spain

P1.069 Tunable generation of correlated vortices in open superconductor micro- and nanotubes
V M Fomin, Institute for Integrative Nanosciences, Germany

P1.070 Noise rectifier based on two-dimensional electron gas
M Cheremisin, A.F. Ioffe Physical-Technical Institute, Russia

P1.071 The spectral properties of the Doppler's effect in dispersive metamaterials
G Burlak, Universidad Autónoma del Estado de Morelos, México

P1.072 Changes in nanoparticle's spectroscopic signal mediated by the local environment
A Corbani Ferraz, Universidade de São Paulo, Brazil

P1.073 High-magnetic-field thermopower in layered electron systems
S Figarova, Baku State University, Azerbaijan

P1.074 Achieving broadband transparency with multishelled spherical metamaterial coatings
K W Yu, Chinese University of Hong Kong, China

P1.075 Electronic transport in InAs nanowires
M Sourribes, University College London, UK

P1.076 Profile of the potential step in semiconductors and the example of Galium nitride
B Santic, Roder Boskovic Institute, Croatia

P1.077 SnO_2 nanobelts: back-to-back Schottcky diodes theory in analysis and extraction of electrical parameters
L Araujo, Universidade Federal de São Carlos, Brazil

P1.078 Electron temperature in isolated quantum dot structures
P Chapman, Hitachi Cambridge Laboratory, UK

P1.079 Microwave manipulation of electrons in silicon quantum dots
P Chapman, Hitachi Cambridge Laboratory, UK

P1.080 Structure and evolution of a gold nanowires at the room temperature: a kinetic monte carlo investigation
K Andrey, Lomonosov Moscow State University, Russia

P1.081 The study of electron scattering mechanisms in single crystal oxide nanowires
O Berengue, Universidade Federal de São Carlos, Brazil

P1.082 HRTEM and XPS study of highly dispersed palladium on the surface of Pd/CeO_2 catalysts
O Stonkus, Institute of Catalysis, Russia

P1.083 Interactions of nano and micro objects with MEMS and NEMS devices
V Afonina, Kotelnikov, Russia

P1.084 Functional properties of NI-TI shape memory alloy processed by ECAP for medical applications
V Kalashnikov, Kotelnikov, Russia

P1.085 Atom-sized contacts of HCP metals and their conductance at room temperature
A Sakai, Kyoto University, Japan

P1.086 Silver-doped CeO_2 thin film catalysts prepared by magnetron sputtering on carbon substrates
M Chundak, Charles University, Czech Republic

P1.087 Light emission from single-walled carbon nanotube on Au(111) induced by scanning tunneling microscope
S Katano, Tohoku University, Japan

P1.088 First principles study on the oxygen-vacancy migration in $LaGaO_3$
T Wungu, Osaka University, Japan

P1.089 Photodesorption and thermal desorption of water from nanostructured carbon surfaces
A Clemens, Chalmers University of Technology, Sweden

P1.090 In-situ measurement of Piezo-driven nanomechanical resonators in a Scanning-Electron-Microscope
H Wang, London Center for Nanotechnology, UK

P1.091 Fractal morphology of water on chromium oxide ultra-thin films
K Esat, Istanbul Technical University, Turkey

P1.092 Combining selected plastic materials with diamond-like carbon coatings
C B Fischer, University Koblenz-Landau, Germany

P1.093 Fabrication and characterization of CdTe nanocrystals thin films embedded in a polystyrene matrix
B Fahima, University Mentouri, Algeria

P1.094 Synthesis and characterisation of PbS nanoparticle thin films for use in solar photovoltaics
D Cant, University of Manchester, UK

P1.095 Towards the transparent and flexible field emission displays using Ion-induced conical nanocarbon structures
M Tanemura, Nagoya Institute of Technology, Japan

P1.096 Thermocouple of a single metal
S Xu, Peking University, China

P1.097 Synthesis and properties of antihistamine-layered double hydroxide nanocomposites based on cetirizine
M Z Hussein, Universiti Putra Malaysia, Malaysia

P1.098 Hole transport properties in modulation doped Germanium heterostructure
A Hassan, University of Warwick, UK

P1.099 Structure transition of annealing Zn nanoparticles
J-H Lin, National Dong Hwa University, Taiwan

P1.100 Effect of annealing on the structural, optical and electrical properties of sol-gel derived Zinc oxide thin films
V Luthra, Gargi College, India

P1.101 In situ X-ray scattering investigations of semiconductor nanowires during their growth by UHV-CVD
T Zhou, Combustion Engineering Association (CEA), France

P1.102 Two-qubit parametric amplifier and stochastic resonance in qubits: Large amplification of weak signals
Z Washington, Loughborough University, UK

Non-covalent interactions

P1.103 Benzene strongly adsorbed on metal surfaces: chemisorption, physisorption, or both?
W Liu, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Polymer surfaces and interfaces

P1.104 Dielectric and electro-optic behavior of liquid crystal dispersions exhibiting planar or homeotropic anchoring at the liquid crystal/polymer interface
M Boussoualem, University of Science and Technology Lille (USTL), France

P1.105 Nanocomposites based on porous silicon for ammonia gas sensing
N Chiboub, University of Science and Technology Lille (USTL), France

P1.106 The molecular order in P(NDI2OD-T2) and PBTTT thin films
L Thomsen, The Australian Synchrotron, Australia

Polymers/biology

P1.107 Modelling the cell cytoskeleton and understanding how eukaryotic cells move
E Tjhung, The University of Edinburgh, UK

P1.108 Solution-phase visible laser processing of Pi-conjugated polymers: optical detection of transition between different molecular states
A Tomioka, Osaka Electro-Communication University, Japan

P1.109 Identification of mitochondrial proteins of malaria parasite using Chou's pseudo amino acid composition
C Yi, Inner Mongolia University, China

P1.110 The thermomechanical properties and morphological characteristics of agar gel
M Lounis, LAAR Laboratory, Algeria

Semiconductors

P1.111 Thermoelectric properties of uniaxial strained Bi wires
A Gilewski, International Laboratory of High Magnetic Fields and Low Temperatures, Poland

P1.112 Anisotopic magnetoresistance and magnetometry studies of GaSb based dilute magnetic semiconductors
B Howells, Nottingham University, UK

P1.113 Electrical and structural properties of thermally grown GeO_2 on epitaxial Ge on Si(001) substrate
C Antunes Casteleiro, University of Warwick, UK

P1.114 Electronic properties of site-controlled (111)-oriented zinc-blende quantum dots
E O'Reilly, Tyndall National Institute, Ireland

P1.115 Theory of the electronic structure of dilute bismide and bismide-nitride alloys of GaAs
E O'Reilly, Tyndall National Institute, Ireland

P1.116 Effect of heat treatment on physical properties of ZnO thin films deposited by DC reactive sputtering
B Abdrahmane, USTHB, Algeria

P1.117 Ion beam analysis for Hall Scattering Factor measurements in antimony-implanted silicon
T Alzanki, Public Authority for Applied Education and Training (PAAET), Kuwait

P1.118 InGaN light-emitting diodes with a reduced barrier thickness
C-L Tsai, Chang Gung University, Taiwan

P1.119 Electronic and optical properties of amorphous semiconductors: a-SiO_2 and a-TiO_2 bulk, solid solution, and interface
M Landmann, Universität Paderborn, Germany

P1.120 Surface states influence in Al Schottky barrier of Ge nanowires
H Kamimura, Universidade Federal de São Carlos, Brazil

P1.121 Interface-induced cation ordering in InGaAs/InP(100) heteroepitaxial structures observed by reflectance difference spectroscopy
R Kanemura, Yakohama National University, Japan

P1.122 Photoemission and ellipsometry measurements of GeO_2 and Y_2O_3 films on Ge substrates
M Althobaiti, University of Liverpool, UK

P1.123 Polaronic effect on impuritiy state in Wurtzite Nitride Semiconductor Quantum Dot under an electric field and hydrostatic pressure
Z Yan, Inner Mongolia Agricultural University, China

P1.124 Aharonov-Bohm quantum rings in microcavities
A Alexeev, University of Exeter, UK

P1.125 Effect of weak magnetic fields treatment on photoluminescence of gallium arsenide and gallium phosphide single crystals
R Red'ko, The National Academy of Sciences of Ukraine, Ukraine

P1.126 Charge Carrier Density at the $(Na/K)TaO_3$ / $SrTiO_3$ Interfaces
S Nazir, King Abdullah University of Science and Technology (KAUST), Saudi Arabia

P1.127 High Mobility of the Strongly Confined Hole Gas in $AgTaO_3/SrTiO_3$
S Nazir, King Abdullah University of Science and Technology (KAUST), Saudi Arabia

P1.128 The Interface of the Ferromagnetic Metal CoS_2 and the Non-magnetic Semiconductor FeS_2
S Nazir, King Abdullah University of Science and Technology (KAUST), Saudi Arabia

P1.129 Oscillator strengths for intersubband transitions in the multi-layered nano-antidots with haydrogenic impurity
Y Naimi, Islamic Azad University, Iran

P1.130 Ion beam analysis for hall scattering factor measurements in antimony-implanted silicon
T Alzanki, Public Authority for Applied Education and Training (PAAET), Kuwait

Theory/computational physics

P1.131 Strain dependence of polarization and dielectric response in epitaxial $(Ba_xSr_{1-x})TiO_3$ Thin Films
S Binomran
King Saud University, Saudi Arabia

P1.132 Charge-transfer excitations in oxo and peroxo dicopper complexes modelled within TDDFT and MBPT
M Rohrmüller, Universität Paderborn, Germany

P1.133 Ferroelectric transition in $LiNbO_3$ calculated from first principles
S Sanna, Universität Paderborn, Germany

P1.134 Break down of one-dimensional free fermion picture on equilibrium crystal shape for sticky steps I: PWFRG calculations
N Akutsu, Osaka Electro-Communication University, Japan

P1.135 Structure and IR spectra of $Na_8[AlSiO_4]6\ (BH_4)_2$ sodalite: Comparison between theoretical predictions and experimental data
M Marcus, Rheinische Friedrich-Wilhelms Universtät Bonn, Germany

P1.136 Phase transitions pressure and lattice dynamical properties of lead polonide
B Yamina, Mostaganem University, Algeria

P1.137 Scalable coarse-grained spin dynamics simulation
F Buijnsters, Radboud Universiteit Nijmegen, The Netherlands

P1.138 Progress in the development of the Cyclic Cluster model at ab initio level
M F Peintinger, University of Bonn, Germany

P1.139 Cyclic cluster implementation of DFTB/DFTB-SCC
T Claff, University of Bonn, Germany

P1.140 The pressure coefficients of the superconducting transition temperatures of ferromagnetic superconductors
R Konno, Kinki University Technical College, Japan

P1.141 Quantum chemical simulations of surface reactions
A Funk, University of Siegen, Germany

P1.142 Polarization-dependent methanol adsorption on lithium niobate Z-cut surfaces
A Riefer, Universität Paderborn, Germany

P1.143 First-principles non-adiabatic molecular dynamics simulations using local basis DFT Fireball code
P Hapala, Institute of Physics of the Czech Academy of Science, Czech Republic

P1.144 Monte Carlo calculation of the final backscattering energy and the backscattering coefficient of electron in solids: the effect of the transport cross section
A Bentabet, Centre Universitaire de Bordj Bou-Arréridj, Algeria

P1.145 Developing a forward flux sampling plugin for multiple applications
R Allen, The University of Edinburgh, UK

P1.146 First-principle studies of phonons in wurtzite structure III-N compound semiconductors
G Zhao, Inner Mongolia University, China

P1.147 Dirac superplasmons in a honeycomb structure of metallic nanoparticles
C Woollacott, University of Exeter, UK

Thin carbon layers/graphene

P1.148 On the Quantum Hall Effect in graphene
M Cheremisin, A.F. Ioffe Physical-Technical Institute, Russia

P1.149 Na induced changes in the electronic band structure of graphene on C-face SiC
L Johansson, Linköping University, Sweden

P1.150 Coupling epitaxy and chemical bonding at the local scale in transition metal supported graphene
C Bromley, University of St Andrews, UK

P1.151 Adhesion of graphene on rough substrates, and substrates with nanoparticles
P-L Olivier, CNRS/LPMCN, France

P1.152 Effective interaction between hydrogen atoms adsorbed on graphene
Y Saito, Okayama University of Science, Japan

P1.153 Electronic properties of super-periodic structures due to dislocated graphene on HOPG
D Yıldız, Istanbul Technical University, Turkey

P1.154 Gap opening of graphene by dual doping method
J-W Yang, Pohang University of Science and Technology, South Korea

P1.155 Graphene/h-BN heterostructures: shaping Dirac fermions for applications and testing QED$_{2+1}$
J Slawinska, University of Lodz, Poland

P1.156 Lattice spin in graphene and spin from isospin
P Maslanka, University of Lodz, Poland

P1.157 Hot carrier relaxation in HOPG probed at the H-point by means of time-resolved XUV photoemission
G Rohde, Christian-Albrechts-Universität zu Kiel, Germany

P1.158 X-ray photoelectron study (XPS and XPD) of few-layer graphene (FLG) on ^{6}H-SiC (0001)
F Djawhar, Université de Lyon, France

P1.159 Growth and atomic structure of graphene on Ir(332)
V Mikšić Trontl, University of Zagreb, Croatia

P1.160 Diamond like carbon (DLC) film by laser ablation for industrial application
M Khalid, National Institute of Vacuum Science and Technology (NINVAST), Pakistan

P1.161 Characterization of graphene growth on commercial available cubic-SiC(001)/Si standard wafers
V Aristov, Institute of Solid State Physics, Russia

P1.162 Chemical termination of graphene nanoribbons – simulation and experiment
L Talirz, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

P1.163 Electronic transport in quasiperiodic graphene p–n–p junctions
M Vasconcelos, Universidade Federal do Rio Grande do Norte (UFRN), Brazil

P1.164 Adsorption energy of metal-phthalocyanines on graphene/Ir(111)
M Scardamaglia, Università di Roma La Sapienza, Italy

P1.165 Stamp transferred suspended graphene mechanical resonators for radio frequency electrical readout
X Song, Low Temperature Laboratory of Helsinki University of Technology, Finland

P1.166 Conductance anomaly near the Lifshitz transition in strained bilayer graphene
D Gradinar, Lancaster University, UK

Topological insulators

P1.167 Interpretation of 2DEG states in topological insulators
T Menshchikova, Tomsk State University, Russia

P1.168 Impurity induced electronic scattering in the protected surface state of Bi(111)
C Klein, University Duisburg-Essen, Germany

P1.169 Electronic structure of Fe and Co magnetic adatoms on Bi_2Te_3 surfaces
L Collins-McIntyre, Oxford University, UK

Poster programme

Poster session ECOSS/ECSCD (C/D)
Wednesday 5 September and Thursday 6 September

Biological interfaces

P2.001 Electron spectroscopic analysis of stratum corneum lipids: Plasma-induced changes in lipid composition
M Marschewski, TU Clausthal, Germany

P2.002 Mechanistic control of amyloid fibril oligomer populations
K Eden, The University of Edinburgh, UK

Complex systems: large organic molecules, self-assembly and self-organisation

P2.003 Monte Carlo simulation of the self-assembly of cross-shaped molecules adsorbed on a solid surface
A Kasperski, Maria Curie-Skłodowska University, Poland

P2.004 Nanopatterning of Si(001) by a self-organized bottom-up process
H Hosseinzadeh, Johannes Kepler University of Linz, Austria

P2.005 Properties of Asp, Glu, Gly and Leu on the Fe_3O_4-(111)-surface: a forcefield simulation study
A Bürger, Ruhr-University Bochum, Germany

P2.006 Ordering of copper phthalocyanine adsorbed on Ag-passivated Si(111)-$\sqrt{3}$x$\sqrt{3}$R30° studied by SPALEED and STM
T Wilkens, University of Bremen, Germany

P2.007 Interface state formation at the PTCDA/Ag(100) interface studied with 2PPE
M Marks, Philipps-Universität Marburg, Germany

P2.008 Interaction between metal-phtalocyanines and metallic substrates
E Rauls, Universität Paderborn, Germany

P2.009 Adsorption of PTCDA on KCl and NaCl surfaces
E Rauls, Universität Paderborn, Germany

P2.010 Adsorption of diindenoperylene on Cu(111) surfaces
E Rauls, Universität Paderborn, Germany

P2.011 Monte Carlo modelling of molecular rhombus tilings
A Stannard, University of Nottingham, UK

P2.012 Chain-length and temperature dependences of the structures of alkylthiolate self-assembled monolayers on metal (111) surfaces
Y Wang, Universidad Autonoma de Madrid, Spain

P2.013 Ordering of Schiff base diamines on Au(111)
M Räisänen, University of Helsinki, Finland

P2.014 Bonding configurations of C_{60} molecules on Au(111)
L Tang, University of Birmingham, UK

P2.015 Construction of 2-D metal organic architectures on Au{111}
C Baddeley, University of St Andrews, UK

P2.016 Organic heteroepitaxy of PTCDA and SnPc on single crystalline metals
R Forker, Friedrich-Schiller-University Jena, Germany

P2.017 Adsorption of EP-PTCDI films grown on Cu (100) studied by STM, LEED and DFT calculations
J C Moreno-López, Centro Atómico Bariloche - Comisión Nacional de Energía Atómica and CONICET, Argentina

P2.018 1,4-benzenedimethanethiol self-assembled monolayers on Au(111) and Ag(111) from vapour phase: stability with surface temperature
L Salazar Alarcon, Centro Atómico Bariloche - Comisión Nacional de Energía Atómica and CONICET, Argentina

P2.019 Long range ordered binary monolayers of sulphur containing donor molecules and TNAP on Au(111) investigated by LEED and STM
B Fiedler, Universität Bonn, Germany

P2.020 Comparison of self-assembly of TMPyP and TTMAPP porphyrin molecules on an iodine-modified Au(100) surface
T Kosmala, Universität Bonn, Germany

P2.021 Effects of electron-beam irradiation on phospholipid/amino acid complexes
R Panajotovic, University of Belgrade, Serbia

P2.022 Spectroscopic study of the orientation and electronic states of α-sexithiophene on chemically modified Si(001) surfaces
M Tanaka, Yokohama National University, Japan

P2.023 Orientation changes of n-Alkane in a monolayer on graphene modified Pt(111) studied by C K-NEXAFS
O Endo, Tokyo University of Agriculture and Technology, Japan

P2.024 Optical properties of liquid crystal placed in nonuniform electrical field
M Boussoualem, University of Science and Technology of Lille (USTL), France

P2.025 Adsorption height of benzene and azobenzene on Ag(111) and Cu(111)
M Willenbockel, Forschungszentrum Jülich, Germany

P2.026 The adsorption of pentacene on quasicrystalline surfaces
J Smerdon, University of Liverpool, UK

P2.027 Charging and switching of metallo-organic complexes on ultrathin, insulating films supported by a metal support: a density functional theory study based on a perfect conductor model
I Scivetti, University of Liverpool, UK

P2.028 Self-assembly of reactants for an on-surface click-reaction: azides and acetylenes on Cu(111)
S R Vadapoo, Aarhus University, Denmark

P2.029 A molecule-like composite nanostructure by self-selective growth
Y Xie, Nanoscale Physics Research Laboratory, China

P2.030 Aging of organic nanowires
F Balzer, University of Southern Denmark, Denmark

P2.031 An STM and UPS study of thermally polymerised 5,10,15,20-tetrakis(4-aminophenyl)-porphyrin (TAPP) films
A Cafolla, Dublin City University, Ireland

P2.032 Hybrid organic–inorganic systems: Al, Ag and Au nanoparticles self-assembled in CuPc
O Molodtsova, DESY, Germany

P2.033 Low temperature scanning tunneling microscopy study of Co-Phthalocyanine molecules on graphene/Ir (111)
S Bouvron, University of Konstanz, Germany

P2.034 Supramolecular self-assembly of 1,3,5-triethynyl-benzene and 1,3,5-triethynylphenyl-benzene molecules on Ag(111)
F Klappenberger, Technische Universität München, Germany

P2.035 Bonding and reaction of self-assembled monolayers on ferromagnetic metal surfaces
F Allegretti, Technische Universität München, Germany

P2.036 2D adaptive nanoporous networks with random features from flexible molecular modules
D Ecija, Technische Universität München, Germany

P2.037 Adsorption of R, S-Phenylglycine on Au(111)
F Grillo, University of St Andrews, UK

P2.038 Thickness-dependent dielectric constant of organic ultra-thin films
C Albonetti, CNR-ISMN, Italy

P2.039 Hierarchical assembly of keratin intermediate filament structures inside skin cells
D Bray, University of Warwick, UK

P2.040 Covalent immobilization of molecularly imprinted nanoparticles on (3-glycidoxypropyl) trimethoxysilane functionalized glass
T Kamra, Lund University, Sweden

Electronic structure of surfaces

P2.041 Photoemission, ion scattering and electron diffraction studies of the CdO(001) surface
M Walker, University of Warwick, UK

P2.042 Strongly anisotropic surface conductivity of diamond(001) surfaces upon N-doping
N J Vollmers, Universität Paderborn, Germany

P2.043 Collapse of shockley surface state by randomly adsorbed Bi atoms at Ag(111) surfaces
H Hirayama, Tokyo Institute of Technology, Japan

P2.044 Spatial mapping of surface plasmons in nanoscale Ag islands on graphite using scanning probe energy loss spectroscopy
L Tang, University of Birmingham, UK

P2.045 Photoemission study of the hydrogenated Si(111)-1x1 surface
W Srour, SOLEIL Synchrotron, France

P2.046 Nanoscopic insight ino recombination active defects at silicon heterojunctions
U Gerstmann, University of Paderborn, Germany

P2.047 Stability of In/Si(111)-(4x1) nanowires
M Babilon, University of Paderborn, Germany

P2.048 The surface electronic structure of Al(100) revisited with the first-principle calculation
D-A Luh, National Central University, Taiwan

P2.049 Image potential states on manganese phthalocyanine thin films
I Yamamoto, Saga University, Japan

P2.050 Atomic and electronic structure of the (2√3x2√3)R30° reconstruction of Sn/Ge/Si(111)
A Tejeda, CNRS/Institut Jean Lamour, France

P2.051 Quantum degeneracy revealed by the relation between the tunneling current and the chemical force.
M Ondráček, Institute of Physics of the Czech Academy of Science, Czech Republic

P2.052 The Role of van der Waals potential on the electronic spectra of solids and interfaces
A Ambrosetti, Fritz Haber Institut der MPG, Germany

P2.053 Theoretical reconstruction of MIES spectra
W Beenken, Ilmenau University of Technology, Germany

P2.054 Cs doping of organic semiconducting monolayers: probing the electronic and geometric structure with angle resolved UPS
E M Reinisch, Karl-Franzens-University, Austria

P2.055 Optical vibration modes and electron-phonon interaction in spherically capped core-shell quantum dots
Y Xing, Inner Mongolia University, China

Liquid-solid interfaces incl. water and electrochemistry

P2.056 The (100)-pyrite-water interface: a molecular dynamic simulation study supporting GIXRD-experiments
S Meis, Ruhr-University Bochum, Germany

P2.057 Water-hydroxyl phases on Cu(110): breaking the ice rules
J Carrasco, Spanish National Research Council (CSIC), Spain

P2.058 Use of multivariate analysis in optimization process of black electroplated Cu-Ni coatings preparation
Ł Skowroński, University of Technology and Life Sciences, Poland

P2.059 Interaction of some atmospheric oxygenated volatile organic compounds (OVOCs) with H_2O, $HNO_3.3H_2O$, and pure HNO_3 ice surfaces
J Lasne, Heriot-Watt University, UK

P2.060 Effect of Ions Y_{3+} inhibitor on mild steel corrosion in 0.5 N NaCl
S Abderrahmane, University of Badji-Mokhtar, Algeria

P2.061 Water adsorption on lithium niobate studied from first principles
R Hölscher, Universität Paderborn, Germany

P2.062 From HCl oxidation to the formation of water on the Cu(100) surface
M Gladys, University of Newcastle, UK

P2.063 Adsorption and desorption of SO_2 on the ionic liquids $[C_2C_1C_1Im][Tf_2N]$ and $[C8C_1Im][BF_4]$
M Buckley, University of Nottingham, UK

P2.064 Continuum solvent model for adsorption processes on periodic surfaces
M Witte, Universität Paderborn, Germany

P2.065 Adsorption of cysteine modified silicon substrates in electrolyte solution studied by means of surface differential reflectance spectroscopy
Y Fujimori, Yokohama National University, Japan

P2.066 Metal-induced anisotropic etching of Ge(100) surfaces in water with dissolved oxygen
K Arima, Osaka University, Japan

P2.067 Atomic surface structure of Cs-terminated muscovite mica determined using SXRD
S Pintea, European Synchrotron Radiation Facility, France

P2.068 Characterization of Ionic Liquid interfaces with metastable induced electron spectroscopy (MIES) and photoelectron spectroscopy (UPS/XPS)
O Höfft, TU Clausthal, Germany

P2.069 Amplitude-modulation AFM-derived heights under suspicion
J Fraxedas, Centre d'Investigació en Nanociència i Nanotecnologia, Spain

P2.070 Electrochemical oscillation in the additives-assisted copper electroplating: a mechanistic study on the role of intermediate species at the copper/electrolyte interface
H Nguyen, University of Bern, Switzerland

P2.071 Redox-active Safranine/Janus Green B leveler additives at Cu(100)/electrolyte interface: EC-STM and electrochemical studies
H Nguyen, University of Bern, Switzerland

P2.072 LEED - IV study of the co-adsorption of chlorine and water on Cu (100)
D Hesp, University of Liverpool, UK

P2.073 Gly-Cys-Gly-Cys immobilization on porous silicon nanostructure for electrochemical detection of metals
N Chiboub, Unité de Développement de la Technologie du silicium (UDTS), Algeria

P2.074 Electrochemical study and mechanical investigation of zinc alloy electrodeposition in the presence of solanum tuberosum juice extract as additive
O S Fayomi, Tshwane University of Technology, South Africa

Metal surfaces

P2.075 Growth of perfect metallic nanowires on Cu (100) vicinal surfaces: a kinetic Monte Carlo study
A Ben Haj Hammouda, Faculy of Science of Monastir, Tunisia

P2.076 Surface structure of Ag-In-RE (Gd,Tb,Yb) 1/1 approximants
S Hars, Liverpool University, UK

P2.077 Effect of surface preparation on the bond strength of aluminum alloy 2024
M Khabiri, Malek-Ashtar University of Technology, Iran

P2.078 Investigation of ultrathin Fe films on Ag(001) by multi-photon photoemission
T R F Peixoto, Max Planck Institute of Microstructure Physics, Germany

P2.079 Influence elements (V and Nb) on the microstructure and corrosion behaviour of a stainless steel type 309
A Himour, University Badji Mokhtar, Algeria

P2.080 Optical properties of the Cu, β-Sn and In nanoscale films on glass substrates
Ł Skowroński, University of Technology and Life Sciences, Poland

P2.081 Proprieties of Ti-C-N coating deposited by magnetron sputterings
S Nadia, Centre for the Development of Advanced Technologies (CDTA), Algeria

P2.082 Oxidation state analysis of Cr in the oxide layer between stainless steel and metallic tin by AES
S Fukushima, National Institute for Materials Science, Japan

P2.083 Surface diffusion involved intermixing of ultrathin In and Ag layers and formation of Ag_xIn_{1-x} surface alloys on the tungsten surface
K Okulewicz, University of Technology and Life Sciences in Bydgoszcz, Poland

P2.084 Self-organization of magnetic nanostructures embedded into Cu(100) surface
S Kolesnikov, Lomonosov Moscow State University, Russia

P2.085 Stress relief by trenches on nitrogen-adsorbed Cu(001) surfaces at near-saturation coverage
M Yamada, University of Tokyo, Japan

P2.086 H_2O adsorption on Cu{100}-c(2x2)-Cl Surface
M Puisto, Lappeenranta University of Technology, Finland

P2.087 DFT study of Pentacene adsorption on aperiodic copper film
M Lahti, Lappeenranta University of Technologym, Finland

P2.088 The surface electronic and magnetic structures of the oxidized ultrathin iron film on the Ir(001) surface
F Maca, Institute of Physics of the Academy of Sciences, Czech Republic

P2.089 Structure and magnetic properties of Fe/W(110)
I Zasada, University of Lodz, Poland

P2.090 Stress evolution during polycrystalline thin film growth studied in-situ by video-rate STM
A Saedi, Leiden University, The Netherlands

P2.091 Structure and formation of PdIn surface alloys
G McGuirk, Institut Jean Lamour, France

P2.092 Photon scanning tunneling microscopy of alloyed gold surfaces
O Gürlü, Istanbul Technical University, Turkey

P2.093 X ray-induced reversible switching of dimetacyano azobenzene on Bi(111)
A Krüger, Freie Universität Berlin, Germany

P2.094 Exploiting resonance effects on Bi(111)
P Kraus, Technical University Graz, Austria

P2.095 Investigation of Au(100) film epitaxial growth on Ir(100) surface
O Fedchenko, Sumy State University, Ukraine

P2.096 An STM/XPS study of the oxychlorination of Cu(111) and Cu(110) surfaces
H Altass, Cardiff University, UK

P2.097 Protection against corrosion: thermally oxidized stainless steel studied by atomic force microscopy and scanning Kelvin probe force microscopy
C Pirri, University of Mulhouse, France

P2.098 Anomalous hall effect in ferromagnetic metals: role of phonons at finite temperature
A Shitade, Kyoto University, Japan

P2.099 AC magnetic susceptibility measurements at high pressure in uranium intermetallics
C O'Neill, The University of Edinburgh, UK

P2.100 NISXW study of Si adsorbed on an Al-Co-Ni quasicrystal
D P Woodruff, University of Warwick, UK

P2. 101 Studying the nanostructure of the copper surface after ion bombardment
T E Amos, University of Edinburgh, UK

Novel methods: instrumentation, facilities and computation

P2.102 Inverse simulation technique for the determination of amorphous structures
J Los, Johannes Gutenberg University, Germany

P2.103 XAFS on thin films and surfaces at SAMBA, the general purpose hard X-ray beamline of SOLEIL
E Fonda, Synchrotron SOLEIL, France

P2.104 Bulk molybdenum tip for scanning tunneling microscopy
P Carrozzo, Politecnico di Milano, Italy

P2.105 Scanning capacitance microscopic studies on the stability of the electrical junction width formed by microwave annealing
M-N Chang, National Chung Hsing University, Taiwan

P2.106 Alignment apparatus for magnetic resonance force microscopy
S Won, Korea Institute of Materials Science, Korea

P2.107 Photoluminescence imaging of high temperature aluminide coatings for turbine engine applications
S Greenwell, University of Bristol, UK

P2.108 Miniaturized pattern formation at soft interfaces
J Sarkar, Indian Institute of Technology Delhi, India

P2.109 Border search method - potential energy surface mapping technique alternative to metadynamics
P Hapala, Institute of Physics of Czech Academy of Science, Czech Republic

Oxide surfaces

P2.110 Theoretical insights into the Ag doping in monolayer and bilayer ZnO armchair nanoribbons: edge effect and position-dependent properties
Y Li, University of Paderborn, Germany

P2.111 Self-limited growth of ZnO films on Ag(111)
B-H Liu, Fritz Haber Institute, Germany

P2.112 Resistive switching in TiO_2 crystals
M Rogala, University of Lodz, Poland

P2.113 Electronic structure and optical properties of tin monoxide bulk and its (001) surface
S Küfner, Friedrich-Schiller-Universität Jena, Germany

P2.114 Adhesion forces at zinc/ α-Al_2O_3 (0001) interface
R Cavallotti, University of Pittsburgh Medical Center (UPMC), USA

P2.115 Distinct physicochemical properties of the first ceria monolayer on Cu(111)
O Stetsovych, Charles University, Czech Republic

P2.116 Oxide layers on the surface of polycrystalline gold foil produced by RF discharge in oxygen: XPS and TPD study
A Stadnichenko, Boreskov Institute of Catalysis, Russia

P2.117 Morphology and thermal stability of thin AlF_3 films on Cu(100)
J Ferrón, Universidad Nacional del Litoral, Argentina

P2.118 HR-EELS studies on oxide nanoparticles
S Frey, Ruhr-Universität Bochum, Germany

P2.119 DFT+U study of adsorption of small molecules on model CeO_2/Cu(111) catalysts
L Szabova, Charles University in Prague, Czech Republic

P2.120 STM and LEED studies on reduced TiO_2 (001) surface
A Busiakiewicz, University of Lodz, Poland

P2.121 Preventing fouling with silicon carboxides films synthesized by DBD-APCVD
J Guillot, CRP-Gabriel Lippmann, Luxembourg

P2.122 Growth of thick ceria films on Cu(111)
F Dvorak, Charles University in Prague, Czech Republic

P2.123 Oxidation of iron
M Soldemo, Royal Institute of Technology, Sweden

P2.124 Surface evolution of (100) magnetite during oxidation
J de la Figuera, Instituto de Química-Física "Rocasolano", Spain

P2.125 Ab initio study of low-coordinated sites on the MgO(001)-surface using hybrid functionals
M Bockstedte, Universitaet Erlangen-Nuernberg, Germany

P2.126 Interaction of atomic and molecular hydrogen with ZnO
C M Kim, Kyungpook National University, South Korea

P2.127 XPS quantification of ZnO(000-1) polar surfaces irradiated with 0.5-5 keV Ar ions
M Krawczyk, Polish Academy of Sciences, Poland

P2.128 Study of fractal properties of MnO_2 pyrolytic films
L Skatkov, Argo Printed Circuit Board (PCB), Israel

P2.129 Tuning the morphology of carbon substrates by oxygen plasma treatment
I Khalakhan, Charles University in Prague, Czech Republic

Semiconductor surfaces

P2.130 Atomic-scale wires on Si(553)-Au: observation of current-dependent periodicity
S Polei, Universität Rostock, Germany

P2.131 Depth profiling of melting and metallization in Si(111) and Si(001) surfaces
R Gunnella, University of Camerino, Italy

P2.132 Faceting transitions in polysilicon films
T Rodionova, Kiev National Taras Shevchenko University, Ukraine

P2.133 Surface preparation and polarity determination of GaN(0001) and InN(0001)
M Walker, University of Warwick, UK

P2.134 Desorption-induced structural changes of metal/Si(111) surfaces – kinetic Monte Carlo simulations
P Kocan, Charles University in Prague, Czech Republic

P2.135 Probing the diffusion and structure of Te and CdTe on Cu(111)
M King, University of Glasgow, UK

P2.136 Structural study of the Si(111)-√3x√3-Pd by transmission X-ray diffraction
H Tajiri, Japan Synchrotron Radiation Research Institute, Japan

P2.137 Adsorption of Al on the Si(100) surface studied by STM and KMC simulations
M Kučera, Charles University in Prague, Czech Republic

P2.138 Isolated silicon dangling bonds (IDBs) on water saturate Si (001)-2 x 1 surface
D Pierucci, LCPMR/Synchrotron Soleil, France

P2.139 Ethylene adsorption on silicon surfaces modified by group III and IV metals studied by STM
P Zimmermann, Charles University, Czech Republic

P2.140 Strain induced intermixing of Ge into Si epitaxial layer
Y Shigeta, Yokohama City University, Japan

P2.141 Effect of electron-optical phonon interaction on resonant tunneling in wurtzite GaN/In$_x$Ga$_{1-x}$N double barrier structures
S Ban, Inner Mongolia University, China

P2.142 Transport and mechanical properties of molecular junctions formed by acetophenone deposited on Si (100) surface
O Krejčí, Institute of Physics of Czech Academy of Science, Czech Republic

P2.143 A combined STM and SXRD investigation into the ZnO(0001) polar surface
L Deacon, University of Reading, UK

P2.144 Ultrasoud influence on the Si-SiO$_2$ interface properties
D Kropman, Tallinn University of Technology, Estonia

Surface dynamics: space/time/energy-resolved

P2.145 Adsorption of cyclooctyne on clean and hydrogen precovered Si(001) surfaces
G Mette, Philipps-Universität Marburg, Germany

P2.146 Molecular orientation in monolayer H_2 on ionic surfaces
D Jack, Univeristy of British Columbia, Canada

P2.147 H_2 diffraction from a strained pseudomorphic monolayer of Cu deposited on Ru(0001)
C Díaz, Universidad Autónoma de Madrid, Spain

P2.148 Incommensurate sliding of graphene flakes on graphite: effect of pressure, substrate and distortions
M van Wijk, Radboud University Nijmegen, The Netherlands

P2.149 Beyond the oxidation of ferritic stainless steel surfaces: Initial oxidation stages of CrC and CrN enriched Fe-17Cr(100)
M Ahonen, Tampere University of Technology, Finland

P2.150 Dynamics and condensation in alkali metal films on Ni(100)
S Paterson, University of Cambridge, UK

P2.151 Two dimensional C_{60} vapour on graphite(0001)
M Hunt, Durham University, UK

P2.152 A new type of detector for dynamic XPS measurements
K Winkler, Omicron NanoTechnology GmbH, Germany

P2.153 Deposition of alkane fragments on aluminium studied by numerical simulations
C Turgut, CRP Gabriel Lippmann, Luxembourg

P2.154 Sputter deposition of polystyrene (PS) molecular fragments on silver (Ag)
C Turgut, CRP Gabriel Lippmann, Luxembourg

P2.155 Computational simulation of time-dependent porosity in micro-porous molecular materials
M Lewis, University of Liverpool, UK

P2.156 Organic nanofibers as waveguides and emitters of surface plasmon polaritons
S Jauernik, Christian-Albrechts-Universität zu Kiel, Germany

P2.157 Diffusion of hydrogen on the Ni(111) surface studied with helium spin echo
J Zhu, University of Cambridge, UK

P2.158 Monte Carlo study of quasi-orthorhombic acetylene thin films on KCl (001)
A Sallabi, Misurata University, Libya

P2.159 Electron stimulated processes of astrophysically relevant molecules at solid surfaces
D Marchione, Heriot-Watt University, UK

Surface reactions, kinetics and catalysts

P2.160 Temperature induced reaction of Maleic anhydride on Pt (111) surface
G Sinha, Aalto University, Finland

P2.161 Design and commisioning of a new, highly integrated UHV surface science system
E Galloway, AWE Plc, UK

P2.162 Hydrogenation of unsaturated hydrocarbons over Fe_3O_4 supported Pd nanoparticles: activation and reactivity of the pro-chiral molecule isophorone
C O'Brien, Fritz-Haber-Institut, Germany

P2.163 Catalyzed oxidation of aniline to form nitrobenzene, obtained from a graphene oxide layer
H Lee, Sookmyung Women's University, South Korea

P2.164 Adsorption and polymerization of TCPQ molecules on Cu(100) surfaces
Y Wang, Universidad Autonoma de Madrid, Spain

P2.165 Diffusion of particles over heterogeneous surface: a case of patchwise bivariate lattice
A Tarasenko, Institute of Physics of the Academy of Science, Czech Republic

P2.166 XPS and HRTEM study of nanosized CuO oxides active in CO oxidation at low temperatures
D Svintsitskiy, Novosibirsk State University, Russia

P2.167 Thermally-assisted electron-induced atomic manipulation in the STM
L Tang, University of Birmingham, UK

P2.168 XPS study of strongly oxidized palladium nanoparticles
L Kibis, Boreskov Institute of Catalysis, Russia

P2.169 TPD and STM investigations on novel p(3×1)Sn_xPt (110) and p(6×1)Sn_xPt (110) surface alloys
J Zheng, Padova University, Italy

P2.170 XPS and HRTEM study of self-sustained oscillations in the reaction of CO oxidation using Pd/Al_2O_3 catalysts
A Boronin, Boreskov Institute of Catalysis, Russia

P2.171 Thermal desorption spectroscopy of astrophysically relevant molecules on olivine and single crystal forsterite
T Suhasaria, University of Muenster, Germany

P2.172 Surface-bulk phase transitions as a driving force of the active sites formation in Pd/CeO_2 catalysts of low-temperature CO oxidation
R Gulyaev, Boreskov Institute of Catalysis, Russia

P2.173 Methanol decomposition on Pt nanoclusters on a thin film of Al_2O_3/NiAl(100)
M-F Luo, National Central University, Taiwan

P2.174 Density functional theory-based analysis on O_2 molecular interaction with the doped and Un-doped Tri-s-triazine-based graphitic carbon nitride
S Aspera, Osaka University, Japan

P2.175 Mo(CO)$_6$ monolayer growth and decomposition on copper (111) and (100) surfaces
M Petukhov, Université de Bourgogne, France

P2.176 Ultrathin phases of ceria on Cu(111)
V Stetsovych, Charles University, Czech Republic

P2.177 Adsorption and dissociation of hydrogen sulfide on metal surfaces: a first-principles calculation
D Matsunaka, Osaka University, Japan

P2.178 Functional groups on carbon surfaces: how do they influence the deposition of gold?
R Davies, Cardiff University, UK

P2.179 Relation between structure of Pt-ceria catalyst and its tolerance for CO
V Johanek, Charles University, Czech Republic

P2.180 Theoretical and experimental study of H_2 adsorption on Pd atoms deposited on Cu(111)
H F Busnengo, Instituto de Física Rosario (CONICET-UNR), Argentina

P2.181 Study of adsorption of acetophenone and some of its derivatives in aqueous solution on surface of libyan palm charcoal
A A Obeid, Misurata University, Libya

P2.182 Reaction of ethanol on Ru(0001)
M Sturm, Dutch Institute for Fundemental Energy Research (DIFFER), The Netherlands

P2.183 Desorption of O_2, CO and N_2 from astronomically relevant surfaces
J Lasne, Heriot-Watt University, UK

P2.184 Surface reactivity of Anatase 101 e 001 surfce: a DFT periodic study
A M Ferrari, Dipartimento Chimica Univesita' Torino, Italy

P2.185 The reactivity of the ZnS(110) surface: a periodic DFT study
A M Ferrari, Dipartimento Chimica Univesita' Torino, Italy

P2.186 Spontaneous ester formation controlled by concentration at the liquid -solid interface
N T N Ha, Chemnitz University of Technology, Germany

P2.187 Investigating interactions between polycyclic aromatic hydrocarbons and atomic hydrogen
A Cassidy, Aarhus Univeristy, Denmark

P2.188 CO oxidation over ultrathin ZnO films on Pt(111)
Y Martynova, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

P2.189 Evaluation of paper surface chemistry during ageing by ToF-SIMS
S Bialczak, Åbo Akademi University, Finland

P2.190 Low-pressure oxidation behavior of FeAl –alloys on 600-800°C
H Izzuddin, Max-Planck-Institut für Eisenforschung, Germany

P2.191 H-abstraction reaction from methane in straight channel of H-ZSM-5 zeolite containing O(3P) atom: A D-DFT study
A Palma, CNR – Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Italy

Plenary speakers - biographies

Masakazu Aono

International Center for Materials Nanoarchitectonics, Japan

Masakazu Aono is the director general of the International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Japan. He obtained his PhD from the University Tokyo in 1972, and was subsequently a research staff member at the National Institute for Research in Inorganic Materials (NIRIM) [1972-1986], a senior scientist at the Institute for Physical and Chemical Research (RIKEN) [1986-2002], a professor at Osaka University [1996-2005], and the director general of the Nanomaterials Laboratory (NML), NIMS [2002-2006]. He arrived at the present position at MANA in 2007; MANA is one of six research centers in the framework of the World Premier International Research Center Initiative (WPI Program) of the Ministry of Education, Culture, Science and Technology [MEXT], Japan. His main research interests lie in nanoscale science and technology (in particular, "nanoarchitectonics", which is his coined word), nanoelectronics, and surface/interface science and technology. He received Minister of Science and Technology Prize, Minister of MEXT Prize, Japan Surface Science Society Award, Feynman Prize in Nanotechnology, etc., and was elected as a fellow of various societies including the American Vacuum Society (USA), the Institute of Physics (UK), the Japan Society of Applied Physics, etc. He serves on various international editorial board such as Surface Review and Letters, Probe Microscopy, Nanoscience, Nanotechnology, Small, ACS Nano, etc.

Sébastien Balibar

École normale Supérieure, France

After undergraduate studies at the Ecole Polytechnique (Paris, 1966-69), Sébastien Balibar graduated at the Ecole Normale Superieure under the supervision of Albert Libchaber (Paris, 1976). He is presently a CNRS Directeur de Recherche at the same ENS in Paris. After a one year postdoc at Nottingham and Exeter (UK), he founded his own research group at ENS (Paris) where he stayed except for several visits in foreign Universities, including the Ohio State University (Columbus USA) , Konstanz Universität (Germany), Kyoto University (Japan) and Harvard University (Cambridge, USA). His main scientific contributions are in the fields of quantum fluids and solids (quantum evaporation, quantum nucleation, supersolidity, quantum plasticity...), crystal surfaces (roughening, growth dynamics, instabilities...), wetting, phase transitions, cavitation in simple and complex liquids (helium 3 and 4, water). He also worked on musical acoustics and history of science. He published more than 200 scientific articles and gave about 100 invited communications in international conferences. He wrote two popular books ("La pomme et l'atome" Odile Jacob ed. 2005 ("The atom and the Apple", Princeton University Press 2008) and "Je casse de l'eau", Le Pommier ed. 2008) showing a constant interest in scientific information.

Klaus Heinz

University Erlangen-Nuernberg, Germany

Klaus Heinz was a Professor of Physics at the University of Erlangen-Nuernberg. He holds a Diploma from the University of Mainz (1968, thesis on Theoretical High Energy Physics) and a Doctoral degree from the University of Karlsruhe (1972, thesis on Experimental Semiconductor Physics). After moving to Erlangen (1972) he turned to surface physics concentrating largely on surface crystallography (Habilitation 1977, Professor 1980). The main research issues he addressed include structure determination by low-energy electron diffraction, surface reconstruction, structural phase transitions, ordered and disordered adsorption systems, alloy surfaces, metallic epitaxy and, since 2006, epitaxial oxide films.

Richard Jones

The University of Sheffield, UK

Richard Jones is Professor of Physics and Pro-Vice-Chancellor for Research and Innovation at the University of Sheffield. His first degree and PhD in Physics both come from Cambridge University, and following postdoctoral work at Cornell University, U.S.A., he was a lecturer at the University of Cambridge's Cavendish Laboratory. In 1998 he moved to the University of Sheffield. In 2006 he was elected a Fellow of the Royal Society, and in 2009 he won the Tabor Medal of the Institute of Physics for contributions to nanoscience. He is an experimental polymer physicist who specialises in elucidating the nano-scale structure and properties of polymers and biological macromolecules at interfaces. In addition to his work as an experimental physicist, he has written extensively on the wider societal and ethical issues surrounding nanotechnology.

Lars Samuelson

Lund University, Sweden

Lars Samuelson obtained his Ph.D. in Solid State Physics at Lund University in 1977. After a post-doc at IBM Research Laboratories in San José, California, he returned to Lund in 1979. In 1986 he became Professor in Semiconductor Physics at Chalmers/Göteborg University and returned to the Physics Department of Lund University in 1988 to take up a Professorship in Semiconductor Electronics. He is the director of the Nanometer Structure Consortium at Lund University (nmC@LU - www.nano.lu.se), started in 1988, and today the primary interdisciplinary center for Nanoscience in Sweden, engaging more than 175 scientists and PhD-students. He is recognized for his research on low-dimensional structures and the physics and applications thus made possible. In recent years his research has been focused on the formation of ideal one-dimensional nanowires through self-assembly, studies of their physical properties, as well as applications of semiconductor nanowires in electronics, photonics and the life-sciences. He has published more than 500 papers in refereed journals and given about 250 invited/plenary talks at international conferences (h-index≈61). In 2004 he became a Fellow of the Institute of Physics, FinstP, in the United Kingdom, and in 2009 Fellow of the American Physical Society (Materials Physics). He is since 2006 a Member of the Royal Swedish Academy of Sciences, KVA (Physics) and since 2007 of the Royal Swedish Academy of Engineering Sciences, IVA. In 2008 he was awarded as "Einstein Professor" by the Chinese Academy of Sciences. Beside his role as academic researcher and teacher, he has engaged himself in creation of spin-out companies and is the primary founder and Chief Scientific Officer (CSO) of the companies Qumat Technologies AB, QuNano AB, GLO AB and Sol Voltaics AB.

David Vanderbilt

Rutgers University, USA

David Vanderbilt received his BA in Physics from Swarthmore College in 1976 and his PhD in Physics from the Massachusetts Institute of Technology in 1981. He spent three years as a Miller Postdoctoral Fellow at the University of California at Berkeley before joining the faculty of the Physics Department at Harvard University in 1984, first as an Assistant and then as an Associate Professor. He has been a Professor in the Department of Physics and Astronomy at Rutgers University since 1991, and was named Board of Governors Professor of Physics in 2009. Dr. Vanderbilt is an expert in the development of methods for electronic structure calculations and the application of such methods for computational materials theory. His current research interests include the development of methods for treating insulators in finite electric fields, advancing the theory and applicability of Wannier functions, and applying Berry-phase methods to study magnetic systems. One class of applications focuses on the dielectric and piezoelectric properties of novel oxide materials, especially structural phase transitions, lattice contributions to dielectric and piezoelectric activity, and properties of interfaces and superlattices. Another research thrust is concerned with anomalous Hall conductivity, orbital magnetization, magnetoelectric couplings, and topological insulators. Dr. Vanderbilt has published over 230 articles in scientific journals and has a Web of Science h-index of 64. He is a Fellow of the American Physical Society (APS), is a winner of the 2006 Rahman Prize in Computational Physics awarded by the APS, and served as Chair of the Division of Materials Physics of the APS in 2006.

Ellen Williams

BP, UK

Ellen Williams joined BP as Chief Scientist in January, 2010. She is responsible for supporting the basic science that underpins the company's technology programs, as well as its major university research programs around the world. She also provides strategic scientific advice to BP's senior executives on matters of Group significance. Her research background is in the field of nanoscience, where she pioneered the quantitative use of scanned probe microscopy in the statistical mechanics of surfaces and new materials.

Martin Wolf

Fritz-Haber Institute of the Max-Planck-Society, Germany

Martin Wolf studied physics at the Freie Universität Berlin and received his PhD there in 1991with Gerhard Ertl for studies on surface photochemistry. After a postdoc period in Austin, Texas, with Mike White, he set up a laboratory for femtosecond surface spectroscopy at the Fritz-Haber-Institute of the Max-Planck Society and was also a visiting scientist at IBM Yorktown Heights with Tony Heinz. In 2000 he was appointed full professor for experimental physics at the Freie Universität Berlin. Since 2008 he has been director of the Physical Chemistry department at the Fritz-Haber-Institute in Berlin. His research focuses on the dynamics of elementary excitations at surfaces, interfaces and in solids, ultrafast photoinduced dynamics and transient electronic structure in correlated materials, interfacial electron transfer, photochemistry and vibrational spectroscopy at interfaces.

Plenary speakers – abstracts

Monday 3 September

Polymer photovoltaics – sophisticated nanostructures that make themselves

R Jones

The University of Sheffield, UK

Photovoltaic devices made from semiconducting polymers perform less well than their counterparts made from inorganic semiconductors, so they will only be competitive if they can be made very cheaply, at large scale. Yet their effective performance depends on quite precise control of their nanostructure, with abundant internal interface and length scales commensurate with the important electronic processes. However, it turns out that quite complex and effective morphologies can emerge from rather simple processing methods, depending on the deposition of thin films from solvents through coating and printing techniques. To control and optimise this, one needs to understand the rich complexity in the way that nano- and micro- structure emerges from a combination of considerations based on equilibrium thermodynamics and the non-equilibrium kinetics of phase changes taking place during processing. For thin films, these factors are further affected by strong and long-ranged perturbations imposed by surfaces and interfaces. In my talk, I will review the basic physics underlying macro- and micro- phase separation, chain dynamics and crystallisation in bulk and near interfaces, and illustrate these principles with experimental studies of morphology development in organic photovoltaic devices.

Tuesday 4 September

Epitaxial cobalt-oxide films - The importance of surface crystallography

K Heinz and L Hammer

University Erlangen-Nuernberg, Germany

Thin films of transition-metal oxides represent, compared to their bulk phases, systems on their own as the oxide-vacuum and the oxide-support interface lead to new phases. Here, concentration is on cobalt-oxide films grown on (a) a clean Ir(100) surface and (b) on this surface covered by pseudomorphic Co layers. Surprisingly in view of the square symmetry of the support, LEED and STM show that thick CoO and Co_3O_4 films grow in the polar (111) orientation on Ir(100). Even more surprising is that on Co/Ir(100) rocksalt-type CoO grows in the non-polar (100) orientation though the 10% lattice misfit with the support is the same. For ultrathin films the interference of the two interfaces leads to a number of different phases.

Interpretation of these phenomena comes largely by crystallography: Quantitative LEED reveals for CoO(111) that a surface slab of the film is of wurtzite structure which, according to published DFT calculations, makes the surface metallic, so avoiding polarity. Co_3O_4(111) films are terminated by only a fraction of the oxide repeat unit allowing for polarity compensation. In the (100)-oriented growth on Co/Ir(100) the first oxidic layer is of (100)-type with, however, a c(4x2) arrangement of Co vacancies. Due to the modified interface chemistry it is stable on Co/Ir(100) but not on Ir(100) in agreement with DFT calculations. It is a precursor for further defect-free (100) growth. The structural elements of the ultrathin films are pyramids of Co squares or triangles with O ontop developing with varying stoichiometry.

Wednesday 5 September

Controlling atomic- and molecular-scale electrochemical reactions at designated positions

M Aono, T Hasegawa, T Nakayma and Yge Okawa

International Center for Materials Nanoarchitectonics, Japan

It is of great importance both scientifically and technologically to control local atomic- and molecular-scale electrochemical reactions at designated positions on solid surfaces or molecular films; in many cases, it is desirable to control the electrochemical reactions reversibly. In this paper, we demonstrate such controls of electrochemical reactions by taking the following three topics I) - III) as remarkable examples.

Topic I) *Reversibly controlling the chemically unbound and bound states of a few adjacent* C_{60} *molecules at a designated position in a thin film of* C_{60}. We have developed a method that can control the formation and dissociation of a linear dimer, trimer, tetramer or pentamer of C_{60} molecules reversibly at will. The chemical mechanisms underlying the method and the application of the method to single-molecule-level ultra-dense digital memory (~200 Tb/in2) are discussed.

Topic II) *Electrically wiring a single functional molecule (phthalocyanine (Pc)) with conductive linear polymer wires (polydiacetylene (PDA)) via spontaneously formed firm chemical bonding (chemical soldering) by using chain reactions.* Discussions are made regarding the mechanisms of the wiring and chemical soldering and the possibility of the realization of a PDA-Pc-PDA single-molecule resonant tunneling diode.

Topic III) *Reversibly controlling the growth and shrinkage of a cluster of metal atoms as a conduction path.* This is the mechanism of ON/OFF switching of the atomic switch developed in our group. In certain conditions, the atomic switch exhibits interesting characteristics similar to the synapse in the human brain. Due to the synaptic characteristics of the atomic switch, we will be able to create material-based neuromorphic circuits formed by a network of atomic switches.

Research in the energy industry

E Williams

BP, UK

BP provides energy in a world of increasing demand and increasing complexity. Everyone wants secure, reliable, and affordable energy, but climate change, resource scarcity, and technical innovation are transforming the energy landscape. There are many possible pathways to a sustainable energy future, and each presents technical challenges that will influence the global-scale asset and infrastructure deployment that take place with time scales of decades.

BP's energy portfolio encompasses many of the research challenges in this arena. Research topics in condensed matter physics, materials science and nanotechnology cut across the spectrum of development areas. These include applications in the sub-surface environment, structural integrity, energy conversion, chemical conversion and separation, fluid flow, and sensing & actuation. Continuing advances in the power of experimental and computational tools now allow new progress on old problems. Developments in material discovery also open new opportunities.

The process of research in a developmental pipeline will be reviewed, along with a description of BP's distributed approach to innovation. Examples of research activities across the portfolio of BP's energy program will be presented.

Berry phases and curvatures in computational electronic structure theory

D Vanderbilt

Rutgers University, USA

The role of Berry phases in the theory of electric polarization is by now well established. In this talk I will discuss several physical phenomena involving orbital currents, for which the properties of interest can be computed from first principles based on a formulation in terms of Berry phases or Berry curvatures.

First, I will review the formulation of the intrinsic anomalous Hall conductivity (AHC) of ferromagnetic metals in terms of Berry curvature, which involves integrating the Berry curvature over the filled Fermi sea. The approach is illustrated via calculations of the AHC of Fe, Ni and Co using Kubo-formula methods [1] or using the Berry curvature method via Wannier interpolation [2]. Comparison with experiment suggests that the intrinsic terms are dominant for this class of ferromagnetic metals.

Second, I will discuss the calculation of orbital magnetization. Traditionally this has been calculated by integrating orbital currents inside muffin-tin spheres, but a proper formulation again requires calculations of terms involving the Berry curvature in k-space, or a related quantity in which the Hamiltonian is sandwiched inside a Berry curvature [3-6]. Again using elemental ferromagnetic metals as the prototypical system, I will review calculations of these quantities using direct [7] or Wannier-interpolation [8] methods.

As a third example, I will discuss the linear magnetoelectric coupling, using Cr_2O_3 as a prototypical example. We compute both lattice-mediated and electronic contributions in both spin and orbital channels. The most subtle contribution is the electronic-orbital one. The form of this contribution is derived in terms of the variation of the orbital magnetization in the presence of an electric field. One term in this expression involves the integration of a Chern-Simons three-form over the three-dimensional Brillouin zone [9-12]. Finally, I will briefly explain the connection between this Chern-Simons coupling and the theory of strong topological insulators in three dimensions.

[1] Y. Yao et al., Phys. Rev. Lett. 92, 037204 (2004).
[2] X. Wang, J.R. Yates, I. Souza, and D. Vanderbilt, Phys. Rev. B 74, 195118 (2006).
[3] D. Xiao, J. Shi, and Q. Niu, Phys. Rev. Lett. 95, 137204 (2005).
[4] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. 95, 137205 (2005).
[5] D. Ceresoli, T. Thonhauser, D. Vanderbilt, and R. Resta, Phys. Rev. B 74, 024408 (2006).
[6] J. Shi, G. Vignale, D. Xiao, and Q. Niu, Phys. Rev. Lett. 99, 197202 (2007).
[7] D. Ceresoli, U. Gerstmann, A.P. Seitsonen, and F. Mauri, Phys. Rev. B 81, 060409(R) (2010).
[8] M.G. Lopez, D. Vanderbilt, T. Thonhauser, and I. Souza, Phys. Rev. B 85, 014435 (2012).
[9] X.-L. Qi, T. L. Hughes, and S.-C. Zhang, Phys. Rev. B 78, 195424 (2008).
[10] A. M. Essin, J. E. Moore, and D. Vanderbilt, Phys. Rev. Lett. 102, 146805 (2009).
[11] A. Malashevich, I. Souza, S. Coh, and D. Vanderbilt, New J. Phys. 12, 053032 (2010).
[12] S. Coh, D. Vanderbilt, A. Malashevich, and I. Souza, Phys. Rev. B 83, 085108 (2011).

Thursday 6 September

Transient electronic structure and ultrafast dynamics of solids

M Wolf

Fritz-Haber Institute of the Max-Planck-Society, Germany

The electronic properties of complex materials are often governed by strong electron-phonon coupling and many-body correlation effects leading to phenomena like metal insulator transitions or superconductivity and the formation of broken symmetry ground states. On example for the coupling between electronic and phonon degrees of freedom are thermally or optically induced phase transitions in charge-density wave (CDW) materials whereby a periodic lattice distortion leading to an opening of an electronic gap at the Fermi surface. Ultrafast optical excitation can induce non-equilibrium phase transitions as well as electronic and geometrical structure changes of such complex materials on femtosecond timescales. We use time- and angle-resolved photoemission spectroscopy (trARPES) to probe directly the resulting transient evolution of the electronic structure and the collective phonon dynamics of the system through their influence on the quasiparticle band structure. Using this technique, we present a systematic study of the tri-telluride CDW system and the high T_c cuprate BSCCO. Finally we discuss the prospects of low-energy excitations (coherent phonons, magnons) to optically control and probe transient states of matter.

Friday 7 September

Semiconductor nanowires for optoelectronic and energy applications

L Samuelson

Lund University, Sweden

Semiconductor nanowires can be grown with a high degree of perfection and find their use into various kinds of devices. Research on the growth of nanowires has led to many unique opportunities, such as a high degree of freedom in combining different semi-conductors into 3D heterostructures. Interesting nanowire-specific challenges are also dealt with, such as the ambiguity in the stacking sequence in grown nanowires, easily leading to mixtures of cubic (zinc-blende) and hexagonal (wurtzite) structures.

I will present the present degree of control of growth and top-down guided bottom-up, or self-assembly, of ideal arrays of designed nanowires. I will also give examples of growth of ideal heterostructures for basic physics as well as for device applications, including opportunities for growth of compound nanowires on silicon substrates. Specifically, I will describe recently resolved details of how III-nitride nanowires nucleate and how their growth can be controlled in a 1D nanowire fashion.

Finally, I will present recent progress in the field of nanowire device applications, such as ultra-low power wrap-gate and tunnel field-effect transistors, as well as for on-silicon photonic devices, in a “more than Moore”-fashion. Finally I will describe how III-V nanowire arrays show great promise for important energy applications, such as for the conversion of sunlight into electricity, i.e. in solar cells, and for the opposite process of conversion of electrical energy into light, i.e. in light emitting diodes.

The quantum plasticity of helium crystals

S Balibar, A Haziot, X Rojas, A Fefferman and J Beamish

École normale Supérieure, France

The plasticity of crystals is usually attributed to the motion of their dislocations. Solid helium offers unique opportunities to study the basic principles of plasticity. This is because it can be prepared at low temperature without any impurity and with very low dislocation densities. We will show video sequences to explain how we measure the elastic properties of helium crystals as a function of their orientation. Taking advantage of these exceptional properties, we have discovered that, in the absence of impurities, helium crystals do not resist to shear in particular directions.

Our series of measurements demonstrate that this exceptional softening is due to dislocations gliding by quantum tunneling along the basal planes of the hexagonal structure. This "quantum plasticity" disappears as soon as traces of ^{3}He impurities bind to dislocations and apparently suppress their mobility. I will explain why this plasticity is an alternative explanation for the rotation anomalies of the same crystals, which has been attributed to their possible "supersolidity".

Invited speakers - biographies

Jong-Hyun Ahn

Sungkyunkwan University, South Korea

Jong-Hyun Ahn obtained his PhD from POSTECH, Republic of Korea in 2001. From 2004 to 2008, he was a research associate at the University of Illinois at Urbana/Champaign. In 2008, he joined Sungkyunkwan University, Republic of Korea, where he has been an associate professor and SKKU fellow since 2012. His research interests focus on graphene growth and their application in flexible electronics.

Morgan Alexander

The University of Nottingham, UK

Morgan Alexander is Professor of Biomedical Surfaces at the School of Pharmacy, University of Nottingham and a Royal Society-Wolfson Research Merit Award holder. He received his Bachelor of Science in Materials in 1988 and his PhD from the same department at The University of Sheffield in 1992. He leads the Laboratory of Biophysics and Surface Analysis which consists of 8 independent academics with complementary expertise in solving fundamental and applied biomolecular, biomaterial and (bio)formulation problems.

His work comprises developing materials for application in biological environments and characterising relationships between the surface and biological response. Understanding these relationships is critical in the development of biomaterials and is the theme running through his group's work across a variety of biomedical application areas spanning bacterial adhesion to controlling stem cell response.

He has contributed to books on surface chemical modification and analysis and has authored over 130 papers dealing with surfaces in high quality peer reviewed publications, including research articles in Nature Materials, PNAS, Nature Communications, Advanced Materials, and Biomaterials. This research is highly interdisciplinary, involving collaborators from a wide variety of fields including regenerative medicine, neuroscience, developmental biology, pharmaceutics, materials processing, plasma physics and nanofabrication. This work is funded by The Wellcome Trust, EPSRC, BBSRC, EMDA, MRC, DSTL and industry.

Maria-Carmen Asensio

Synchrotron SOLEIL, France

Currently, permanent research staff of the SOLEIL synchrotron, she is also permanent associated staff of the Institute of Material Science of Madrid, since 1991. She has commenced her academic career in Argentina, where after completing her Bsc degree in Physical Chemistry, she finished her PhD degree in Surface Science. Then she held a two-year Senior Lecturer in Physics at the Autonomous University of Madrid, followed by a two-year post-doctoral position at the Warwick University in the group of Prof. Woodruff. Following her work in photoelectron diffraction studies of adsorbed molecules, she joined the Fritz Haber Institute of the Max-Planck in Berlin, collaborating in a large European Research Consortium. Her research has involved a wide range of fundamental studies using synchrotron radiation based techniques devoted to the characterization of novel materials, in the area of Solid State Physics. In particular, her work has been centered on the structural determination of ordered interfaces using angular and energy scanned photoelectron diffraction techniques and the electronic structure determination by angle resolved photoelectron spectroscopy (ARPES). Lately, she has developed an innovative technique by combining ARPES and microscopy, named Nano-ARPES. She is author of more than 145 scientific publications in refereed journals and gives regularly invited talks in international conferences.

Christopher Bell

Stanford University, USA

Christopher Bell completed his Ph.D. at Cambridge University in 2004, and continued there in a Post-Doctoral position for one year, before moving to the University of Leiden for two years. He was a Canon Foundation in Europe Fellow at The University of Tokyo, from 2007 to 2008, then a Post-Doctoral researcher until 2010, when he became a Research Assistant Professor. From May 2011 he has been an Associate Staff Scientist at SLAC National Accelerator Laboratory, Stanford University. He has research interests ranging from the physics of low dimensional transport, including superconductivity, magnetism and novel proximity effects, to the materials science and chemistry of interfaces and surfaces.

Gabriel Bester

Max-Planck-Institut für Festkörperforschung, Germany

Dr. Gabriel Bester studied physics at the University of Stuttgart where he obtained his Master of Science in 1997. His Master's thesis focused on the connection between the thermodynamic properties of defect formation and its microscopic origin. By combining "ab-initio" density functional calculations (DFT) with a thermodynamic model, he gained access to the energetics of atomic defects and their concentrations. He applied the theory to intermetallic compounds. In 2001 he obtained his PhD based on the work he did at Max-Planck institute for Metal Research in Stuttgart in the group of Prof. Manfred Fahnle. The work focused on the interpretation of results obtained in the framework of DFT in the language of bonding/antibonding interatomic interactions. The connection to this intuitive chemical language was established by defining a bond strenght (Ecov) valid for periodic systems. Following his PhD he joined the group of Dr. Alex Zunger at the National Renewable Energy Laboratory (NREL) as a Postdoc, where he worked on the calculation of the electronic and optical properties of nanostructures. From 2004 until 2007 he worked in the Solid State Theory group at NREL as Senior Scientist on the development of numerical methods and the application of these methods to a variety of problems in the realm of quantum dot physics. In 2007 he was appointed as independent junior research group leader at the Max Planck Institute for Solid State Research. In 2012 he obtained the hablitation from the University of Stuttgart.

Peter Beton

The University of Nottingham, UK

Peter Beton joined the University of Nottingham in 1988 as a postdoc and, following a period as a Royal Society University Research Fellow, was appointed to the academic staff in 1994. His research interests lie at the intersections between materials science, physics, chemistry and device technology and his recent work has been focussed on supramolecular templates, random tiling, two-dimensional covalent networks and the deposition of polymers and polymer nanorings on metal surfaces.

Maria Blanco-Rey

Donostia International Physics Center (DIPC), Spain

Maria Blanco-Rey carried out her PhD in the Materials Science Institute of Madrid (belonging to CSIC) on the topic of theory of Low-Energy Electron Diffraction, and got her doctorate degree from the Autonomous University of Madrid in 2006. From 2007 to 2010, she joined the Surface Science Group of the Department of Chemistry in the University of Cambridge (UK) as a Postdoctoral Research Fellow. Her research subjects during that period were catalysis on palladium oxide surfaces an surface chirality using ab-initio methods. Since December 2010, she works as a Research Fellow at the Donostia International Physics Center in San Sebastian (Spain), where she investigates dynamical processes on surfaces.

Volker Blum

Fritz-Haber-Institute, Germany

Volker Blum received his doctorate in physics at the University of Erlangen-Nuernberg on surface crystallography of alloy surfaces in 2002. After a stay at the National Renewable Energy Laboratory in Golden, Colorado (2002-2004, structure and thermodynamics of metallic alloys from first principles), he joined the Fritz Haber Institute (Berlin), where he is a research group leader today. His primary interest is the prediction, from quantum-mechanical first principles, of the structure, dynamics, electronic and vibrational properties of nanostructured molecules and surfaces. Where necessary, this work involves pushing out the computational limits of electronic structure theory in the context of the FHI-aims all-electron electronic structure code.

Christine Boeglin

IPCMS, France

C. Boeglin is a Research Director at CNRS in France. After her Ph.D. from Université de Strasbourg, she spent one year at Freie Universität Berlin in the groups of Prof. J. Kirschner. She is an expert in the field of X-ray spectroscopy and X-ray magnetic circular dichroism in condensed-matter physics. Her current research focuses on the study of dynamical processes in magnetic nanostructures, using picosecond and femtosecond X-ray pulses. Recently her group distinguish for the first time the ultrafast dynamics of the spins and of the orbital magnetic moments excited by an Infra Red laser pulse. Reference : C. Boeglin, E. Beaurepaire, V. Halté, V. Lopez-Flores, C. Stamm, N. Pontius, H. Dürr, J. -Y. Bigot "Distinguishing the ultrafast dynamics of spin and orbital moments in solids " Nature 465, 458-461 (2010).

Kirill Bolotin

Vanderbilt University, USA

Dr. Kirill Bolotin received his undergraduate degree from the Moscow Institute of Physics and Technology and his PhD from Cornell University. His thesis work was focused on developing metal-nanoparticle single-electron transistors and studying the quantum analog of anisotropic magnetoresistance. He then became a postdoctoral scientist at Columbia University, working with the groups of Horst Stormer and Philip Kim. There he discovered the approaches to fabricate ultrahigh mobility graphene, found several new phenomena - such as the Fractional Quantum Hall effect -- in such devices, and participated in development of ultrasensitive graphene nanomechanical resonators. Since 2009, Bolotin is an assistant professor at Vanderbilt University. The Bolotin group explores the limits of mobility in graphene devices, explores applications of graphene resonators, and studies novel classes of materials obtained by stacking different 2D crystals. Bolotin was recently awarded the NSF Career and the Sloan foundation awards.

Hans Boschker

University of Stuttgart, Germany

Hans Boschker studied applied physics at the University of Twente. He graduated in 2006, working on superconducting electronic devices under thesupervision of Prof. Hilgenkamp. For his PhD thesis, he worked on the conducting $LaAlO_3/SrTiO_3$ interface, $La_{0.67}Sr_{0.33}MnO_3$ thin films, $La_{0.67}Sr_{0.33}Mn_{03}$ magnetocrystalline anisotropy and

$La_{0.67}Sr_{0.33}Mn_{03}/SrTiO_3$ interfaces under the supervision of Prof. Rijnders and Prof. Blank at the University of Twente. He graduated Cum Laude in 2011. He presently works at the Max Planck Institute for Solid State Research in Stuttgart in the group of Prof. Mannhart.

Alexandre Bouhelier

Centre National de la Recherche Scientifique, France

Alexandre Bouhelier is a permanent researcher at the CNRS working at the University of Burgundy, Dijon France. He holds a doctorate in Physics (2001) from the University of Basel, Switzerland, where he worked in near-field optics. His interests are focused on the fundamental aspect of plasmonics and near-field optics. He was a distinguished fellowship of the Center for Nanoscale Materials, Argonne N'tl laboratory and Fellowship of the Swiss National Science Foundation. A Bouhelier is author or co-author of more than 60 scientific publications, 2 patents, and 4 contributed book chapters.

Peter Broekmann

University of Bern, Switzerland

Peter Broekmann studied chemistry at the University of Bonn, where he gained a PhD in physical chemistry in 2000. After a postdoctoral stay in the group of Prof. Bene Poelsema at the University of Twente (Netherlands) he started a habilitation project at the Institute of Physical Chemistry in Bonn. Since October 2007 he is member of the BASF copper plating team. In October 2008 he accepted a lecturer position for interfacial electrochemistry at the University of Bern. His research is focused on copper electrochemistry utilizing in-situ scanning probe techniques, in-situ X-ray diffraction and ex-situ photoelectron spectroscopy

Jane Brown

Loughborough University, UK

I was born in 1932 in Scotland in the rural village of Baldernock. I spent my Undergraduate and Post Graduate years at Cambridge as a member of Newnham College reading for the Natural Sciences Tripos with Part II in Physics and subsequently undertaking research for a PhD in the Cavendish laboratory on the Structures of some intermetallic compounds. I did two years post doctoral research in the USA at Brookhaven National laboratory where I had my first encounter with neutron diffraction and in particular with polarised neutrons. On my return to Cambridge as fellow of Newnham College and Assistant Director of research in the Cavendish laboratory I started a group working on magnetic crystallography in association with the solid state division at Harwell. 12 years later when the British joined France and Germany in signing the treaty to exploit the ILL research reactor I moved there as senior scientist responsible for the diffraction group. At the ILL my research was mainly in the field of polarised neutrons, developing techniques for their use and programs for evaluating and exploiting the results. I retired officially from the ILL staff in 1994 but continued as a long term Visitor and visiting Professor at Loughborough University until October 2011. I am now living in Cambridge and trying to work through a backlog of incompletely treated data.

Harald Brune

École Polytechnique Fédérale de Lausanne, Switzerland

Harald Brune is Full Professor at the Swiss Federal Institute of Technology in Lausanne (EPFL). He has obtained his Diploma in Physics at Ludwig Maximilians University in Munich in 1989 and 1992 his PhD in Physical Chemistry under the guidance of Profs. G. Ertl (2007 Nobel laureate in Chemistry) and R. J. Behm at the Fritz-Haber Institute of the Max-Planck Society in Berlin. He has joined the group of Prof. K. Kern as Post Doctoral Fellow at EPFL, where he earned the Latsis Award 1996 for his studies on the self-assembly of metal nanostructures at metal surfaces. In 1998 he has been nominated Reader (MER) in Nanophysics at EPFL, has received an offer for a Chair (C4) at Philipps University of Marburg, and accepted the counteroffer of EPFL, where he has been nominated Associate Professor in 1999 and promoted to Full Professor in 2005. He is Fellow of the American Physical Society and member of the research council of the Swiss National Science Foundation. His research focuses on the self-assembly and on the physical and chemical properties of metallic nanostructures on single crystal surfaces. Atomic scale control during growth and in-situ analysis of magnetic, catalytic, and electronic properties aim at a fundamental understanding of the role of every constituent atom with the perspective of atomic scale engineering.

Mark Buitelaar

University of Cambridge, UK

Mark Buitelaar is a Royal Society Dorothy Hodgkin research fellow at the Cavendish Laboratory in Cambridge. He received his Ph.D. from Basel University on electron transport in carbon nanotube quantum dots; pioneering work on coupling quantum dot devices to superconductors. He then moved to the Cavendish Laboratory where he performed experiments demonstrating charge pumping in individual carbon nanotubes driven by surface acoustic waves. His current research interests include the study of the spin systems of carbon nanotube and graphene quantum dots, with an emphasis on quantum coherence.

Pepa Cabrera-Sanfelix

Donostia International Physics Center (DIPC), Spain

Pepa Cabrera-Sanfelix achieved her PhD in physics in 2005 from the Surface Science Research Centre-Department of Chemistry at the University of Liverpool, working in the area of computational studies of molecule-surface interactions and dynamics. After her PhD, she moved to the Donostia International Physics Center (DIPC) in San Sebastián, Spain, where she currently occupies an independent researcher position within the Fellows Gipuzkoa program. Her research focuses on the interaction of small molecules with surfaces. In particular, she has contributed to the modelling of water ice on ionic substrates and graphitic surfaces relevant for atmospheric physics and astrophysics. The behaviour of water at transition metal and transition metal oxide surfaces has also been a subject of her research, relevant for electrochemistry and the understanding of corrosion and surface reactivity.

Robert Carley

Free University of Berlin, Germany

Robert studied chemistry at King's College London. Following a PhD in the coherent control of Rydberg electron wavepackets at University College London, he applied femtosecond pulseshaping to the optical isomerization of benzene, also at UCL. He then spent a short time working on laser-driven plasma physics at Imperial College before moving into ultrafast studies of solids and surfaces at the Max Born Institute in Berlin, in the group of Martin Weinelt. There, in addition to studies of molecular switches, he has been involved in the construction of a femtosecond extreme ultraviolet beamline for time- and angle resolved photoemission spectroscopy based on high-order harmonic generation and its use in ultrafast laser-driven magnetization dynamics. Robert moved to the Free University of Berlin at the end of 2011 and continues to do experiments at the MBI.

Judith Driscoll

University of Cambridge, UK

Judith received her Ph.D. from the University of Cambridge in 1991. She was an IBM Post-doctoral Fellow at Stanford University and IBM Almaden from 1991-1995. She was a Reader at Imperial College from 1995 until 2003. She was then a Long Term visiting staff member at Los Alamos National Lab in 2003 and she has retained that position as a visitor since. In late 2003, she joined the University of Cambridge where she is now a Full Professor in Materials Science. She is also a Fellow of Trinity College in Cambridge. She works on the materials science and applied physics of functional oxide materials, including superconductor, magnetic materials, ferroelectrics and semiconductors. She has published over 250 papers and is holder of an ERC advanced investigator grant on functional oxide interfaces.

Arianna Filoramo

CEA, France

Arianna Filoramo received her Ph.D. degree in Solid State Physics at the ENS (Ecole Normale Superieure) in Paris in 1997 on time resolved spectroscopy of semiconductor hereostructure. In 1998 she joined the Molecular Electronics Research Lab of Motorola where she worked on molecular transport, carbon nanotubes and DNA-based electronics projects. Since 2004 she carries on her activity in the Laboratoire d'Electronique Moleculaire at CEA. Her main topics concerns molecules, DNA scaffolds and carbon nanotubes for biomimetic approaches.

Mark Fox

The University of Sheffield, UK

Mark Fox is Professor of Optical Physics at the University of Sheffield. He received his doctorate from Oxford University in 1987, after which he worked as a post-doctoral member of technical staff at AT&T Bell Laboratories in New Jersey. He returned to Oxford as a Royal Society University Research Fellow, and then moved to the University of Sheffield in 1998. During his career he has worked on the optical properties of low-dimensional semiconductor structures, especially III-V quantum wells and quantum dots, with a particular interest in their application in quantum optics. His current research activities are carried out through two EPSRC-funded programme grants on "Optical Control of Quantum States in Semiconductor Nanostructures" and "Semiconductor Integrated Quantum Optical Circuits". He is the author of two texts in the Oxford Masters Series in Physics: Optical Properties of Solids (2nd edition, 2010) and Quantum optics: an introduction (2006), and is a Fellow of both the Institute of Physics and the Optical Society of America.

Hartmut Fuess

Technische Universität Darmstadt, Germany

Hartmut Fuess studied chemistry and physics at the Universities of Darmstadt (Germany) and Grenoble (France). He was a researcher at the Institute Laue-Langevin (ILL) in Grenoble and at Harwell (GB). In 1975 he was appointed Professor for Crystallography at the University of Frankfurt and 1989 Professor for Materials Science at Darmstadt University. He was responsible for the construction and running of diffractometers at several national and international institutions both for neutron and synchrotron radiation. He served as president of the European Crystallographic Association and chaired numerous committees in the field of neutron and synchrotron sciences.

Stefano Gariglio

University of Geneva, Switzerland

Stefano Gariglio is a Researcher in the Condensed Matter Physics Department at the University of Geneva. After his studies in Genoa (Italy), he obtained his PhD in 2003 at the University of Geneva. His research interests are the physics of complex oxides, in particular phenomena at interfaces and heterostructures, and their integration in functional devices.

Thomas Greber

University of Zürich, Switzerland

Prof. Greber studied Physics at ETH Zurich and obtained his PhD on Two Aspects concerning 4f impurities on metals in 1990. From 1991 to 1994 he was Humboldt and SNF Gastforscher at the Fritz-Haber-Institut in Berlin, where he worked on non adiabatic gas surface reactions. Since 1995 he is senior scientist and lecturer at the University of Zürich. His main interests are sp2 hybridized single layer templates on transition metals and molecules on such surfaces that he investigates with photoemission and scanning tunneling microscopy.

Leonhard Grill

Fritz-Haber-Institut, Germany

After graduation in experimental physics at the University of Graz/Austria (Prof. F. Netzer), L. Grill finished his PhD on ultrathin metallic films on semiconductors at the Laboratorio TASC in Trieste/Italy in 2001 (Prof. S. Modesti). He was research associate at the Free University Berlin (Prof. K.-H. Rieder) until 2006 when started to lead his own group. Since 2009 when he also finished his Habilitation, he is head of the "Nanoscale Science" group at the Fritz-Haber-Institute of the Max-Planck-Society (Dept. of Physical Chemistry). His research focuses on the study and manipulation of single functional molecules on surfaces by scanning tunneling microscopy.

Jens Guedde

Philipps-Universitat Marburg, Germany

Jens Guedde was born in Berlin (Germany) and received a Ph.D. degree in physics in 1995 from the Free University of Berlin for work on high resolution laser spectroscopy of Rydberg atoms. After spending a year as a postdoc at the Max-Born-Institute for Nonlinear Optics and Short Pulse Spectroscopy in Berlin, he returned to the Free University of Berlin and worked on non-linear optics and ultrafast spin dynamics in thin metallic films. In 2000 he joined the surface science group of Prof. Dr. Ulrich Höfer at the Philipps-University in Marburg (Germany), where he started to study ultrafast electron dynamics at metal surfaces using two-photon photoemission and non-linear optical spectroscopy. For this work, he received his habilitation for experimental physics in 2006 and has now a permanent position in Marburg.

Arsen Gukasov

LLB CEA-CNRS, France

After undergraduate studies at the Leningrad Polytechnical Institut (1966-1972), Arsen Gukasov works in Leningrad Nuclear Physics Institut (at present PNPI) of the Academy of Sciences of the USSR until 1992. He obtained his Ph. D from PNPI (1981) for his work in critical neutron scattering and neutron optics. During this period he also works in a tight collaboration with ILL scientists on the magnetic dynamics of complex magnetic systems (antiferromagnetic garnets) using inelastic neutron scattering in combination with symmetry analysis. In 1992-1993 he works as a visiting scientist at ISIS RAL (UK) in the Excitations Group. He joins Leon Brillouin Laboratory CEA-CNRS (LLB) in Saclay in 1993, where he occupies the position of the Neutron Diffraction Group Leader. He also coordinates new instrumentation projects carried out at the LLB. His main scientific contributions are in the fields of neuron optics and diffraction, polarized neutron technique and magnetism (chirality, multiferroics, frustrated magnets, actinides, strongly correlated systems etc.). He published more than 130 scientific articles and gave regularly invited communications in international conferences.

Bjork Hammer

Aarhus University, Denmark

Prof. Hammer obtained his PhD from the Technical University of Denmark in 1993. The following year, he was an Alexander von Humboldt fellow at the Fritz-Haber-Institute, Berlin before returning to the Technical University. In 1997, Prof. Hammer was appointed associate professor at Aalborg University and in 2000 he moved to Aarhus University, where he was appointed full professor in 2009. Prof. Hammer has developed first-principles quantum mechanical methods (the DACAPO computer code) and applied them to surface science problems of interest to heterogeneous catalysis. With prof. Nørskov, he formulated the d-band model for predicting trends in the reactivity of transition metal surfaces with structure and chemical composition. Current research interests of prof. Hammer include defected (e.g. stepped) and chirally modified surfaces.

Ewelina Hankiewicz

Universität Würzburg, Germany

Dr. Ewelina Hankiewicz is a Professor at the Wuerzburg University in Germany. She received her Ph.D. in Theoretical Physics from the Institute of Physics Polish Academy of Sciences in Warsaw in 2001 for the work on the magnetic polarons on the antiferromagnetic lattices. She was a Postdoc and a Faculty for several years in United States. She was a Postdoc at Texas A&M University and the University of Columbia-Missouri and an Assistant Professor at Fordham University in New York. The research of Dr. Ewelina Hankiewicz has been centered on the spin and charge transport in the nanosize systems, the physics of topological insulators as well as competing phenomena of magnetism and superconductivity.

John C Hemminger

University of California, USA

John C. Hemminger earned his B.S. in Chemistry from the University of California, Irvine in 1971. He obtained his M.S. in Chemistry and Ph.D. in Chemical Physics from Harvard University working with William A. Klemperer. Following two years as an NSF postdoctoral fellow at the University of California, Berkeley and Lawrence Berkeley National Laboratory, he joined the Chemistry faculty at UC Irvine, where he has been Chair of the Chemistry Department and Dean of the School of Physical Sciences. He is presently Professor of Chemistry and the Vice

Chancellor for Research at the University of California, Irvine. His research has involved a diverse range of fundamental studies of the chemistry and physics occurring at surfaces and interfaces, with applications to the optical properties of nanostructured surfaces, surface reaction chemistry, catalyst performance, and atmospheric chemistry (with a particular emphasis on the liquid/vapor interface). His research is funded by the Chemistry Division of the NSF, and a program on solar energy that is a joint program of the Chemistry Division, the Division of Materials Research, and the Division of Mathematics, as well as by the U.S. Department of Energy, Office of Basic Energy Sciences. He has published over 190 peer-reviewed papers and mentored over 50 graduate students and 30 postdoctoral researchers. He is a fellow of the American Physical Society, the American Chemical Society, the American Vacuum Society, and the American Association for the Advancement of Science. He has received National Awards from the American Chemical Society (the Arthur W. Adamson award) and from the American Vacuum Society (the Medard W. Welch award). He is a recipient of an Alexander von Humboldt Senior Scientist Award.

Philip Hofmann

Aarhus University, Denmark

Philip Hofmann was born in Berlin in 1967. He studied physics at the Free University, Berlin, and did his PhD research at the Fritz-Haber-Institute of the Max Planck Society, also in Berlin. He stayed at the Oak Ridge National Laboratory, USA, as a Feodor Lynen Fellow of the Alexander von Humboldt Foundation. In 1998, he moved to the University of Aarhus, Denmark, where he is now a professor at the Department of Physics and Astronomy and also associated with the Synchrotron Radiation Source and the Interdisciplinary Nanoscience Center (iNANO). His research is primarily focused on the electronic structure of solids and their surfaces.

Karsten Horn

Fritz Haber Institute of the Max Planck Society, Germany

Karsten Horn studied physics at the Rheinisch-Westfälische Technische Hochschule Aachen, Germany, and obtained his Ph.D. in vibrational spectroscopy of adsorbates on metals at Queen Mary College, London. He is a staff scientist at the Fritz Haber Institute in Berlin, and his work centers around the investigation of the electronic structure of low dimensional structures, semiconductor interfaces, quasicrystalline materials, and low dimensional structures such as metallic quantum wells and graphene, using photoelectron spectroscopy.

Andrew Horsfield

Imperial College London, UK

Andrew Horsfield is a senior lecturer and Director of Undergraduate Studies in the Materials Department at Imperial College. He joined in 2007 as an RCUK Fellow, and is an honorary Research Fellow at the London Centre for Nanotechnology. Previous to this he was the Senior Research Fellow in charge of the theory core project for the IRC in Nanotechnology at UCL where he developed a novel scheme for non-adiabatic molecular dynamics (Correlated Electron-Ion Dynamics). His interest in the interface between biology and physics was made possible by a Career Development Fellowship from the Institute of Physics which he received while working for the Fujitsu European Centre for Information Technology. His interest in efficient electronic structure methods and the development of two electronic structure codes (Plato and OXON) occurred while working in the Department of Materials at Oxford University with Prof. David Pettifor and Prof. Adrian Sutton. This built on his experience with tight binding while studying liquid silicon with Prof. Paulette Clancy at Cornell University as a PDRA and Junior Lecturer. He obtained his MSc and PhD in physics at Cornell University with Prof. Neil Ashcroft. His first-class BA in physics was obtained from Oxford University.

Thomas Ihn

ETH Zürich, Switzerland

Thomas Ihn is experimental physicist at the Solid State Physics Laboratory of ETH Zurich. In December 2007 he was awarded the title of a Professor of ETH Zurich. Thomas Ihn, born in Munich (Germany) on May 28, 1965, studied physics at the Technical University of Munich from 1985 to 1991 finishing with a diploma in physics. He completed his doctoral dissertation under the supervision of Dr. K.-J. Friedland at the Paul-Drude Institute in Berlin (Germany) and submitted the thesis 1994 to Prof. F. Koch at the Technical University of Munich. Between 1995 and 1997 he worked as a postdoc at the University of Nottingham in England. In April 1997 he moved on to ETH Zurich joining the group of Professor Klaus Ensslin. After his habilitation thesis he received the 'Venia Legendi' for experimental physcis in 2003.

The primary research interests of Thomas Ihn are quantum states and the electronic transport in nanostructures. He focuses on the investigation of the electronic properties of novel devices with tailored properties dominated by quantum effects, and based on well-known and also novel materials.

Matthieu Jamet

CEA-Grenoble and UJF, France

Dr. Matthieu JAMET, 39 years old, is graduated from Ecole Normale Supérieure Lyon (1993-1997) and Agrégé de Physique (teaching diploma). He received his Master degree in 1997 in Material Science, his PhD degree in 2001 with highest honour from the University of Lyon 1 on *“Structure and magnetism of cobalt, iron and mixed cobalt-silver nanoclusters embedded in a superconducting niobium matrix. Magnetic properties of a single nanocluster probed by micro-SQUID”* and his HdR (Habilitation à Diriger des Recherches) in 2010 from the University of Grenoble on the *“Study of Ge:Mn ferromagnetic semiconductor”*. In 2001-2002, he was awarded an Alexander von Humboldt Fellow at the Max Planck Institute of Microstructure Physics in Halle (Germany) to work on the self-organization of nanomagnets. Since the end of 2002 he is a permanent researcher at the CEA-Grenoble. His research interests are: semiconductor spintronics (hybrid ferromagnet/semiconductor systems, group IV ferromagnetic semiconductors, spin injection in Si and Ge), MgO-based magnetic tunnel junctions and perpendicular anisotropy materials. Since 2007, he is the head of the NM Lab (Nanostructures and Magnetism) of the CEA-Grenoble. This lab comprises 11 permanent staff members among which 8 researchers, 3 technicians and an average of 10 students (Post-docs, PhD and master students). The topics are currently: spintronics in semiconductors and metals, nanomagnetism in thin films and nanoparticles, magneto-electric effects, magnetic domain wall dynamics in nanotructures. He coordinated two projects in semiconductor spintronics: one French PNANO ANR project GeMO (2007-2010, 500 k€) dealing with the ferromagnetic semiconductor Ge:Mn and one RTRA project (Nanoscience Foundation of Grenoble) IMAGE (2008-2011, 250 k€) on spin injection in germanium. He supervised 2 post-docs, 3 Master internships and 8 PhD students. He is the author of ~ 40 publications, 4 patents, 1 book.

Fedor Jelezko

Ulm University, Germany

Wonho Jhe

Seoul National University, South Korea

Professor of Physics, Seoul National University, Seoul, Korea (1992-present)
Director of Center for Creative Research (1997-2005)
Director of Center for Nano-liquid (2006-present)
Postdoc, Harvard University (1989-1992)
Ph.D. in Physics, Yale University (1989)
B.S. in Physics, Seoul National University (1982)
National Academy of Science of Korea Award (2006)

Peter D Johnson

Brookhaven National Laboratory, USA

Peter D. Johnson is a Senior Physicist and Chair of the Condensed Matter Physics and Materials Science Department at Brookhaven National Laboratory. He obtained a B.Sc from Imperial College, London in 1972 and a Ph.D from Warwick University in 1978. After a period as a Research Associate at Warwick University working on Photoemission and Photoelectron Diffraction he joined Bell Laboratories in 1981 to work on Inverse Photoemission. In 1983 he joined the Physics Department at Brookhaven National Laboratory and continued the developments of the Inverse Photoemission technique, Spin Polarized Photoemission and more recently High Resolution Photoemission. Significant accomplishments include the first experimental identification of Image States, a new class of surface electronic state, spin polarized quantum well states in thin film and multilayer systems, mass renormalization in the cuprate superconductors, and, recently, a particle-hole asymmetry in the underdoped cuprate superconductors. He introduced new methods of analysis into photoemission including the now widely used Momentum Distribution Curves. Peter was awarded the 2001 Brookhaven Science and Technology Award and the 2011 Oliver E. Buckley Prize of the American Physical Society. He is a Fellow of the American Physical Society, the American Association for the Advancement of Science and the Institute of Physics in the UK.

Lev Kantorovich

King's College London, UK

Lev Kantorovich obtained his PhD in Riga, Latvia (former USSR) in 1985 in the area of theoretical condensed matter physics. In 1993-4 he spent one year in Oviedo (Spain), as an invited Professor. In 1994-6 he worked for 2.5 years with Mike Gillan at Keele University (U.K.) and then between 1996 and 2002 with Marshall Stoneham and Alex Shluger at UCL. Since 2002 he is at King's College, first as a lecturer, followed by a Reader in 2005 and, finally, promoted to a Professor in 2009. He published over 155 papers in peer-reviewed journals as well as contributed (around 10) chapters in books. He co-wrote one book in 1991 in Latvia and published one on his own in 2004, entitled "Quantum theory of the solid state: an introduction", which appeared in the series "Fundamental Theories of Physics", by Kluwer. Two of his PhD students won in 2007 and 2010 a prestigious Tadion Rideal Prize for the best PhD at KCL (and a runner up in 2006), and one was awarded Springer Thesis Prize in 2011 with a book based on her Thesis to be published by Springer. His research interests span various areas of computational and theoretical condensed matter physics, ranging from ab initio thermodynamics, modeling imaging, dissipation and manipulation with scanning probe techniques, self-assembly of organic molecules on crystal surfaces, including thermodynamic and kinetic aspects, quantum and classical statistical mechanics of equilibrium and non-equilibrium open systems, quantum transport, free energy calculations, electronic embedding techniques, etc. A large portion of his work has been done in collaboration with experimental groups.

Rustem Khasanov

Paul Scherrer Institute, Switzerland

Rustem Khasanov received his doctorate in physics at the University of Zurich on the group headed by prof. Hugo Keller in 2003. After a stay at the Ames National Laboratory (Iowa, Ames), he joined the bulk muon-spin rotation (µSR) group in Paul Scherrer Institut (Villigen, PSI), where he takes responsibility on the high-energy µSR spectrometer GPD. His research is focused on studies of high-temperature and low-temperature superconducting materials.

Phil King

University of St Andrews, UK

Phil King received a MPhys degree in physics from the University of Oxford, UK, in 2005, and a Ph.D. in condensed matter physics from the University of Warwick, UK, in 2009, for which he was awarded the Roy prize of the Institute of Physics. He was a postdoctoral research fellow at the University of St Andrews, UK, from 2009 until 2012. In April 2012, he took up a Kavli postdoctoral research fellowship at Cornell University, USA. His research is primarily focused on the electronic structure of novel quantum materials such as correlated oxides and topological insulators.

Mathieu Kociak

Laboratoire de Physique des Solides, France

Mathieu Kociak is a researcher at the Centre National de la Recherche Scientifique (CNRS). He received a Ph.D from the University of Paris XIth on superconductivity and plasmons in carbon nanotubes in 2001. He then moved to the Meijo University (Nagoya, Japan) where he performed in situ transport measurements on individual carbon nanotubes. Afterwards, he spend one year in the Condensed Matter Laboratory (SPEC) working on designing a Magnetic Force Microscope. He then got a position at the Laboratory for Solid States Physics (LPS) in Orsay, France. His main research interests include the study of the correlations between the structure, and the optical and electronic properties of individual nanoobjects. He is currently working especially on nanooptics with fast electrons using Electron Energy Loss Spectroscopy and nanocathodoluminescence. Mathieu's awards include the Guinier Prize of the french Physical Society (2002).

Matti Krusius

Aalto University, Finland

Matti Krusius is a researcher in the Low Temperature Laboratory of Aalto University. Currently his work deals with superfluids. The interest centers on the dynamics of these quantum systems in the largely unexplored zero-temperature limit. Particularly the isotropic B-phase of the fermion p-wave ^{3}He superfluids is at the forefront at temperatures below 0.5 mK which can be explored only in 3 or 4 laboratories. New dissipation sources are identified in both turbulent and laminar vortex flow and new processes have been described by which the equilibrium state is reached when fluid flow is disturbed. One of the central questions is the loss of coupling of the superfluid to the external experimentally controlled reference frame in the limit of vanishing density of quasiparticle excitations. The work is performed with a rotating refrigerator where the lowest temperature is reached using adiabatic demagnetization cooling of a nuclear paramagnet. Only 2 or 3 such installations have been constructed so far and the apparatus at Aalto is unique in reaching the zero-temperature limit in rotation for the ^{3}He superfluids.

Christian Kumpf

Forschungszentrum Jülich, Germany

Christian Kumpf graduated at the University of Erlangen-Nürnberg and received the doctoral degree from University of Rostock. After a Postdoc phase at Risø National Laboratory in Roskilde/Denmark with Prof. R. Feidenhans'l and Prof. C. Bechgaard he obtained his Habilitation at University of Würzburg under guidance of Prof. E. Umbach in 2006. In 2008 he moved to the Forschungszentrum Jülich, and recently he was offered a professorship at RWTH Aachen University. Since 1995 he is working in the field of Thin Films and Surface Science, at first on Metal-Silicide thin films as well as group-IV, III-V and II-VI semiconductor surfaces. In 2001 he moved on towards molecular adsorbate systems, with special focus on interaction phenomena at metal-organic and hetero-organic contacts.

Cait MacPhee

The University of Edinburgh, UK

Cait MacPhee is a Professor of Biological Physics at the University of Edinburgh. She started her undergraduate life in Australia in the biosciences, gradually moving across to physics during the course of her career. Her postdoc was in the Oxford Centre for Molecular Sciences with Prof. Chris Dobson, where she was awarded a Dorothy Hodgkin Fellowship by the Royal Society. Her first academic post was in the Cavendish Laboratory at the University of Cambridge, where she co-founded the Biological Physics Group with Tom Duke. She was awarded a University Research Fellowship by the Royal Society in 2002. In 2005 she moved to the School of Physics and Astronomy at the University of Edinburgh, where she remains to the present day. She acts as Theme Leader for the pan-Scotland Physics and Life Sciences initiative under the auspices of the Scottish Universities Physics Alliance (SUPA). She has interests in protein structure-function relationships, protein evolution, nanobiotechnology and astrobiology. Cait tweets as @sciorama.

Davide Marenduzzo

The University of Edinburgh, UK

Davide Marenduzzo is a Reader in Biophysics at the University of Edinburgh. Before then, he has held postdoctoral appointments at the University of Oxford and at the University of Warwick, followed by a SUPA Fellowship at Edinburgh. He obtained his PhD in Statistical and Biological Physics at the International School for Advanced Studies SISSA/ISAS in Trieste. His interests are currently DNA biophysics, biopolymers, liquid crystals, and soft condensed matter, including active matter.

Keith McKenna

The University of York, UK

Keith McKenna obtained his PhD in 2005 from the University of Leeds. From 2005-2009 he was employed as a Research Fellow at University College London, and from 2009-2011 as an Assistant Professor at Tohoku University. Since 2011 he has held a Lectureship in the Department of Physics at the University of York. His diverse research interests include the electronic properties of grain boundaries and dislocations, charge trapping and electron transfer in oxides, mechanisms of resistive switching and the structure and properties of nanoparticles.

Fiona Meldrum

University of Leeds, UK

Fiona Meldrum is a Professor at the School of Chemistry, University of Leeds, UK. She obtained her undergraduate degree in Natural Sciences from the University of Cambridge in 1989, and her doctorate in biological crystallization from the University of Bath in 1992. Following a postdoctoral position at the University of Syracuse, USA she carried out further postdoctoral work at the Max Plank Institute of Polymerforschung, Mainz, Germany under award of a Humbold Research Fellowship. Fiona then joined the Australian National University in Canberra as a Research Fellow, before returning to the UK to take up a lectureship at Queen Mary, University of London in 1998. In 2003, she moved to the School of Chemistry, University of Bristol and was appointed Reader in 2007. She joined the University of Leeds in 2009 where she holds a Chair in Inorganic Chemistry, and was awarded an EPSRC Leadership Fellowship in the same year. Her research focuses on crystallization, with particular emphasis on biomineralization and bio-inspired crystal growth, where natural systems are used as an inspiration for the design and synthesis of crystalline and amorphous minerals. She currently has particular interests in the effects of confinement on crystallization and the formation of crystals with composite structures.

Jörg Meyer

TU München, Germany

Jörg Meyer studied physics at the University of Hannover. He received his diploma degree with distinction focusing on theoretical work on the adsorption of functionalized organic molecules on metal surfaces. Diving deeper into first-principles based theory but moving to gas-surface dynamics at the Fritz-Haber-Insitute for his PhD, he finally graduated summa cum laude at the Free University Berlin. This work earned him a best poster prize in the young investigator competition at the Gordon Research conference on dynamics at surfaces in 2011. At present, he works in the group of Prof. Karsten Reuter at TUM, evaluating implications of an atomistic perspective on electron and phonon dynamics at interfaces for fundamental energy research.

Karina Morgenstern

Ruhr-Universität Bochum, Germany

Karina Morgenstern received her education in physics and computer science at the Rheinische Friedrich - Wilhelms - University in Bonn, Germany, and the University of Tennessee, Knoxville, U.S.A. She pursued her PhD work in surface science at the Research Center in Jülich, Germany, and the University of Aarhus, Denmark, and graduated from the University of Bonn in 1996. After her PhD, she spent three years as a PostDoc at the University in Lausanne, Switzerland, and six years at the Free university in Berlin, Germany. From 2005 to 2012 she was a professor for Solid State Physics at the University of Hannover, Germany. Currently, she is a professor for physical chemistry at the Ruhr University in Bochum, Germany. Her major research interests include the kinetics of metallic nanostructures, interactions and reactions of molecules on surfaces and non-adiabatic transfer reactions.

Alberto Morpurgo

University of Geneva, Switzerland

Christine Mottet

CINaM - CNRS / AMU, France

Christine Mottet is a researcher of the department of Theory and Numerical Simulations of the Interdisciplinary Centre of Nanoscience in Marseille (France). After a thesis on metallic clusters and a post-doc at the University of Genova, Italy, in the group of the professor Ferrando on the growth of metallic surfaces, she enters the CNRS as researcher in the group of modelisation of Guy Tréglia in the Research Centre on Crystal Growth Mecanisms in Marseille. She works on the modelling by numerical simulations of the structure and dynamics of metallic nanoparticles. She has been member of the Council of the French Physical Society and of the National Council of the Universities. She is co-director of a CNRS research network of a fifteen of laboratories in France on nanoalloys. She is also a member of the Manager Comity of a COST Action on nanoalloys.

Enzo Orlandini

University of Padova, Italy

Enzo Orlandini received his education and PhD degree in physics at the Physics Department- University of Bologna, Italy. After the PhD he spent two years as PostDoc at the University of Toronto, Canada, two years as Marie Curie fellow at the sub-department of Theoretical Physics in Oxford and two years as researcher at the Service de Physique Theorique in Saclay, France. From 1998 to 2004 he has held a researcher position at the INFM in Padova and in 2004 he became Associate professor in Physics at the Padova University, Italy. His major current research interests include knots in polymers, liquid crystals, non-equilibrium phenomena and active matter

Niko Pavliček

University of Regensburg, Germany

Born May 21st, 1984 in Stuttgart (Germany), I have studied Physics at the University of Regensburg from 2004 to 2009. I obtained my diploma degree for studies on "Electronic coupling of anthracenedicarbonitrile dimers on ultrathin insulating films" in the research group of Prof. Jascha Repp. Currently, I am finishing my PhD thesis in the same group. My research interests are in low temperature scanning tunneling and noncontact atomic force microscopy of single molecules on ultrathin insulating films.

Walter Pfeiffer

Bielefeld University, Germany

Walter Pfeiffer received the Ph.D. in physics from the University of Constance, Germany in 1993 in the field of nuclear solid state physics. In 1994 he joined the Faculty of Physics of the University of Würzburg, Germany, as postdoctoral fellow working in the field of ultrafast laser spectroscopy of surface dynamics. In 2000 he became assistant professor at the University of Würzburg focussing his research in the field of ultrafast nanooptics and time resolved spectroscopy of nanoscale electronic transport phenomena. Since 2006 he is Professor in the Faculty of Physics of the Bielefeld University, Germany. His current research interests include coherent control of electronic excitations, ultrafast nanophotonics, plasmonics, time-resolved photoelectron spectroscopy, and molecular optoelectronics.

Frederic Pierre

CNRS, France

Frédéric PIERRE is an experimentalist in the field of mesoscopic physics. He is project leader at the Laboratory of Photonics and Nanostructures (LPN-CNRS, Marcoussis, France), which is part of the Saclay scientific pole south of Paris. The 'Quantum transport' team explores the quantum mechanical phenomena in nanometer-scale electrical circuits. In a first research line, this study is performed through the energy distribution spectroscopy of low-dimensional electronic systems driven out of equilibrium. In a second research line, the quantum electrodynamics of mesoscopic circuits is investigated through conductance and noise measurements, using quantum point contacts as test-beds for coherent conductors and field effect to tune in-situ the electromagnetic environment. See http://www.lpn.cnrs.fr/en/PHYNANO/TQ.php for more information.

Angus Rockett

University of Illinois, USA

Angus Rockett is a Professor and Chief Advisor of the Department of Materials Science and Engineering at the University of Illinois. He is Past President and a Fellow of the American Vacuum Society, a member of the Governing Board of the American Institute of Physics, the Program Chair for the 2011 Photovoltaic Specialists Conference, and was a rotating Research Program Administrator at the Office of Basic Energy Sciences at the Department of Energy in 2000. He holds a Sc.B. in Physics from Brown University (1980) and a Ph.D. in Materials Science from the University of Illinois (1986). He has won numerous awards for teaching and advising from the College of Engineering at the University of Illinois. His teaching has ranged from introductions to materials engineering for business and engineering students to senior and graduate courses on electronic materials (including a book The Materials Science of Semiconductors). His research has concerned ion-assisted growth of semiconductors and fundamental science of growth of materials by molecular beam epitaxy. This was extended to theoretical treatments of the same subject by lattice Monte Carlo and density functional theory methods. At the same time he worked on sputtered hard coatings deposited by reactive magnetron sputtering. He has studied the basic science of solar cell materials and the operation of solar cell devices for 25 years using virtually all of the common materials microchemical and microstructural analysis techniques from SIMS and TEM to STM and photoluminescence. He has also worked on self-assembled nanostructures, MEMS devices, silicide reactions for VLSI contacts, Si-Ge oxidation kinetics for gate dielectrics, superconducting cavity resonators as temperature probes, and optical spectroscopic analysis of combustion. He is an AVS Short Course Instructor for the Photovoltaics and Sputter Deposition of Thin Films short courses. He has also given short courses in fundamentals of thin film solar cells at the IEEE Photovoltaic Specialists Conference, on characterization of photovoltaic materials at the Materials Research Society, and has given short courses on sputter depostion, thin films, and photovoltaics in China, Mexico, Sweden, Israel, Brazil, Korea, Argentina and elsewhere. He has over 150 published works and has given many invited and plenary talks on subjects related to his research.

John Rodenburg

The University of Sheffield, UK

John Rodenburg undertook his PhD, a two-year RA position, and then a ten-year Royal Society Research Fellowship at the Cavendish Laboratory, University of Cambridge. In 1999 he moved to a Research Chair at the Materials Research Institute (now MERI) at Sheffield Hallam University. Since 2003 he has been at the University of Sheffield where he holds a Personal Chair in the Department of Electronic and Electrical Engineering. His early work was on instrument development in electron microscopy and its application to material science. More recently, he has developed a number of computational methods for solving the phase problem, thus enabling the use diffraction data to reconstruct transmission images at higher resolution and with greater sensitivity than that achievable with lenses alone. This has potentially wide application in sub-atomic electron imaging and sub 50-nanometre scale X-ray imaging. One of these approaches - iterative ptychographic imaging - is now being widely taken up in the X-ray microscopy community and has just been used to demonstrate that electron lens resolution can be improved upon by a factor of five. Although the work with electrons is still at an early stage, it has the potential to make an enormous impact in the ultra-high resolution imaging of condensed matter.

Angelo Rosa

Sissa, Italy

In 2012 I have been appointed faculty member (research fellow) of the 'Statistical and Biological Physics' Sector at SISSA (Trieste, Italy). In 2003 I earned the PhD in 'Statistical and Biological Physics' at SISSA, and I spent the following 7 years in different research centers across Europe: Ecole Polytechnique Federale de Lausanne (Switzerland), 'Max-Planck Institute for the Physics of Complex Systems' in Dresden (Germany), and the 'Institute for Biocomputation and Physics of Complex Systems' in Zaragoza (Spain). Finally, in 2010 I came back to Trieste. My research interests mainly focus on the applications of Polymer Physics to understand the behavior of macromolecules of biological relevance, like DNA and chromosomes. I have co-authored 21 papers in peer-reviewed physical and bio-physical journals.

Wolf-Gero Schmidt

University of Paderborn, Germany

Wolf Gero Schmidt was born in 1968. He studied physics in Jena, Germany. He graduated in physics in 1993, and received his Ph.D. degree in 1997 (Bechstedt group), followed by a post-doctoral stay at North Carolina State University (Bernholc group). In 2005 he became Associate Professor at Massey University, New Zealand. Since 2006, he has been a Full Professor of Theoretical Physics at Paderborn University, Germany. His research interests are the physics and chemistry of surfaces and interfaces, nanoscale science, and computational physics.

Steven Schofield

University College London, UK

Steven Schofield is a lecturer at the London Centre for Nanotechnology and Department of Physics & Astronomy, University College London (UCL); he also holds an EPSRC Career Acceleration Fellowship (2009-14). Steven was an Australian Postdoctoral Fellow at the University of Newcastle (2005-08). He obtained his PhD from the University of New South Wales (2000-04), where he established a technique for positioning donor atoms in silicon with atomic-scale precision in the groups of Michelle Simmons and Robert Clark. Steven's current research is focussed on the creation and measurement of novel atomic-scale quantum structures using scanning tunnelling microscopy and spectroscopy, with potential applications in device physics and materials research; and the organic functionalisation of semiconductor surfaces for single-molecule conductance and hybrid silicon-organic devices.

Michelle Simmons

Australian Research Council Centre of Excellence for Quantum Computation and Communication Technology, Australia

Professor Simmons is the Director of the Australian Research Council Centre of Excellence for Quantum Computation and Communication Technology, a Federation Fellow and a Scientia Professor of Physics at the University of New South Wales. Following her PhD in II-VI solar cells at the University of Durham in the UK in 1992 she became a

Research Fellow at the Cavendish Laboratory in Cambridge, UK, working with Professor Sir Michael Pepper FRS in GaAs-based quantum electronics. In 1999, she was awarded a QEII Fellowship and went to Australia where she established a large research group dedicated to the fabrication of atomic-scale devices in silicon using the atomic precision of a scanning tunneling microscopy. Her group has developed the world's thinnest conducting wires in silicon and the smallest transistors made with atomic precision. She has published more than 300 papers in refereed journals and presented over 80 invited and plenary presentations at international conferences. In 2005 she was awarded the Pawsey Medal by the Australian Academy of Science and in 2006 became the one of the youngest elected Fellows of this Academy. In 2008 she was awarded a second Federation Fellowship by the Australian Government and was named the NSW Scientist of the Year in 2011.

Arthur R Smith

Ohio University Nanoscale & Quantum Phenomena Institute, USA

Arthur R. Smith obtained his Ph.D. in physics from the University of Texas at Austin under the direction of Ken Shih in 1995 in the area of GaAs/AlGaAs heterostructures and superlattices studied by cross-sectional scanning tunneling microscopy. After doing post-doctoral work on GaN surfaces with Randall Feenstra at Carnegie Mellon University for 2 1/2 years, he joined the Physics and Astronomy department at Ohio University as Assistant Professor in 1998. His research interests include surface epitaxial growth processes and surface structures investigated using STM, with a focus on magnetic/spintronic materials. In 2000, he received the U.S. Presidential Early CAREER Award in Science and Engineering. He was promoted to Associate Professor in 2003 and to Full Professor in 2008. Since 2005, he has also been Director of the Ohio University Nanoscale and Quantum Phenomena Institute, now serving in his 3rd term. He has published to date 70 papers in various scientific journals and frequently speaks at international conferences and workshops.

Andrzej L Sobolewski

Institute of Physics of the Polish Academy of Sciences, Poland

Andrzej L. Sobolewski received his MSc in Physics from the Warsaw University in 1977 and was employed as assistant in the Institute of Physics of the Polish Academy of Sciences (IPPAS) where he received his PhD in 1981. He worked for two years as a postdoctoral Humboldt fellow at the Technical University of Munich. Having received the Habilitation degree in 1989 in the IPPAS, he got professor position there. His research interests include, among others, theoretical investigation of elementary photochemical processes in molecular systems, e.g., excited-state proton and electron transfer, and pathways of ultra-fast radiationless energy relaxation. He is a winner of the 2007 prize of the National Foundation for Sciences, Copernicus Award (2008), and Smoluchowski-Warburg Medal (2009).

Gary Steele

TU-Delft, The Netherlands

Dr. Gary Steele was born in Toronto, Canada, and studied Physics at McGill before moving to MIT to pursue his doctoral degree imaging the quantum Hall liquid with a scanning probe microscope with Ray Ashoori. After his Ph. D., he joined the group of Leo Kouwenhoven at TU-Delft studying carbon nanotubes. During his postdoctoral work, he developed a new technique for making suspended carbon nanotube devices, leading to a breakthrough it both their electronic and mechanical properties. In July 2010, Gary joined the Kavli Institute of Nanoscience as an Assistant Professor. His research group in Delft now focusses on quantum nanomechanics with NEMS devices made from carbon nanotubes and graphene which are coupled to superconducting microwave circuits.

Andreas Stierle

DESY and University of Hamburg, Germany

Andreas Stierle studied Physics at the Ruhr-Universität Bochum (Germany), where he received his PhD in 1996. From 1996-1998 he was employed as a postdoctoral fellow at the European Synchrotron Radiation Facility in Grenoble (France) working in the field of surface and interface physics. Using surface x-ray diffraction as a main characterization tool, he investigated oxidation processes on metal and alloy surfaces. From 1998 to 2009 he held a position at the Max Planck Institute for Metals Research (Stuttgart, Germany) as a senior scientist, responsible for the construction and operation of a hard x-ray beamline at the Angströmquelle Karlsruhe (KIT, Germany) dedicated to in-situ studies of nanomaterials. In addition, he led a research group on nano-oxidation and corrosion. In 2009 he was appointed as a professor for solid state physics at the University of Siegen (Germany). Since 2012, he is holding an appointment as a professor for nanoscience at the University of Hamburg, in combination with a position as leading scientist at DESY (Hamburg, Germany). His main research interests are in-situ investigations of surfaces and interfaces under reaction conditions employing advanced surface sensitive x-ray diffraction schemes.

Fabio Taddei

NEST, NANO-CNR, Italy

Fabio Taddei is a researcher at NEST, Istituto Nanoscienze-CNR in Pisa (Italy). He graduated at the University of Milan (Italy) in 1995 and got his PhD degree at Lancaster University (UK) in 2000. He was a postdoctoral fellow at ISI Foundation in Turin (Italy), and at the University of Catania (Italy). His research activity is within the quantum transport theory of nanostructures. In particular, he has been recently working in the following subjects: Spintronics in hybrid superconductor/ferromagnet systems; Time-dependent transport and adiabatic pumping; Heat transport and cooling effect in hybrid systems; Transport in semiconductor in the quantum Hall regime; Superconducting circuits: mesoscopic Josephson junctions and quantum bits; Graphene.

Alexandre Tkatchenko

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Alexandre Tkatchenko obtained his bachelor degree in Computer Science, and PhD in Physical Chemistry in Mexico. During 2008 -- 2010, he was an Alexander von Humboldt Fellow in the Theory Department at the Fritz-Haber-Insitut der MPG in Berlin, Germany. Currently, he leads an ERC-funded group on Functional Materials and Intermolecular Interactions at the same Institute. Alexandre has received the Gerhard Ertl Young Investigator Award, and was selected for the Volker Heine Young Investigator Award.

M Todorova

Max-Planck-Institut für Eisenforschung, Germany

Mira Todorova studied physics at the Technical University Darmstadt, Germany, and then moved to the Fritz-Haber-Institute in Berlin (Scheffler group) to pursue her PhD. She investigated the oxidation of palladium surfaces and graduated from the Technical University Berlin in 2004. After her PhD she spent two years in Australia as a PostDoc at the University of Sydney (Stampfl group), before returning to Germany to work at the Max-Planck-Institut für Eisenforschung in Düsseldorf (Neugebauer group). Her research centres on ab-initio based multi-scale modelling of materials properties, in particular the physics and chemistry of surfaces and interfaces, and the linking of first-principles calculations with thermodynamic and statistical concepts.

Ruud Tromp

Leiden University, The Netherlands

Patrick Unwin

The University of Warwick, UK

Patrick Unwin founded the Warwick Electrochemistry and Interfaces Group in 1992 and has been Professor of Chemistry since 1998. He was founding director of the Warwick-EPSRC Centre for Analytical Science (2008) and is currently Co-Editor of Journal for Electroanalytical Chemistry. The author of more than 250 papers and winner of numerous international awards for his research, a major focus is the development and application of multi-functional imaging techniques with applications across a broad range of science.

Milko van der Boom

Weizmann Institute of Science, Israel

Milko E. van der Boom received his B.Sc. degree (1992) from the Amsterdam University of Applied Sciences, The Netherlands, and a M.Sc. degree (1994) in Inorganic Chemistry at the University of Amsterdam (with Prof. Kees Elsevier). He earned his Ph.D. degree with distinction in 1999 from the Weizmann Institute of Science in Israel (with Prof. David Milstein). After 3 years of postdoctoral research with Prof. Tobin J. Marks at Northwestern University in the United States, he became a Faculty member in the Weizmann Institute's Department of Organic Chemistry. He is the incumbent of the Bruce A. Pearlman Professorial Chair in Synthetic Organic Chemistry. Prizes and honors include an Alon Fellowship from the Israel Council for Higher Education, the Gutwirth Award, and the Israel Chemical Society Prize for Young Scientists. His current research interests include molecular logic and computing, surface-confined assemblies, and halogen bonding.

Luca Vattuone

Università degli Studi di Genova, Italy

Luca Vattuone graduated in Physics with laude in the University of Genoa in 1990, he got then his PhD in 1994 with a Thesis in experimental surface science under the supervision of Prof. Mario Rocca. In 1995 he joined the group of Prof. Sir David A. King at the University of Cambridge as a post-doctoral research associate. From 1996 to 1998 he worked as a post-doc of Genoa University first and of the National Institute for the Physics of Matter (INFM) afterwards. In 1999, after serving as a physicist of the Navy Hydrographic Institute for a few months, Dr. Vattuone was appointed as a staff University Researcher in the Physics Department of the University of Genoa. His research activity is focussed on the experimental investigation of gas-surface interaction (by HREELS, XPS, Supersonic Molecular beams, STM and Single Crystal Calorimetry) and of surface electronic excitations but it includes also the application of Montecarlo methods to surface science. His latest achievements include the discovery of the Acoustic Surface Plasmon and the investigation of the role of molecular alignment in the adsorption dynamics. Dr. Vattuone co-organised the International Conference on Vibrations at Surfaces VAS 12 with Prof. Giorgio Benedek, and was a member of the organising committee of ECOSS 26 and of ICSFS 16 as well as Guest-Editor of its Proceedings. In 2011 he joined the Editorial Board of ISRN Physical Chemistry. For the full list of his papers and his contact details see: www.fisica.unige.it/~vattuone/

Thomas Wandlowski

University of Bern, Switzerland

Thomas Wandlowski studied Chemistry and Mathematics in Halle, Germany. After completion of his PhD with Prof. Kretschmer in 1986 (Electrocapillary studies at meta/electrolyte interfaces), he joined the J. Heyrovsky Institute of Physical Chemistry and Electrochemistry (Prague, with Prof. Koryta), as Research Fellow. He completed his Habilitation in 1990 with a topic on phase formation at electrochemical interfaces. After three years as Research Assistant Professor at Georgetown University (Washington DC), he returned to Germany in 1994 as Heisenberg and joined the Department of Electrochemistry at Ulm University. In 1999 he accepted the position as Head of the Electrochemistry Group, Research Centre Jülich, Institute of Surfaces and Interfaces, and was teaching as Privatdocent at the RWTH Aachen. Since 2007 he is Full Professor of Physical Chemistry and Electrochemistry at the University of Berne (Switzerland).Thomas Wandlowski's research interests covers a wide range of topics, such as Interfacial electrochemistry at well defined electrodes, structure and reactivity of nano-objects and single molecules at electrified solid/liquid interfaces, self-assembly and charge transport at surfaces and interfaces, electrocatalysis, surface enhanced vibrational spectroscopy (SEIRAS, SHINERS, MCBJ-Raman), in-situ scanning probe microscopy (STM/STS, CP-AFM). He has published more than 135 Research Papers and 5 Book Chapters.

Roland Widmer

Empa, Switzerland

Roland Widmer is a senior scientist at the Swiss Federal Laboratories for Materials Science and Technology (Empa) in Dübendorf, Switzerland. After he performed his Diploma and PhD thesis in electrolytic in-situ scanning probe microscopy at the Department of Chemistry and Biochemistry at the University of Bern under the supervision of Prof. H. Siegenthaler, he joined Empa in 2003 and visited the group of Prof. K. Horn at the FHI in Berlin for a sabbatical in 2008. The main focus of his research is to understand the structure and reactivity of (complex) surfaces and processes at surfaces at a molecular and atomic level mainly applying scanning probe and X-ray photoelectron emission techniques.

Roland Wiesendanger

University of Hamburg, Germany

Roland Wiesendanger, born 1961, studied physics at the University of Basel, where he received his Ph.D. in 1987 and his Habilitation degree in 1990, working in the field of scanning tunnelling microscopy. In 1992 he received an offer for a full professor position from the University of Hamburg related with the launch of the Microstructure Advanced Research Center Hamburg (MARCH). In Hamburg, Roland Wiesendanger has initiated the Center of Competence in Nano-scale Analysis "HanseNanoTec", the Interdisciplinary Nanoscience Center Hamburg (INCH), the Collaborative Research Center 668 of the German Research Foundation entitled "Magnetism from the single atom to the nanostructure", and the Cluster of Excellence "Nanospintronics" of the Free and Hanseatic City of Hamburg. Since end of the eighties, Roland Wiesendanger pioneered the technique of Spin-Polarized Scanning Tunnelling Microscopy and Spectroscopy which allowed the first real-space observation of magnetic structures at the atomic level. Roland Wiesendanger also contributed significantly to the development of Magnetic Force Microscopy (MFM) and Magnetic Exchange Force Microscopy. Roland Wiesendanger is author or co-author of 450 scientific publications and 2 textbooks, and editor or co-editor of 7 monographs and 7 conference proceedings. He presented more than 430 talks worldwide. For his outstanding research contributions, Roland Wiesendanger has been awarded with the Gaede-Prize of the German Vacuum Society in 1992, the Max Auwärter Prize in 1992, the Karl Heinz Beckurts Prize in 1999, the Philip Morris Research Prize in 2003, the ERC Advanced Grant Award in 2008, and the Nanotechnology Recognition Award of the American Vacuum Society in 2010. He is an elected member of the German Academy of Sciences "Leopoldina" (since 2000), the Hamburg Academy of Sciences (since 2005), and the German Academy of Technical Sciences (since 2008). Since 2012, he is Honorary Professor of the Harbin Institute of Technology (China).

Ludger Wirtz

University of Luxembourg, Luxembourg

Ludger Wirtz studied physics at Bonn University, Germany, and at the University of Tennessee in Knoxville, USA. He received the PhD from the Vienna University of Technology, Austria, in 2001. After a postdoctoral stay in the group of Prof. A. Rubio at the University of the Basque Country, San Sebastian, Spain, he joined the Institute of Electronics, Microelectronics, and Nanotechnology (IEMN) in Lille, France, as a permanent researcher of the CNRS in 2004. In February 2012 he was appointed professor of theoretical solid-state physics at the University of Luxembourg. His research interests include semiclassical methods in mesoscopic physics, the theory of ion-surface interaction, and the theoretical/computational spectroscopy of nanostructured materials (graphene, nanotubes, nanocrystals).

Phil Woodruff

The University of Warwick, UK

Phil Woodruff completed his first degree at the University of Bristol before moving to the (then new) University of Warwick for his PhD, working on the solid/melt interface. He then switched his interest to the solid/vacuum interface and established a research group working on the structural, electronic and chemical properties of well-characterised surfaces, using a wide range of techniques. For some years his primary focus has been on quantitative surface structure determination, mainly of molecular adsorbates on metal and oxide surfaces. Much of this work has involved the use of established and new synchrotron-radiation based methods. In addition to his role as Professor of Physics at the University of Warwick, he held visiting positions at the Fritz Haber Institute in Berlin during the period 1999-2011.

Boris I Yakobson,

Rice University, USA

Dominik Zumbuhl

University of Basel, Switzerland

Dominik Zumbühl, born 1974 in Zürich, received a diploma in physics in 1998 from ETH Zürich. Subsequently, he started working on his doctorate in mesoscopic physics at Stanford University in the lab of Prof. Charles Marcus. In 2000, Dominik relocated together with Dr. Marcus's group to Harvard University, where, in 2004, he obtained a Ph. D. with the title "Coherence and Spin in GaAs Quantum Dots". He then joined the group of Prof. Marc Kastner at MIT as a postdoctoral fellow. In April 2006, Dominik was appointed as a tenure track assistant professor at the Department of Physics at the University of Basel.

In 2008, Dominik was among the first series of recipients of the prestigious Starting Grant of the European Research Council (ERC), adding significantly to research funding over a five year period.

Monday 3 September

Organic layers and polymers 1

(invited) Surface confined assemblies and polymers for sensing and molecular logic

M van der Boom

Weizmann Institute of Science, Israel

Since the development of molecule-based sensors and the introduction of molecules mimicking the behavior of the AND gate in solution by de Silva in 1993, molecular (Boolean) Logic and Computing (MBLC) has become increasingly popular. The molecular approach toward Boolean logic resulted in intriguing proofs of concepts in solution including logic gates, half-adders, multiplexers, and flip-flop logic circuits. Molecular assemblies can perform diverse logic tasks by reconfiguring their inputs. Our recent research activities, which will be presented, focus on MBLC with electrochromic polymers and immobilized polypyridyl complexes on solid support. We have designed a series of coordination-based thin films that are formed linearly by stepwise wet-chemical deposition or by self-propagating molecular assembly. The electrochromic properties of these films can be used for (i) detecting various analytes in solution and in the air, (ii) MBLC, (iii) electron-transfer studies, and (iv) interlayers for efficient inverted bulk-heterojunction solar cells. Our concept toward MBLC with functionalized surfaces is applicable to electrochemical and chemical inputs coupled with optical readout. Using this approach, we demonstrated various logic architectures with redox-active functionalized surfaces. Electrochemically operated sequential logic systems (e.g., flip-flops), multi-valued logic, and multi-state memory have been designed, which can improve computational power without increasing spatial requirements. Applying multi-valued digits in data storage and information processing could exponentially increase memory capacity. Our approach is applicable to highly diverse electrochromic thin films that operate at practical voltages (< 1.5 V).

Electron dynamics in self-assembled monolayers of azobenzene alkanethiols on gold

C Gahl[1], S Paarmann[2] and M Weinelt[1]

[1]Freie Universität Berlin, Germany, [2]Freie Universität Berlin / Max-Born-Institut, Germany

Integration of photochromic azobenzene moieties into self-assembled monolayers (SAMs) is of high interest for the functionalization of surfaces. Charge and energy transfer processes between chromophore and metal substrate can strongly influence the photo-isomerization yield. Therefore the electronic structure and femtosecond electron dynamics of self-assembled monolayers of azobenzene functionalized alkanethiols on gold have been investigated with time-resolved two-photon photoemission spectroscopy (2PPE).

Two excited electronic states at 2.4 and 3.6 eV above the Fermi level are attributed to unoccupied states in the chromophores, which are populated via charge transfer from the metal substrate. Their lifetimes in the order of 100 fs are in agreement with charge transfer times deduced from resonant photo-emission of core-levels.

Additional to the ultrafast dynamics we observe a continuous change of the monochromatic 2PPE spectra on the time scale of hours. While at a photon energy of hν=4.2 eV the SAM is irreversibly modified by the UV illumination, reversible changes attributed to photo-isomerization occur at hν=3.6 eV. The low cross-section of $<10^{-22}$ cm^2 is in accordance with earlier experiments where within the experimental error no optical response to UV light was observed.

Towards a unified structural model for alkanethiol self-assembled monolayers on Au(111)

Q Guo[1], F Li[2] and L Tang[1]

[1]University of Birmingham, UK, [2]Tsinghua University, China

Self-assembled alkanethiol monolayers on Au(111) play important roles in technological fields such as passivation of Au nano-particles. Although SAMs on Au(111) have been studied for more than two decades, the atomic structure of the interface is still not resolved. A recent STM study has shown that the well-accepted $\sqrt{3}$ x $\sqrt{3}$ sructure for a full layer of methylthiolate on Au(111) has in fact never existed. Here we attempt to explain what causes the misunderstanding that exists for such a well-known system and try to provide a unified model for all structures that have been observed.

[1] L. Tang, F. Li, W-C. Zhou, and Q. Guo, “The structure of methylthiolate and ethylthiolate monolayers on Au(111): Absence of the ($\sqrt{3}\times\sqrt{3}$)R30° phase”, Surf. Sci. 606, (2012), L31.
[2] F. Li, L. Tang, W-C. Zhou and Q. Guo, J. Am. Chem. Soc., 132 (2010) 13059.
[3] F. Li, F. W-C, Zhou, and Q. Guo, Phys. Rev. B. 79 (2009) 113412.

Adatoms, solvent polarity, and co-adsorption in the design of self-assembled dithiol monolayers

A Sharif, D N Buckley and C Silien

University of Limerick, Ireland

Even though the preparation and generic properties of saturated standing-up self-assembled monolayers (SAMs) of alkanedithiols on Au(111) and of other dithiols incorporating aromatic moieties are generally known, it has also appeared that the conditions of self-assembly are critical in determining the final structural properties of the films. However, with the ubiquity of thiol chemistry and the extensive implications of dithiols in nanoelectronics, a more refined understanding of the growth of SAMs is highly desirable. Rationalizing that the factors determining the initial growth are emphasized for low dithiol concentrations, and accounting for the capacity of STM to image surfaces with molecular resolution, we have studied by STM the self-assembly of a series of dithiols from dilute solutions [1,2]. Our STM experiments resolve the involvement of the Au adatoms, of the initial adsorption of lying-down dithiols asymmetrically bonded to the substrate, and of the co-adsorption of solvent molecules; and we discuss how these effects further combine with the solvent polarity to stabilize different SAM interfaces.

[1] Sharif, A. M.; Buckley, D. N.; Buck, M.; Silien, C. J. Phys. Chem. C 2011, 115, 21800-21803.
[2] Sharif, A. M.; Buckley, D. N.; Silien, C. submitted 2012.

Atomic force microscopy with C_{60} molecular probes

A Stannard[1], A Sweetman[1], S Jarvis[1], L Kantorovich[2] and P Moriarty[1]

[1]University of Nottingham, UK, [2]King's College London, UK

We discuss a variety of results obtained using AFM tips terminated, precisely, with a buckminsterfullerene (C_{60}) molecule. Chemical interactions between silicon-terminated AFM tips and surface-adsorbed C_{60} molecules have been studied previously [1]. However the site-specific chemical interactions in this experimental configuration are determined by silicon tips with undefined apexes. To resolve this problem, and unambiguously define the tip apex, the situation can be reversed using a tip-adsorbed C_{60} molecule to probe adatoms on the Si(111)-(7x7) surface. In this instance, the molecular orientation of a tip-adsorbed C_{60} molecule is revealed via the appearance of the silicon adatoms, e.g. imaging with a pentagonal face of a C_{60} molecule gives rise to an adatom appearance with five-fold symmetry.

By performing site-specific spectroscopy measurements, chemical bonds between C_{60} molecular probes and adatoms of the Si(111)-(7x7) surface can be measured. The observed chemical forces are found to agree very well with density functional theory (DFT) calculations, with peak attractive forces of 1.3 nN observed both experimentally and theoretically.

Finally, confidence in the nature of the tip apex termination allows probing of the interaction between tip-adsorbed and surface-adsorbed C_{60} molecules. The attractive component of this interaction is purely van der Waals in nature, and the full potential, including Pauli repulsion, has been predicted analytically by Girifalco [2]. Our experimental observations are in very good agreement with this prediction, especially with respect to the equilibrium binding energy.

[1] C. Chiutu et al, Chem. Commun. 47, 10575 (2011).
[2] L. Girifalco, J. Phys. Chem. 95, 5370 (1991).

Carbon, graphene 3

(invited) The phonon dispersion of graphene in interaction with different substrates

L Wirtz, A Molina and A Allard

University of Luxembourg, Luxembourg

We present ab-initio calculations of the vibrational properties of graphene on different metallic and non-metallic substrates. The phonon dispersions display peculiar changes due to the interaction with the substrate. Phonon measurements via Raman or high-resolution electron-energy loss spectroscopy (HREELS) can thus give important information on the graphene-substrate interaction.

The changes in the phonon dispersion on metallic substrates can be quite pronounced depending on the degree of hybridization of the carbon pi-bands with the surface states [1]. In particular, in the case of chemisorption on a Ni(111) surface, the Kohn-anomalies in the highest optical branch are suppressed and the strong Raman signal disappears.

The changes on non-metallic substrates are more subtle but nevertheless well visible in the Raman spectra if one compares, e.g., the spectra of graphene on silicon dioxide with the spectra of suspended graphene [2] and graphene on hexagonal boron nitride [3]. We show that the screening by the substrate influences the electron-phonon coupling between the highest optical phonon branch at K and the pi-bands. This mechanism is responsible for the shift of the Raman 2D line on different substrates.

[1] A. Allard and L. Wirtz, Nano Lett. 10, 4335 (2010).
[2] S. Berciaud, S. Ryu, L.E. Brus, T.F. Heinz, Nano Lett. 9, 346 (2009).
[3] Collaboration with F. Forster, A. Meier, K. Watanabe, T. Taniguchi, and C. Stampfer.

Graphene on weakly interacting metals: pristine surfaces and point defects

D Fernández-Torre[1], M M Ugeda[2], H González-Herrero[2], I Brihuega[2], P Pou[1], A J Martínez-Galera[2], R Pérez[1] and J M Gómez-Rodríguez[2]

[1]Universidad Autónoma de Madrid, Spain, [2] Departamento de Física de la Materia Condensada Universidad Autónoma de Madrid, Spain

Understanding the coupling of graphene with its local environment is critical to integrate it in tomorrow's electronic devices. Previous studies have shown that highly perfect sheets of graphene can be obtained by epitaxial growth on metal surfaces, and for some transition elements, like Cu or Pt, the interaction is very weak and many characteristic properties of graphene are preserved [1,2]. In this work, we show how the presence of these two metallic substrates affects the properties of an atomically tailored graphene layer. To this end, we combine low temperature scanning tunneling microscopy (LT-STM) experiments [3] with density functional theory calculations (DFT) and non-equilibrium Green's functions (NEGF) methods to model the electronic transport [4]. For the non-defective graphene adsorbed on Pt(111), our calculations show that the periodic modulations typically observed by STM on the Moiré patterns can be explained as a purely electronic effect, because the simulated image is anticorrelated with the topmost regions of the corrugated sheet. For graphene on Cu(111), topographic effects play a more important role. When vacancies are present on graphene/Pt(111), the calculations help us associate the observed STM images with the positions of the atoms. Vacancy sites become reactive, leading to an increase of the coupling between the graphene layer and the metal substrate at these points. This gives rise to a rapid decay of the localized state and the quenching of the magnetic moment associated with carbon vacancies in free-standing graphene layers [5].

[1] A.J. Martínez-Galera et al., Nano Letters, 11 (2011) 3576.
[2] P. Sutter et al, Phys. Rev. B, 80 (2009) 245411.
[3] M. M. Ugeda, doctoral thesis, Universidad Autónoma de Madrid (to be published)
[4] J.M. Blanco et al, Prog. Surf. Sci., 81 (2006) 403.
[5] M.M. Ugeda et al, Phys. Rev. Lett., 107 (2011) 116803.

(invited) Self assembly for nanoelectronics and biomimetic approaches with carbon nanotubes

A Filoramo, S Campidelli and V Derycke

CEA, France

Thanks to their exceptional electrical, mechanical and chemical characteristics, carbon nanotubes are very promising building blocks for future nanoelectronic technologies. However, the future of this class of SWNT-based devices is to a large extent related to the development of a bottom-up self-assembly technique.

Here, we will first present our approaches to the fabrication of carbon nanotubes devices by self-assembly [1, 2]. Nanotransistors are important key enabling elements and one can envision enhancing functionalities of circuits by designed nano-constructions. We will show that additional functionalities and control can be added to nanotube devices [3, 4] and how they can provide an elegant solution to implement adaptive circuits [5].

[1] (a) E. Valentin et al. Microelect. Eng., 61, 491 (2002); (b) E. Valentin et al. MRS proceedings, 772, 201 (2003) ;(c) S. Auvray et al. Nano Lett., 5, 451 (2005).
[2] (a) S. Lyonnais et al. Chem. Commun., 683 (2009); (b) S. Lyonnais et al., Small, 4, 442 (2008); (c) K. Nguyen et al. Adv. Mater., 20, 1099 (2008).
[3] S. Campidelli et al., J. Am. Chem. Soc., 130, 11503 (2008); T. Palacin et al. J. Am. Chem. Soc., 131, 15394 (2009).
[4] (a) J. Borghetti et al. Adv. Mater., 18, 2535 (2006); (b) C. Anghel et al. Nano Lett., 8, 3619 (2008).
[5] (a) G. Agnus et al. Adv. Mater., 22, 702 (2010). W.S Zhao et al. Nanotechnology , 21, 175202 (2010); (b) G. Agnus et al. Small, 6, 2659 (2010).

Two-phonon scattering in graphene in the quantum Hall regime

A Alexeev[1] and M Portnoi[1,2]

[1] University of Exeter, UK, [2] International Institute of Physics, Brazil

One of the most distinctive features of graphene is its huge inter-Landau-level splitting in experimentally attainable magnetic fields resulting in the room-temperature quantum Hall effect. We calculated the longitudinal conductivity due to two-phonon scattering in graphene in quantizing magnetic fields over a broad range of temperatures. The multi-phonon scattering mechanism [1] is known to be negligible for conventional two-dimensional systems under the quantum Hall conditions apart from exotic cases such as magneto-roton dissociation in phonon spectroscopy [2]. However, our calculations show that this mechanism dominates in the high-temperature quantum Hall regime in graphene, since at elevated temperatures the energy of an acoustic phonon with a wavevector comparable to the inverse magnetic length is much smaller than the temperature; therefore, a number of such phonons increases drastically. Single-phonon processes in pristine graphene in this regime remain suppressed due to momentum and energy conservation requirements. We show that the two-phonon scattering mechanism provides a significant error in Hall conductivity measurements and it is therefore the major obstacle in using graphene as a room-temperature quantum Hall standard of resistance.

[1] V.N. Golovach and M.E. Portnoi, Phys. Rev. B 74, 085321 (2006).
[2] V.M. Apalkov and M.E. Portnoi, Phys. Rev. B 66, 121303 (2002).

Electron acceptors adsorption on a nanostructured graphene surface

D Stradi[1], C Diaz[2], M Garnica[3], S Barja[3], F Calleja[4], A Arnau[5], D Sanchez-Portal[6], M Alcami[2], N Martin[7], A Lopez Vazquez de Parga[3], F Martin[8] and R Miranda[3]

[1]Universidad Autonoma de Madrid & IMDEA Nanociencia, Spain [2]Departamento de Quimica, Universidad Autonoma de Madrid, Spain, [3]Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid & IMDEA Nanociencia, Spain, [4]IMDEA Nanociencia, Spain, [5]Materials Physics Center & Donostia International Physics Centre & Departamento de Fisica de Materiales, Spain, [6]Materials Physics Center & Donostia International Physics Centre, Spain, [7]Departamento de Quimica Organica, Universidad Complutense de Madrid & IMDEA Nanociencia, Spain, [8]Departamento de Quimica, Universidad Autonoma de Madrid & IMDEA Nanociencia, Spain

The growth of graphene on metallic substrates constitutes one of the most effective ways to achieve large and relatively defect-free monolayer graphene samples[1]. Similarly to what happens in ultrathin films of alkali-halides[2] or oxides[3], graphene act as a buffer layer, decoupling the electronic structure of the adsorbed molecular species from that of the underlying metallic substrate[4,5]. This makes it possible to image the spatial distribution of molecular orbitals in Scanning Tunneling Microscopy experiments, and, even more important, analyze with unprecedented detail the effect of the surface on the electronic structure of the adsorbate. Nevertheless, in several cases, such as in graphene grown on Ru(0001), the analysis is complicated by the fact that the strong interaction between graphene and the metallic substrate alters significantly the graphene morphology, which becomes corrugated, and affects its electronic structure, which is no longer homogeneous[6,7]. Due to the complexity of such situation, theoretical calculations are needed in order to interpret the experimental results. In this contribution, Density Functional Theory calculations that shed light on the electronic properties of the graphene/Ru(0001) surface will be presented[8], as well as results concerning the adsorption of electron acceptor molecules.

[1] J. Wintterlin and M.-L. Bocquet, Surface Science 603, 1841 (2009).
[2] X. H. Qiu, G. V. Nazin and W. Ho, Science 299, 542 (2003).
[3] J. Repp et al., Science 312, 1196 (2006).
[4] H. T. Zhou et al., Appl. Phys. Lett. 99, 153101 (2011).
[5] S. Barja et al., Chem. Comm. 46, 8198 (2010).
[6] A. L. Vázquez de Parga et al., Phys. Rev. Lett. 100, 056807 (2008).
[7] D. Stradi et al., Phys. Rev. Lett. 106, 186102 (2011).
[8] D. Stradi et al., Phys. Rev. B 85, 121404 (2012).

Alkali-metal intercalated graphene on Ir(111)

P Pervan[1], M Petrović[1], I Šrut[1], I Pletikosić[2], M Milun[1], M Kralj[1], S Runte[2], C Busse[2], T Michely[2], R Brako[3], D Šoićkčev[3], J Sadowski[4] and T Valla[4]

[1]Institut za fiziku, Serbia, [2]Universität zu Köln, Germany [3]Institute Ruđer Bošković, Croatia, [4]Brookhaven National Laboratory, USA

Graphene on Ir(111) is unique by its structural quality and by the electronic structure which resembles that of a free standing graphene [1], which makes it very attractive to serve as a model system for chemical doping experiments by the adsorption and intercalation of alkali atoms (Li, Na, K, Cs). We have studied adsorption and intercalation of alkali metals into graphene/Ir(111) system by the application of scanning tunnelling microscopy (STM), low energy electron microscopy (LEEM), X-ray Photoemission Spectroscopy (XPS) and Angle Resolved Photoemission

Spectroscopy of high-resolution in energy and momentum (ARPES). The systems are modelled by density functional theory (DFT) calculations.

All alkali metals induce a substantial Dirac point shift of about 1.3 eV which is associated with the alkali metal atoms positioned between Ir surface and graphene layer. However, at a small coverage Cs shows tendency to form a domain which consist of diluted adsorbed layer on top of graphene. This domain is accompanied by the Dirac point shift of 0.3 eV to higher binding energies. These two different domains are clearly distinguished by STM and LEEM. They exhibit different local work functions as measured by ARPES. The LEEM study of Cs intercalation process clearly points to the importance of the graphene wrinkles which are formed due to stress relaxation during final cooling of grown graphene layer. We have also studied electron-phonon-coupling (epc) induced renormalization of the graphene π-band when intercalated by an alkali-metal. The epc values determined in our experiments are isotropic and within the range of 0.2.

[1] Kralj, M.; Pletikosić, I.; Petrović, M.; Pervan, P.; Milun, M.; N'Diaye, A. T.; Busse, C.; Michely, T.; Fujii, J.; Vobornik, I. Graphene on Ir(111) characterized by angle-resolved photoemission Phys. Rev. B 2011, 84, 075427.

Reactions on surfaces 1

(invited) Beating the heat atomistically: watching phonons cool down during oxygen dissociation on Pd(100)

J Meyer

TU München, Germany

Energy conversion at interfaces is at the centre of the rapidly growing field of basic energy science. One particular example is the conversion of chemical energy into heat which comes as an unavoidable by-product of all exothermic elementary reaction steps in heterogeneous catalysis. Engineers routinely deal with important consequences on a macroscopic scale based on well-known continuum theories relying on empirically determined effective parameters, for which an atomistic understanding is very limited at best.

Aiming at multiscale modelling, our novel QM/Me approach extends the power of embedding techniques to metallic systems - including a proper description of the electronic band structure. A huge atomistically described bath can thus be included in ab initio molecular dynamics simulations of chemical reactions at catalyst surfaces.
Applied to oxygen dissociation on Pd(100) as a representative showcase system, for which electron-hole pair excitations are unlikely to act as dominant primary energy dissipation channel [1], we quantify concomitant phonon excitations based on a newly developed projection scheme. Thanks to the phononic details implicitly incorporated in the bath, we obtain a high resolution for individual modes over the entire surface Brillouin zone.

We can thus unravel the role of surface phonons as well as question the validity of the harmonic approximation for the solid during the dynamics - commonly employed in generalized Langevin equations and other model Hamiltonians - from an unprecedented first-principles perspective. The latter also allows to make comparisons to Fourier's law.

[1] J. Meyer and K. Reuter, New J. Phys. 13, 085010 (2011).

Observation of a large steric effect in the initial oxidation of Si(100)

M Kurahashi and Y Yamauchi

National Institute for Materials Science, Japan

The rate of surface oxidation could depend on the geometry of an O_2 molecule relative to the surface because of the anisotropic shape of the molecule. Such steric effects in oxidation have been investigated for several metallic surfaces using an aligned O_2 beam produced by collisional alignment method[1]. No such steric effects however have been reported for the oxidation of semiconductor surfaces. We have recently succeeded in producing a single spin-rotational state [(J,M)=(2,2)] selected O_2 beam, for which the alignment as well as the spin state of O_2 molecules are well defined. In the present study[2], we have applied this beam to the study of the steric effect in the initial oxidation of Si(100) and found that the initial sticking probability (S_0) depends strongly on the alignment of O_2 molecules. The temperature and translational energy dependence of S_0 indicates that oxidation via the direct process gives a sticking probability ratio of 1.7 between "helicopter" and "cartwheel" geometries while the indirect process dominant at low temperatures and low translational energies exhibits no appreciable steric effects. This reveals that oxidation via the direct process strongly prefers the geometry in which the molecular axis is parallel to the surface. The steric effects persist even at the translational energy >0.3 eV, indicating that the activation barrier for the perpendicular geometry is much higher than 0.3 eV.

[1] L. Vattuone et al. Prog. Surf. Sci., 85, 92 (2010).
[2] M. Kurahashi et al., Phys. Rev. B(R) (in Press).

(invited) Surfaces, interfaces, and their impact on photovoltaic energy conversion

A Rockett

University of Illinois, USA

This talk reviews some of the issues on the importance of surfaces and interfaces to photovoltaic energy conversion and describes some of the results my group has obtained on chalcopyrite materials in particular. Surfaces represent points of recombination and hence loss of minority carriers generated by photons in the device. As such passivation of surface defects is crucial to producing an efficient device. Surface passivation in Si photovoltaics can be accomplished with dielectrics such as SiO_2 but more usefully by hydrogenated amorphous Si (a-Si:H) as in the "HIT" contact technology developed by Sanyo. In $CuInSe_2$ and related compounds have exceptional surfaces low energy despite being polar by nature. The clean surfaces show pinning of the Fermi level near the middle of the energy gap by photoelectron spectroscopy and tunneling spectroscopy but formation of the heterojunction unpins the junction and forms a good contact. Examples are presented of tunneling spectra for $CuInSe_2$ and $AgInSe_2$ illustrating the large differences in behavior and the implications for device operation. Contacts are also crucial to device operation. Surface doping can reduce the impact of some contacts, as is the case for CdS on $CuInSe_2$ but other junctions are less well behaved.

Energy transfer in molecule-substrate interactions studied by Pt-SiO_2-Si chemoelectronic thin film devices

M Scheele, I Nedrygailov, D Diesing and E Hasselbrink

Universität Duisburg-Essen, Germany

Energy flow in chemical surface reactions comprise excitation and relaxation of reacting molecules as well as heating and electronic excitation of the substrate. On the other hand, molecules can also take up energy from a substrate. Both, energy loss of molecules to the substrate as well as energy take up from the substrate can be detected by means of chemoelectronic devices. These devices are thin film metal-semiconductor or metal-insulator-metal junctions with a top metal electrode of nanometre thickness acting as the substrate. The energy transfer from a metal film to a molecular beam of hydrogen, helium and nitrogen can be monitored as a change of the device current driven by a constant bias voltage. The current changes can be a result of a temperature difference across the device. The sensitivity of the device can be tuned by the magnitude and the polarity of the bias voltage and the base temperature of the device. Moreover model calculations show a large sensitivity of chemoelectronic devices to temperature differences in the milli Kelvin range.

A first-principles insight to the properties of hydrogenated amorphous silicon

M Legesse, M Nolan and G Fagas

Tyndall National Instittute – UCC, Ireland

Amorphous silicon (a-Si) is the prototypical material to understand the properties of structurally disordered semiconductors. The properties of a-Si have been studied extensively due to its technological relevance for thin film photovoltaics and transistors in large display electronics. Hydrogenation has emerged as a standard technique to improve the properties of a-Si by removing charge trap states. The optical properties are also affected through a blue shift in the band gap of hydrogenated a-Si. Nevertheless, the role of hydrogen is still under debate and fundamental understanding from atomic-scale modelling has a major contribution to make.

In this presentation we discuss the dependence of the conductivity and optical gap on the nature of mid-gap states in ideally, under- and over- saturated hydrogenated a-Si. Our central finding is that the magnitude of the band gap does not only depend on the hydrogen concentration but also on sample preparation, and the number of possible trap states depends critically on their interplay. Our results are based on empirical potential and quantum mechanical density functional theory (DFT) studies of models of 512 atom supercells. Our amorphous structures are obtained via a heat and quench approach. The radial distribution function and the electronic density of states are used respectively for the structural and electronic characterisation of our samples. These compare well with experimental results. A detailed analysis of the band gap and the localised states in the Urbach tails and the mid-gap follows by examining the charge density, the inverse participation ratio and the dielectric function.

Magnetism 1

Observations of spin dependent transport using optically orientated photocurrents

S Clowes[1], J Li[1], A Gilbertson[2] and L Cohen[2]

[1]University of Surrey, UK, [2]Imperial College London, UK

The realization of efficient semiconductor based spin filters and manipulators is essential for semiconductor spintronics to achieve its promised potential as a route to faster and more energy efficient electronics. One of the challenges is the creation of spin polarized currents within inherently non-magnetic semiconductors. The conventional approach to achieve this has been via the incorporation of magnetic materials. However, it may be possible to produce non-magnetic spin filters with very high efficiency by exploiting the strong spin-orbit interaction present in a number of semiconductors. An important feature of these devices is that the transport regime is predominantly ballistic. In this respect, p-GaAs quantum wells (QWs) have been the material of choice due to their very large hole mobilities and the strength of spin-orbit coupling in the valence band. Recent advances in the growth of n-InSb QWs have resulted in mobilities in this material that now exceed 100,000 $cm^2V^{-1}s^{-1}$ and have resulted in mean free paths of around 2 μm. In addition to this InSb has the strongest Rashba coefficient of all the III-Vs making it an ideal candidate for ballistic spintronic devices.

We have investigated spin dependent transport in InSb QW nanoscale structures using spin polarised photocurrents. We have demonstrated transverse magnetically focussing of photocurrent signals in an InSb/InAlSb quantum well device. Using optical spin orientation by modulated circularly polarized light an electron spin-dependent signal has been observed due to the spin-orbit interaction. In addition to this, simulations of the focusing signal have been performed using a classical billiard ball model, which includes both spin precession and a spin-dependent electron energy. The simulated data suggests that a signal dependent on the helicity of the incident light is expected for a Rashba parameter $\alpha>0.1$ eVÅ and that a splitting of the focusing signal is not expected to be observed in linear polarized photocurrent and purely electrical measurements. This demonstrates the spin dependent focussing effect without the need of quantum point contacts or large in-plane magnetic fields to lift the spin degeneracy of these contacts.

We will also report on measurements of spin dependent transport in InSb nanowires using the same optical orientation technique described above. By applying weak magnetic fields (~200 mT) we have observed a spin filtering effect which is caused by spin dependent back scattering of electrons from the sidewalls of classical origin.

Voltage control of magnetisation and magnetic domain configurations in magnetostrictive epitaxial $Fe_{1-x}Ga_x$ thin films and devices

D Parkes[1], S Cavill[2], A Hindmarch[3], P Wadley[1], F McGee[1], K Edmonds[1], A Rushforth[1] and B Gallagher[1]

[1]University of Nottingham, UK, [2]Diamond Light Source, UK, [3]Durham University, UK

The control of ferromagnetic domains and domain walls by electrical means is a desirable objective for applications in many existing and proposed information storage[1,2] and logical processing[3] devices. One route to achieve this goal is via hybrid ferromagnet/piezoelectric transducer devices [4-6] in which a voltage applied to the transducer induces mechanical strain in the ferromagnet affecting the magnetic anisotropy through the inverse magnetostriction effect. We have implemented epitaxially grown thin films of $Fe_{81}Ga_{19}$ on a GaAs substrate in such a device. Through a combination of magnetotransport measurements, magneto-optical Kerr effect (MOKE) and high resolution photoemission electron microscopy (PEEM) we demonstrate that our epitaxial films possess an exceptionally large magnetostriction (enhanced over that previously observed in bulk samples[7]) and a strong cubic magnetocrystalline anisotropy. We exploit these properties to achieve voltage control of the magnetisation and magnetic domain walls, including the reconfiguration of ordered domain patterns in structured geometries, and non-volatile switching of the magnetisation in the absence of external magnetic fields. Such functionalities will be directly applicable to information storage and processing technologies.

[1] W.J. Gallagher and S.S.P. Parkin, IBM J. Res. & Dev. 1, 5 (2006).
[2] S.S.P. Parkin, M. Hayashi, and L. Thomas, Science 320, 190 (2008).
[3] D.A. Allwood, et al. Science 309, 1688 (2005).
[4] Sang-Koog Kim et al., J. Mag. Mat. Res. 267, 127 (2003).
[5] J-W Lee et al., Appl. Phys. Lett. 82, 2458 (2003).
[6] A.W. Rushforth et al., Phys. Rev. B. 78, 085314 (2008).
[7] A.E. Clark, et al. J. Appl. Phys. 93, 8621 (2003).

Magnetization reversal of individual Co nanoislands

S Ouazi, S Wedekind, G Rodary, H Oka, D Sander and J Kirschner

Max Planck Institute of Microstructure Physics, Germany

We investigate the field induced magnetization reversal of individual Co islands on Cu(111) in the size range of 700 to 18000 atoms by spin-polarized scanning tunneling microscopy at 8 K. The switching field H_{SW} changes with island size in a non-monotonous manner: it increases with island size and reaches a maximum value of 2.4 T at 5500 atoms, and it decreases for larger islands.

We extract the energy barrier for magnetization reversal as a function of island size. Our analysis reveals that the Co islands are magnetically inhomogeneous. The outer rim is magnetically soft, whereas the center region is magnetically hard. Thus, Co islands may be regarded as an exchange spring nanomagnet [1]. For larger islands, we propose that the magnetization reversal occurs by domain nucleation and growth. Our results elucidate a crossover of the magnetization reversal from an exchange spring behavior to domain wall formation with increasing size [2].

[1] H. Zeng, J. Li, J. Liu, Z. Wang, and S. Sun, Nature 420, 395 (2002).
[2] S. Ouazi, S. Wedekind, G. Rodary. H. Oka, D. Sander, and J. Kirschner, Phys. Rev. Lett. 108, 107206 (2012).

(invited) Ultrafast magnetization dynamics using pulsed X rays

C Boeglin[1], V Lopez-Flores[1], V Halte[1], C Stamm[2], N Pontius[2] and E Beuarepaire[1]

[1]IPCMS, France, [2]HZB –BESSY, Germany

Ultrafast magnetization dynamics is an important issue for both fundamental science and for applications in order to optimize spin manipulation on a microscopic level. Since the first observation of laser induced spin dynamics [1], the mechanisms of angular momentum dissipation at picosecond timescales have been widely debated. It has now been shown that it is possible to probe absolute values of magnetization with a high temporal resolution (100 fs) using the f-slicing source at HZB-BESSY. In this context, we have used ultrashort optical laser pulses (60 fs duration) to induce changes of the magnetization in ferromagnetic CoPd alloy films with perpendicular anisotropy. The optical laser pulses are used to excite ferromagnetic CoPd, probed at Co L2,3 edges with ultrashort circularly polarized femtosecond X-ray pulses using a pump-probe set-up [2,3]. We show that the two components of the magnetic moments (L, S) lead to different ultrafast dynamics and that the spin-orbit coupling related to the magneto-crystalline anisotropy in the ultrashort time scales. We will compare our results with other alloys were the chemical selectivity has been used to study different ultrafast dynamics due to exchange.

[1] Beaurepaire et al. Phys. Rev. Lett. 76, 4250 (1996).
[2] Stamm et al. Nature Mater. 6, 740-743 (2007).
[3] C. Boeglin, E. Beaurepaire, V. Halté, V. Lopez-Flores, C. Stamm, N. Pontius, H. Dürr, J. -Y. Bigot "Distinguishing the ultrafast dynamics of spin and orbital moments in solids" Nature 465, 458 (2010).

Electronic interface effects in FeCu alloy films grown on self-assembled Pb islands

F Luque[1], I A Kowalik[2], T O Mentes[3], A Locatelli[3], R Miranda[4], J J de Miguel[1], D Arvanitis[5] and M Ángel Niño[6]

[1]Universidad Autónoma de Madrid, Spain, [2]Institute of Physics, Polish Academy of Sciences, Poland, [3]Sincrotrone Elettra, Italy, [4]Dpto. de Física de la Materia Condensada, Universidad Autónoma de Madrid, and IMDEA-Nanociencia, Campus UAM, Spain, [5]Uppsala University, Sweden, [6]IMDEA-Nanociencia, Spain

Metastable fcc $Fe_{50}Cu_{50}$ alloy films are prepared by UHV codeposition with the aid of a surfactant Pb monolayer [1]. XMCD-PEEM micrographs obtained at the Nanospectroscopy beamline of synchrotron Elettra in Trieste (Italy) using circularly polarized x rays tuned at the Fe L_3 absorption edge show that the alloy grown on a Cu(111) single-crystal only becomes ferromagnetic at room temperature for thicknesses above ~18 ML. Nevertheless, the same alloy grown on top of the Pb islands spontaneously formed due to the Stranski-Krastanov growth mode of Pb on Cu(111) is strongly ferromagnetic in-plane at 300 K above ~5 ML thickness and it remains so at least up to 450 K. Micro-LEED I-V measurements demonstrate that all alloy films are fcc with equivalent crystallographic structure and lattice parameter irrespective of the supporting substrate. Hence, the cause of the different magnetic behaviour must be ascribed to electronic effects at the interface between the alloy and the substrate.

The origin of the enhanced magnetic ordering in the films grown on Pb has been investigated by XMCD measurements at beamline I1011 of synchrotron MAXlab in Lund, Sweden. Sum-rule analysis of these data allows us to determine the spin and orbital magnetic moments of the Fe atoms and discuss the interfacial anisotropy in the context of the intense spin-orbit coupling of the bulk Pb substrate and the electronic state of the Fe and Cu ionic cores.

[1] J. Camarero et al., Surf. Sci. 482-485, 1077 (2001).

Ballistic-like persistent currents in disordered normal metal rings: Origin of large experimental values

J Feilhauer and Martin Mosko

Slovak Academy of Sciences, Slovakia

Quantum physics predicts [1] that a mesoscopic resistive metal ring will support a persistent current corresponding to the current carried by a single electron diffusing around the ring at the Fermi energy. Recent experiments confirm this prediction [2,3], but a puzzle of mesoscopic solid-state physics is the observation of currents resembling a single electron moving around the ring ballistically rather than diffusively [4]. The importance of this experimental puzzle for physicists can be illustrated by the fact that it has been addressed by about four hundred papers in two decades [5]. We explain the puzzle by calculating persistent currents in rings with realistic disorder. If disorder is due to polycrystalline grains, we find the expected diffusive current. However, if disorder is mainly due to the rough ring edges, we find the ballistic-like current even for the ring lengths hundred times larger than the electron mean free path, like in the milestone experiment. This ballistic-like current is inherent to the metallic rings with rough edges; it is carried by a single electron which moves (classically speaking) in parallel with the edges and thus does not feel the roughness.

[1] H. F. Cheung et al., Phys. Rev. Lett. 62, 587 (1989).
[2] H. Bluhm et al., Phys. Rev. Lett. 102, 136802 (2009).
[3] A. C. Bleszynski-Jayich et al., Science 326, 272 (2009).

[4] V. Chandrasekhar et al., Phys. Rev. Lett. 67, 3578 (1991).
[5] W. Shanks, (Yale PhD. Thesis) (2011) http://arxiv.org/abs/1112.3395.

Low temperature physics 1

(invited) Gate tunable normal and superconducting transport through a 3D topological insulator

A Morpurgo

University of Geneva, Switzerland

We report on transport experiments though very thin Bi_2Se_3 layers, exfoliated from high quality single crystals. The Bi_2Se_3 layers are transferred onto a Si/SiO_2 substrate acting as a gate, and superconducting electrodes are attached using conventional nano-fabrication techniques. Low-temperature measurements of magneto-resistance exhibit clear Shubnikov de Haas oscillations, which can be tuned by applying a gate voltage. The plot of the resistance as a function of magnetic field and gate voltage exhibit a clear fan diagram of Landau levels originating from both electrons and holes at the surface closer to the gate electrode. A quantitative analysis of the fan diagram allows to index the electron and hole Landau levels, and we find that their degeneracy agrees with what is expected from Dirac fermions (the so-called half integer Hall effect with a zero energy Landau level shared bay valence and conduction gap). Shubnikov de Haas oscillation due to carriers on the surface far away from the gate are also observed, as features in the fan diagram that do not depend on the gate voltage, since the effect of the gate voltage second surface is screened by the first and by carriers in the bulk. A quantitative analysis of the data show that an impurity band is present inside the bulk bands of Bi_2Se_3, with a large density of states, that coexist with the surface states. Finally, at zero magnetic field, we observe Andreev reflection due to the superconducting electrodes together with a clear proximity induced supercurrent. The critical current is gate tunable and exhibits a bipolar behavior, with a minimum at the same gate voltage observe from extrapolating the fan diagram of Landau levels. This observation indicates that at least part of the supercurrent is carried by Dirac electrons and holes at the surface. These results demonstrate the possibility to use nano-devices for the investigation and control of surface states in 3D topological insulators.

Noise spectral analysis of environmental noise in SQUID and superconducting qubit type circuits using a Cavity Bifurcation Amplifier

G Ithier, J Burnett, G Tancredi and P Meeson

Royal Holloway, University of London, UK

We present a novel technique for the characterisation of noise in superconducting quantum bit circuits which has the new advantage of directly accessing the frequency dependence of the environmental noise spectrum.

Due to their potential scalability superconducting circuits provide a promising framework for Quantum Information Processing, however, despite dramatic improvement in recent years quantum coherence times are still insufficient for the performance of non-trivial calculations. Superconducting quantum circuit coherence times are limited by their strong coupling to environmental noise sources. Exploring, understanding and reducing environmental noise sources is a thus a key issue in the quest for a useful quantum computing architecture.

To our knowledge, all previous characterisations of noise sources in superconducting quantum bit circuits have used the decay of NMR type coherence functions such as the Ramsey or Hahn echo ones. These techniques are sensitive, they operate at low temperature and low probing power, but they do not give straightforward access to the frequency dependence of the noise. Our new technique relies on the repetitive use of a threshold detector, including those typically used for quantum bit state measurement. The power of this method is demonstrated through the use of a non-linear superconducting resonator exhibiting a bifurcation phenomenon, the so called Cavity Bifurcation Amplifier. We demonstrate independent access to the noise spectra of frequency fluctuations and magnetic flux noise. We also show that the sensitivity is close to the fundamental shot noise limit of a weak continuous measurement making this implementation one of the most sensitive available for probing environmental noise. We further benefit from the low dissipation of the bifurcation phenomenon and the low probing energy involved ($\sim 10^3$ photons) allowing us to operate the device in a temperature regime inaccessible to other noise probing techniques such as SQUID amplifiers and single electron transistors.

(invited) Evidence for nuclear spin order in GaAs quantum wires at ultra-low temperatures

D Zumbuhl[1], C Scheller[1], G Barak[2] and A Yacoby[2]

[1]University of Basel, Switzerland, [2]Harvard University, USA

The ability to reach low millikelvin or even microkelvin temperatures in nanoscale samples would open up the possibility to discover new physics. For example, mediated by the hyperfine interaction and interacting electrons, helical nuclear spin order in a GaAs 2D electron gas has been predicted around 1 mK at B = 0, constituting a novel type of correlated state. Here, I will present a new method intended to cool nanostructures into the microkelvin regime based on the well established technique of adiabatic nuclear demagnetization. On a parallel network of nuclear refrigerators, temperatures of 185 microK have been reached upon demagnetization, thus completing the first step towards ultracold nanostructures.

Further, I will present evidence of a nuclear ordered state in GaAs cleaved-edge overgrowth quantum wires. In this 1D system, the predicted nuclear ordering temperature is ~80 mK [1], much higher than in the 2D system. The conductance values of the plateaus are strongly suppressed below the universally expected multiples of 2e2/h [2]. For the lowest mode, the plateau conductance saturates at ~1 e2/h at T < ~100 mK, though it is clear that the sample cools well below 100 mK. This suggests that the spin degeneracy is lifted, consistent with recent theory [1] predicting helical nuclear magnetism in the Luttinger liquid regime.

[1] "Nuclear magnetism and electron order in interacting one-dimensional conductors", Bernd Braunecker, Pascal Simon, and Daniel Loss, Phys. Rev. B80, 165119 (2009).

[2] "Nonuniversal Conductance Quantization in Quantum Wires", A. Yacoby, H. L. Stormer, Ned S. Wingreen, L. N. Pfeiffer, K. W. Baldwin, and K. W. West, Phys. Rev. Lett. 77, 4612 (1996).

Extending the operating temperature range of ultra-low noise nanoSQUIDs

L Hao, D Cox and J Gallop

National Physical Laboratory (NPL), UK

NanoSQUIDs made from Nb thin films have been produced with nanometer loop sizes, using weak-link junctions with dimensions lees than 60 nm. These composite (W/Nb) single layer thin film devices, patterned by FIB milling, have shown extremely good low-noise performance ~250nphi0 [1] at temperatures between 5 K and 8.5 K and can also operate in rather high magnetic fields (up to 1T). However the devices produced so far have a limited operating temperature range, typically only 1-2 K. It would be useful to extend the operating range down to much lower temperatures if possible. With this in mind we have been experimenting with controlled charged particle beam exposure of the Nb films, to suppress their transitions temperatures and to extend the useful range of operation. We report results on these, including exposure dependent onset of hysteretic behaviour of the SQUID I-V characteristics. The results may be explained in terms of induced damage to the crystal lattice and the onset of amorphisation.

[1] L. Hao et al., Appl. Phys. Lett. Vol. 92, 192507 (2008).

Non-linear dynamics of nanoelectromechanical systems

J Owers-Bradley[1], K Lulla[1], R Cousins[1], M Patton[1], C Mellor[1], A Venkatesan[2] and A Armour[1]

[1]University of Nottingham, UK, [2]IISER Mohali, India

The non-linear dynamics of nanoelectromechanical systems (NEMS) is of practical importance as it can limit their use as sensors operating in the linear regime. The very high operating frequencies of NEMS devices (typically in the MHz range) make them ideal for investigating fundamental aspects of non-linear dynamics. Because NEMS devices are engineered systems and their nonlinearities can be extensively tuned, it should be possible to use them to study complex non-linear phenomena in which different mechanical modes interact. Furthermore, when cooled to very low temperatures, the non-linear behaviour in nanomechanical devices would provide important signatures of the transition from classical to quantum regimes. Non-linearity can arise in a wide variety of different ways in NEMS devices. For example when a doubly clamped beam is excited its displacement leads to a stretching of the beam which generates a Duffing type nonlinearity in a given mode as well as generating inter-mode couplings. We present a systematic study of the nonlinear response of three of the flexural modes of a nanomechanical beam resonator, together with the associated inter-mode couplings. We report the results of a series of measurements taken at 100 mK on the fundamental, third and fifth harmonics of a doubly-clamped beam fabricated from high-stress (~ 1 GPa) silicon nitride. When we excite one single mode at a time and find a Duffing like behaviour which can be understood quite naturally in terms of the nonlinearity arising from the stretching of the beam. We then drive two modes at the same time, with the shift of one mode acting as a probe of the displacement of the other. The high tensile stress and the low temperature mean that the Q-factor of the modes is high enough to allow us to observe the higher mode resonance signals as well as the frequency shifts induced by nonlinear mode-mode couplings which are much larger than the linewidth. Using the single-mode results to calibrate our measuring scheme we are able to make a detailed quantitative comparison (without the need for any fitting parameters) between our results and the predictions of a simple model of the stretching nonlinearity.

Nonlinear dynamics in nanomechanical resonators

E Collin, M Defoort, K Lulla, OBourgeois, Y Bunkov and H Godfrin

CNRS, France

Nanomechanical devices have attracted recently the interest of physicists for both applications and their fundamental understanding. Indeed, these artificial mechanical devices can be studied and controlled in such an accurate way that they become model systems in which fundamental issues of (here classical) mechanics can be addressed.

We present results on a special type of goalpost-shaped nanomechanical devices studied at low temperatures. Particular care is taken in calibrating the setup and understanding the resonance properties of the system [1]. Using a linear excitation technique (magnetomotive) combined with a strongly nonlinear one (capacitive), we can efficiently tune nonlinear effects in the nanoresonator. Parametric amplification with an exceptional gain has been realized and applied to the study of thin films anelasticity [2]. Audio-mechanical mixing has been demonstrated [3]. Finally, the physical issue of dynamic bifurcation, of ubiquitous interest in physics (linked to thermal activation of Josephson junctions, the kinetics of chemical reactions, the dynamics of magnetic macro-molecules…), is presented [4].

[1] E. Collin et al., Rev. Sci. Instrum. In press (04/2012).
[2] E. Collin, T. Moutonet, J.-S. Heron, O. Bourgeois, Yu. M. Bunkov, H. Godfrin, Phys. Rev. B 84, 054108 (2011).
[3] M. Defoort, K. Lulla, J-S. Heron, O. Bourgeois, E. Collin, and F. Pistolesi, Appl. Phys. Lett. 99, 233107 (2011).

[4] Article under preparation.

Electronic structure and topological insulators 1

Influence of magnetic impurities on doping and scattering of topological surface states: Fe on Bi_2Te_3 and Bi_2Se_3

M Scholz[1], J Sánchez-Barriga[1], D Marchenko[1], A Varykhalov[1], E Rienks[1], A Volykhov[2], L Yashina[2] and O Rader[1]

[1]Helmholtz-Zentrum Berlin, Germany, [2]Moscow State University, Russia

The effect of Fe impurities deposited on the surface of the topological insulators Bi_2Se_3 and Bi_2Te_3 is studied by means of ARPES, core-level photoemission and STM. The topological surface state reveals surface electron doping when the Fe is deposited at room temperature and hole doping when deposited at low temperture (T= 10 K). We show that in both cases the topological surface state remains intact and gapless. We analyze the line broadening for pure Bi_2X_3 (X=Se, Te) and after deposition of Fe. We observe that the constant (independent of binding energy) broadening in the bulk band gap range increases by a factor of 2 upon deposition of Fe. Because we deposit the Fe without electron doping, this result is not due to a gain in warping as was recently suggested. We discuss the results based on different types of scattering mechanisms.

Epitaxial Bi_2Se_3 on Graphene/SiC(0001): Structure, growth, and defects.

V Lazarov[1], Y Liu[2], D Gilks[1], M Weinert[2] and L Li[2]

[1]The University of York, UK [2]University of Wisconsin-Milwaukee, USA

Bi_2Se_3 is a 3D topological insulator (TI) that has attracted a lot of research due to theoretical predictions of exotic properties associated with topologically protected helical two-dimensional surface states and one-dimensional states associated with bulk line defects such as dislocations. While the 2D surface states have been experimentally verified using angle resolved photoelectron spectroscopy and scanning tunnelling spectroscopy (STS), the bulk 1D modes, which also depend on the type of the dislocations and the class of the TIs, are yet to be verified experimentally. In this work we use MBE to control the synthesis of the Bi_2Se_3 and understand the growth, film structure and defects formation on atomic scale by using STM, (S)TEM and DFT. TEM show that Bi_2Se_3 film is epitaxially grown with the following crystallographic orientation: Bi_2Se_3(11-20)||SiC(1-100) and Bi_2Se_3(0001||SiC(0001). Based on insitu STM we found that Bi_2Se_3growth on graphene/SiC(0001) initiates with two-dimensional nucleation, and that spiral growth ensues with pinning of the 2D growth fronts at jagged steps of the substrate or domain boundaries created during coalescence of the 2D islands. Winding of growth fronts around these pinning centre leads to spirals. In some cases when grains coalesce formation of anti-phase boundaries was observed and the strain at the boundaries relieves within several atomic planes. Finally the STS results (taken from spiral cores and array of parallel steps) show that 1D helical mode of line defects is not allowed for Bi_2Se_3

Temperature dependent measurements of the phonon dispersion on Bi(111)

A Tamtögl[1], P Kraus[1], M Mayrhofer-Reinhartshuber[1], D Campi[2], G Benedek[2] and W E Ernst[1]

[1]Graz University of Technology, Austria, [2]Universitá di Milano-Bicocca, Italy

There has been an increasing interest in bismuth in the recent years. A phase transition in Bi involving electron pockets that host Dirac electrons has been reported [1] and the present interest in topological insulators (e.g.: Bi_2Se_3) has been a stimulus for helium scattering measurements [2].

We have measured the surface phonon dispersion relation of Bi(111) at surface temperatures of 100 K, 120 K and at room temperature using time-of-flight spectra of inelastically scattered He atoms. The phonon dispersion in both high-symmetry directions exhibits a Rayleigh mode, an optical mode and a flat, nearly dispersionless branch at approximately 4 meV.

The low temperature measurements reveal a higher group velocity of the Rayleigh mode than at room temperature and the agreement with theoretical calculations is fairly good within variations of the experimental data. Indeed, some differences may be based on the fact that even in the bulk case the optical modes could not be reproduced perfectly at a few high-symmetry points [3].

The interpretation of the nearly dispersionless mode remains a puzzling question. It could be caused by a resonance-enhanced bulk mode which is also supported by the strong surface corrugation revealed in recent elastic measurements [4]. Although calculations of the Bi(111) surface phonon dispersion do not favour this explanation, rescaled calculations of the Sb(111) phonon dispersion show a clear surface resonance corresponding to this branch.

[1] K. Behnia, Science 321 (2008) 497.
[2] X. Zhu et al.,Phys.Rev.Lett. 107 (2011) 186102.
[3] Díaz-Sánchez L E et al., X Phys. Rev. B 76 (2007) 104302.
[4] Mayrhofer-Reinhartshuber et al., JPCM 24 (2012) 104008.

(invited) Electronic structure of clean and adsorbate-covered Bi_2Se_3

P Hofmann

Aarhus University, Denmark

The so-called topological insulators are well-known, off-the-shelf materials, but they have a previously overlooked and profound "topological" property that forces their surfaces and edges to be metallic, in contrast to the insulating bulk. Moreover, the one-dimensional (two-dimensional) metal at the edge (surface) of a topological insulator was shown to be inherently robust against disturbances, and to possess special transport properties linked to the electron's spin, leading to many exciting predictions for new physics and potential applications.

In this talk, I will present recent results on the electronic structure and electron dynamics of the prototypical topological insulator Bi_2Se_3. In particular, the effects induced by adsorbates are discussed. Adsorption, intercalation and substitution can drastically modify the electronic states present near the surface, in particular through strong band bending effects that can lead to new quantum-confined and two-dimensional states in both the conduction and valence band of the material.

Electron transmission through atomic steps of Sb surfaces

K Kobayashi

Ochanomizu University, Japan

Topological insulators are intensively studied in recent years due to their novel properties. A characteristic property is the existence of nontrivial surface states, in which electrons are not scattered to the backward direction by imperfections. Surface steps are good structures for studying directly this property. We have already studied theoretically the electron transmission through atomic steps of Bi_2Se_3 and Bi_2Te_3 surfaces, and found new properties such as perfect reflection [1]. In this presentation we show a theoretical study on the transmission properties of Sb surfaces.

Sb is a material having nontrivial surface states [2]. However, since the bulk electronic state is semimetallic, surface and bulk states coexist at the Fermi energy. Therefore, the scattering to bulk states occurs. This point is different from the Bi_2Se_3 and Bi_2Te_3 cases, in which only surface states exist in the bulk band gaps. We calculated the transmission properties through atomic steps of Sb surfaces, and obtained numerical results of transmission probability that are in good agreement with experimental data [3]. Moreover, we found that the transmission properties much depend on the direction of the step lines.

[1] K. Kobayashi: Phys. Rev. B 84 (2011) 205424.
[2] J. C. Y. Teo, L. Fu and C. L. Kane: Phys. Rev. B 78 (2008) 045426.
[3] J. Seo, P. Roushan, H. Beidenkopf, Y. S. Hor, R. J. Cava and A. Yazdani: Nature 466 (2010) 343.

Quantum spin models from flux tubes in correlated topological insulators

M Hohenadler, F Assaad and M Bercx

University of Würzburg, Germany

The adiabatic insertion of a pi flux into a quantum spin Hall insulator gives rise to localised spin and charge fluxon states. Here we first demonstrate that pi fluxes can be used in exact quantum Monte Carlo simulations to identify a correlated quantum spin Hall insulator. We then show that electronic correlations give rise to low-lying spin degrees of freedom with clear signatures in the magnetic susceptibility, and at the same time provide a bosonic mode of magnetic excitons with tunable energy. The excitons act as exchange particles and mediate a dynamical spin-spin interaction of adjustable range and strength. In combination with the freedom to create almost arbitrary spin lattices, correlated topological insulators with pi fluxes represent a novel kind of quantum simulator useful for numerical simulations and experiments.

Normal and superconducting transport in the topological insulator HgTe: Theoretical aspects

G Tkachov, J B Oostinga, E M Hankiewicz, H Buhmann and L W Molenkamp

University of Würzburg, Germany

HgTe quantum wells and topological surface states in 3D HgTe samples exhibit spin-helical (effectively Dirac-like) charge carriers [1]. In this contribution we discuss theoretical aspects of helical charge transport, particularly the anomalous carrier mobility and weak localization effects observed in HgTe quantum wells [2,3]. We also address superconducting transport in Josephson junctions with the HgTe topological insulator as a weak link [4]. Such Josephson junctions are predicted to support topologically protected Andreev bound states which are intimately related to the Majorana bound states. We discuss how to detect the topological bound states via the AC Josephson effect.

[1] B. Buettner, C.X. Liu, G. Tkachov, E.G. Novik, C. Bruene, H. Buhmann, E.M. Hankiewicz, P. Recher, B. Trauzettel, S.C. Zhang, and L.W. Molenkamp, Nature Phys. 7, 418 (2011).
[2] G. Tkachov, C. Thienel, V. Pinneker, B. Buettner, C. Bruene, H. Buhmann, L. W. Molenkamp, and E. M. Hankiewicz, Phys. Rev. Lett. 106, 076802 (2011).
[3] G. Tkachov and E. M. Hankiewicz, Phys. Rev. B 84, 035444 (2011).
[4] L. Maier, J.B. Oostinga, D. Knott, C. Bruene, P. Virtanen, G.Tkachov, E.M. Hankiewicz, C. Gould, H. Buhmann, and L. W. Molenkamp, submitted to Phys. Rev. Lett. (2012).

Semiconductors and their surfaces 1

(invited) In-Si(111)(4x1)/(8x2) nanowires: metal-insulator transition and optical response

W G Schmidt

University of Paderborn, Germany

One-dimensional conductors have been fascinating physicists for a long time. While a strictly 1D material is an academic construct, there are a number of substrate-stabilized quasi-1D systems that can be used for learning the fundamentals of electronic transport in low-dimensional systems. The In-Si(111)(4x1)/(8x2) nanowire array is perhaps the most intensively investigated quasi-1D system [1]. It features a Peierls instability-driven phase transition, the mechanism of which has been controversial since its discovery, cf. Ref. [1].

Here density-functional theory calculations on its structural, vibrational, electronic, and optical properties are presented. The calculated optical response in comparison with measured data settles eventually the long-standing debate on the nanowire ground-state geometry in favour of hexagons [2]. The subtle balance between the lower energy of the insulating phase and the larger vibrational entropy of the metallic wires causes a metal-insulator transition [3]. Ab-initio molecular dynamics simulations shed light on its dynamics, recently studied by ultra-fast time-resolved electron diffraction [4]. Finally, the influence of adatoms on the quantum transport [5,6] and phase-transition [7] is discussed.

[1] PC Snijders, HH Weitering, Rev. Mod. Phys. 82, 307 (2010).
[2] S Chandola et al., PRL 102, 226805 (2009).
[3] S Wippermann, WG Schmidt, PRL 105, 126102 (2010).
[4] S Möllenbeck et al., MRS Symp. Proc. 1230, 3 (2009).
[5] AA Stekolnikov et al., PRL 98, 026105 (2007).
[6] S Wippermann, N Koch, WG Schmidt, PRL 100, 106802 (2008).
[7] WG Schmidt, et al., PRB 84, 115416 (2011).

Self-catalyzed MBE-growth of InAsP nanowires on Si

M Panfilova, I Isakov, M J L Sourribes, H Y Liu and P A Warburton

University College London, UK

Semiconductor nanowires are under intensive study due to their intriguing features and great potential for electronic and optoelectronic devices, among other applications. Of particular interest are III-V semiconductors on Si, exploiting the mature Si technology and superior optoelectronic and electronic properties of III-V compounds. While there have been many studies on the growth of InAs and InP nanowires by metal-organic vapour-phase epitaxy either with or without the use of Au particles as catalyst, there are only a few studies on self-catalyzed growth of such nanowires by molecular beam epitaxy (MBE). Furthermore a variation of the P content in $InAs_{1-x}P_x$ nanowires enables bandgap modulation. However there are no reports about self-catalyzed ternary $InAs_{1-x}P_x$ nanowires grown by MBE.

Here we present self-catalyzed growth of free-standing $InAs_{1-x}P_x$ nanowires with different P content on Si (111) substrates by MBE. The nanowires were investigated by scanning electron microscopy for growth selectivity and nanowire geometry. To obtain further insight into the morphology and structure of the nanowires transmission electron microscopy measurements were carried out. The P composition of $InAs_{1-x}P_x$ nanowires was inferred from the measured lattice constant, using both high resolution X-ray diffraction (HRXRD) and energy-dispersive X-ray spectroscopy.

Density functional theory calculations of In adatoms on In nanowires, Si(111)In-8x2

H-K Kim[1], H Shim[2], G Lee[2] and H Kim[1]

[1]Sookmyung Women's University, South Korea, [2]Inha University, Korea

Indium nanowires self-assembled on Si(111) constitute a quasi-one-dimensional electronic system at room temperature (RT), and undergo a structural phase transition from the high-temperature 4x1 phase to the low-temperature (LT) 8x2 phase at 130 K [1]. This phase transition is accompanied by Metal-insulator transition with a periodic lattice distortion (PLD) [2]. It has been reported that In adatoms lower the transition temperature, compared with a clean 4x1 phase [3]. In-adatom-related features are clearly observed in the form of momomers and dimers on the LT-8x2 phase in scanning tunneling microscopy (STM) images whereas they are invisible on the RT-4x1 phase.

In this presentation, we report the denstiy functional pseudopotential calculations on various In adatom configurations on In/Si(111)-8x2 to identify the experimentally observed in-adatom-induced defects. First, the stable adsorption sites of a single adatom are identified. Then, we investigate the interaction among a few adatoms to explore the possible formation of small In adatom clusters. In-adatom dimer and trimer are found to be energetically favored to an isolated adatom. These results agree with the experimental STM images which show that adatom dimers are much more detected than a single adatom.

[1] H. W. Yeom et al., Phys. Rev. Lett. 82, 4898 (1999).
[2] J. R. Ahn et al., Phys. Rev. Lett. 93, 106401 (2004).
[3] W. Lee et al., J. Kor. Phys. Soc. 56, 943 (2010).

Atomic structure and electronic properties of semiconductor nanowire surfaces studied by scanning tunneling microscopy and spectroscopy

R Timm, M Hjort, OPersson, J Knutsson, S Lehmann, J Wallentin, L Samuelson and A Mikkelsen

Lund University, Sweden

Semiconductor nanowires show fundamental new physics and offer interesting opportunities for device application in energy and information technology. Due to the small size and the large surface-to-bulk ratio, the nanowire surface has a crucial influence on the performance of the entire device. Here, we present Scanning Tunneling Microscopy and Spectroscopy (STM/S) results on polytypic InAs and GaAs nanowires consisting of alternating segments with metastable wurtzite (WZ) and stable zincblende (ZB) crystal structure. The nanowires were cleaned from native oxide by annealing under an atomic hydrogen background[1,2]. STM images on all common low-index nanowire side facets could be obtained, revealing the atomic structure of these surfaces, for different WZ and ZB NW facets. The axial stacking of WZ and ZB segments results in the formation of a type-II heterostructure, as was investigated with STS.

In order to go further in combining structural and electrical characterization of nanowire devices, we have developed a combined Atomic Force Microscopy (AFM) / STM setup, where we can first locate an individually contacted nanowire in AFM mode and then acquire STM images and STS spectra on this specific nanowire under device operation. Finally, we also use the STM to image the nanowires directly from the top[3] and then form a point contact between the STM tip and the Au particle on top of the nanowire to do conductivity measurements on individual wires.

[1] Hilner et al., NanoLett. 8, 3978 (2008).
[2] Hjort et al., Appl.Phys.Lett. 99, 233113 (2011).
[3] Fian et al., NanoLett. 10, 3893 (2010).

Emergence of a state at Fermi level due to the formation of In-Sn heterodimers in Indium atomic chains on the Si(100)-2x1 surface

P Sobotik[1], P Mutombo[2], M Ondracek[2], P Zimmermann[1], M Setvin[2], P Kocan[1], I Ostadal[1] and P Jelinek[2]

[1]Charles University in Prague, Czech Republic, [2]Institute of Physics, Academy of Sciences of the Czech Republic

Co-deposition of metals of groups III and IV on the Si(100)-2×1 surface results in formation of 1D atomic chains. In case of In-Sn chains it has been shown [1], that there is no decomposition into pure Sn and In chains and that formation of heterogeneous In-Sn dimers is preferred. Recently, combining DFT and STM/STS experiments [2], we were able to resolve basic structures in mixed chains at low Sn:In ratio and assign them to theoretically predicted structures. The results were finally confirmed by chemical identification of single atoms in mixed InSn chains by means of nc-AFM and DFT calculations [3]. Pure Sn and In chains are not metallic. Emergence of a state at the Fermi level was predicted for a single In-Sn dimer as well as existence of states close to the Fermi level for In-Sn Sn-In and In-Sn In-Sn structures [3]. We present STM/STS experiments which confirmed this expectation. Spectra measured at different structures will be discussed and interpreted also with respect to the recent finding [3] that the Si atoms can replace the Sn atoms and form In-Si heterodimers.

[1] L. Magaud et al., Phys. Rev. B 65 (2002), 245306
[2] P. Sobotik et al, Emergence of a state at Fermi level due to the formation of In-Sn heterodimers in In atomic chains on the Si(100)-2×1 surface, in preparation
[3] M. Setvin et al, Chemical Identification of Single atoms in Mixed InSn Chains on Si(100) Surface by nc-AFM and DFT, in preparation

Nanostructures 1

(invited) Optical antenna: a paradigm shift for nanoscale wireless telecommunication

A Bouhelier

Centre National de la Recherche Scientifique, France

Optical antennas are devices employed for collecting, confining and redirecting radiation from and to nanometer–scale volumes. These characteristics are usually defined by designed parameters such as antenna’s morphology and the manner the different constituting elements are interacting with each other. In order to actively act on antenna performances, I will discuss the effect of a variable load commanded by an external electrical trigger and demonstrate that this on-demand control opens up the possibility to tune an antenna without changing its geometrical parameters. I will also discuss preliminary results concerning realization of metallic optical nano-antennas transceivers enabling a bilateral transduction between electron and photons. This unique nanometer-scale transducing devices may contribute to the development of short-range on-chip wireless optical data transfer.

Nano-optical measurements of novel superconducting single photon detector designs

R Heath[1], M Tanner[1], J O'Connor[1], L San-Emeterio-Alvarez[2], W Jiang[2], Z H Barber[2], R J Warburton[3] and R Hadfield[1]

[1]Heriot-Watt University, UK, [2]University of Cambridge, UK, [3]University of Basel, Switzerland

Superconducting nanowire single photon detectors (SNSPDs) are a highly promising emerging photon counting technology, offering infrared sensitivity, combined with low dark count rates and sub-100 ps timing jitter[1]. These devices are under consideration for a wide variety of photon counting applications, from quantum cryptography to remote sensing. Next generation device designs based on optical cavities, ultra narrow wires, parallel wire arrays and even nano-antenna enhanced devices are being evaluated to meet the demands of advanced photon counting applications. In this study we use a novel low temperature nano-optical testing setup to investigate a variety of device designs[2]. We are able to probe the local infrared detection efficiency and timing resolution with sub-micrometre resolution. We report on the effects of nano-optical elements, the variation of timing properties with position in non-uniform nanowires[3] and the timing properties with bias of novel parallel wire devices. Enhancing detection probabilities and exploitation of varying timing dynamics with position are investigated.

[1] CM Natarajan et al, Superconducting nanowire single photon detectors: physics and applications Supercond. Sci. Technol. 25 063001 (2012) .
[2] RM Heath, MG Tanner, et al, in Single Photon Workshop (PTB Braunschweig, Germany, 2011).
[3] JA O’Connor et al, Spatial dependence of output pulse delay in a niobium nitride nanowire superconducting single photon detector Applied Physics Letters 98 201116 (2011).

Photoinduced modification of surface states in nanoporous InP observed by terahertz spectroscopy

J Lloyd-Hughes[1], S Mueller[1], G Scalari[2], H Bishop[1], A Crossley[1], M Enachi[3], L Sirbu[3] and I Tiginyanu[3]

[1]University of Oxford, UK, [2]ETH Zurich, Switzerland, [3]TU Moldova

A precise control of the surface properties of semiconductor nanomaterials is vital for their functionality and use in many opto-electronic applications. Terahertz time-domain spectroscopy allows the non-contact investigation of electron transport in semiconductor nanomaterials, without the complication of contact fabrication. The technique allows the photoconductivity to be determined on picosecond timescales, under the assumption that the material's properties are not permanently altered by photoexcitation. Here we demonstrate that this assumption is not always valid.

We report an investigation of nanoporous honeycombs of n-type InP using terahertz time-domain and X-ray photoemission spectroscopies. To account for the THz transmission we derived an expression for the axial dielectric function of an array of infinitely long air pores embedded in a semiconducting host matrix. The Drude model of a free electron plasma was utilized for the complex conductivity of the host material, yielding the electron carrier density n and momentum scattering time in the nanomaterial. The InP honeycombs exhibited a substantially lower electron density than their nominal value, indicating that surface depletion reduces n.

After photoexcitation the dark conductivity was found to increase quasi-irreversibly, recovering only after several hours in air. The calculated electron density for different surface pinning energies suggests that photoexcitation may reduce the density of surface states. This photoinduced modification of porous semiconductors may be useful in material processing as it is a clean, dry, and area-selective method to increase the conductivity.

Simulation of nanowire junctionless transistors from first principles

L Ansari, G Fagas and J Greer

Tyndall National Institute – UCC, Ireland

The 'End-of-the-Roadmap' for nanoelectronics is the point when downscaling of individual transistor sizes reach lengths of few nanometres. We are applying electronic structure methods to explore the behaviour of materials at this length scale and to understand transistor behaviour for nanowire devices. The consequences from confinement in sub-5 nm wires on physical properties such as electron and hole scattering lengths and mobilities can be significant. For example, electron mobilities for [110]-grown silicon nanowires are 6 times larger than those for [100]-oriented wires. This effect cannot be predicted without an explicitly determined form of the deformation potentials. For surface and electron-phonon scattering in small cross section nanowires, scattering lengths are larger than 10 nm implying near-ballistic transport.

Using a combination of scattering calculations and ab initio electronic structure calculations, junctionless silicon nanowire transistors are investigated. Our primary finding is that a Si nanowire junctionless transistor is physically possible at scales of 1 nm wire diameter and 3 nm gate length, although the behaviour of dopants at these small nanowire diameters is significantly different than for bulk doping. The junctionless transistor architecture performance in terms of source-to-drain tunnelling and sub-threshold slope is examined. The difference for current-voltage characteristics calculated from a linear response or non-equilibrium Green's function approach is compared between junctionless transistors fabricated in silicon, germanium and carbon nanotubes. An introduction of how band gap engineering can be introduced into semimetal nanowires is given and a design for obtaining transistor action in a semimetal nanowire is presented.

Silicon nitride mechanical nano-resonators

E Collin, M Defoort, K Lulla, O Bourgeois, Y Bunkov and H Godfrin

CNRS, France

We report on experiments performed in vacuum at low temperatures on nanomechanichal silicon nitride doubly-clamped resonators. Different samples have been studied, with different in-built stresses ranging from low-stress (about 100 MPa) to high-stress (about 1 GPa). The mechanical properties (frequency, Q-factor, non-linear behavior) have been characterized as a function of this intrinsic axial load.

The control of THz radiation with layered superconductors

A Wall-Clarke and S Saveliev

Loughborough University, UK

This paper considers nonlinear effects on the propagation of Josephson plasma waves in the Josephson-vortex photonic crystal in layered superconductors with the possibility of exciting the second harmonic, tuneable by magnetic field. This would enable an increase in the operable frequency of THz superconducting devices such as generators, detectors and filters. We demonstrate numerically that the second harmonic can be strongly amplified for certain resonance frequencies. The linear spectrum for the second harmonic has also been analysed, finding the possible resonance points with the first harmonic spectrum. An analytical approach describing a spatial distribution of the THz Josephson plasma waves at the resonances is also developed. This work has also been extended to the third harmonic, showing a similar resonance behaviour with a smaller maximum amplitude than the second harmonic.

Experimental and simulated Investigation of ternary GaAsN compound for use as laser diode

O Abdallah[1], Y Al-Douri[2], A Abdellaoui[3], M Ghaffour[3] and M Bouslama[3]

[1]Centre Universitaire Khemis Miliana, Algeria, [2]University Malaysia Perlis (UNIMAP), Malaysia, [3]Labmat ENSET ORAN, Algeria

The ternary compound $GaAs_xN_{1-x}$, in which the group V element is partially replaced by nitrogen, has been subject to many recent studies because of its use as low threshold diode laser for applications in medicine diagnostics, optical storage and optical telecommunications.

In our work, trimethyl gallium, arsine AsH_3 and dimethylhydrazine (DMHy) were used to grow GaAsN of thickness 200nm on GaAs substrate. Two samples were prepared one of them was followed by heating at a temperature above 700°C.The heating of GaAs during the growth process is advantageous to eliminate the defects and enables to avoid all charge phenomenon to occur on the surface.

Auger electron spectroscopy (AES) is particularly suitable for analyzing this compound allowing elemental and quantitative analysis of the outmost layers of material because of its surface sensitivity. In addition, electron energy loss spectroscopy (EELS) as a complementary technique, gives information about the interband transitions, plasmon excitations, chemical relationships and the dielectric constant.

The compound surface $GaAs_xN_{1-x}$ was characterized by AES and EELS using an hemispherical analyzer operating in direct mode, N(E). The pass energy E_0 between the deflectors is constant at about 80 eV that corresponds to a good compromise between the resolution and the transmission of the instrument and allows an energy resolution of about 1 eV to be obtained.

The simulated study is related to the energy gap variation with the x concentration. We show that the $GaAs_xN_{1-x}$ gap decreases until the x reached the value of 0.25 and after that it is increases with increasing the concentration x. We follow our simulated study, using the rate equations of semiconductor laser, to plot the corresponding spectral lines.

Oxides and oxide surfaces 1

Hydrogen interaction on RuO_2(110) surface: A combined STM and TPD study

Y Wei, S Wendt and F Besenbacher

Aarhus University, Denmark

In this talk, we present a combined STM and TPD study on the interactions of oxygen and hydrogen molecules with the RuO_2(110) surface. We show that both weakly bonded on-top O species and free Ru-cus sites are required for hydrogen adsorption and dissociation. The most substantial water formation is obtained at low adsorption temperatures and at a medium coverage of pre-adsorbed O on-top species. We propose that the sticking coefficient of hydrogen and the diffusivity of H adatoms play important roles for the hydrogen adsorption and the subsequent water formation reaction.

On the H_2O – OH balance upon water adsorption on TiO_2 single crystal surfaces

A Sandell[1], M Amft[1], L E Walle[2], D Ragazzon[1], A Borg[2], P Uvdal[3] and N Skorodumova[4]

[1]Uppsala University, Sweden, [2]Norwegian University of Science and Technology (NTNU), Norway, [3]Lund University, Sweden, [4]Department of Materials Science and Engineering, Royal Institute of Technology, Sweden

The formation of the interface between water and a solid is a truly challenging fundamental problem. On many surfaces the formation of this interface or wetting layer is accompanied by water dissociation to hydroxyl [1]. The formation of hydroxyl plays an important role in stabilizing the wetting layer but partial water dissociation adds to the complexity of the wetting processes.

We have studied water adsorption on single crystalline TiO_2 of both the anatase and rutile polymorph at the Swedish synchrotron radiation facility MAX-lab [2-4]. Here we present a molecular level mechanism for the adsorption of water and subsequent partitioning into H_2O and OH on the benchmark surface, rutile TiO_2(110). The mechanism is based on the initial formation of stable hydroxyl dimers having a repulsive interaction between themselves and an attractive interaction with respect to water molecules. The experimental input was acquired using surface sensitive photoemission measurements of the O1s level, monitoring the water uptake in real time. The final model was then derived with the aid of DFT calculations and Monte Carlo simulations. In addition, we discuss effects due to surface defects: Dissociation at bridging O vacancies effectively quenches the dissociation on stoichiometric parts. Ti interstitials with a typical density of a few percent have negligible influence on the proposed mechanism.

[1] P. J. Feibelman, Science 295, 99 (2002).
[2] J. Blomquist et al., J. Phys. Chem. C112, 16616 (2008).
[3] L. E. Walle et al., Phys. Rev. B80, 235436 (2009).
[4] L. E. Walle et al., J. Phys. Chem. C115, 9545 (2011).

Dissociation of formic acid on anatase TiO_2 (101) probed by vibrational spectroscopy

M Buchholz[1], M Xu[2], H Noei[3], M Muhler[3], Y Wang[3] and C Wöll[1]

[1] Karlsruhe Institute of Technology, Germany, [2]Shandong University, China, [3] Ruhr University Bochum, Germany

The role of metal oxides is central in many technological areas such as gas sensing, solar energy conversion, water splitting and environmental treatments. It is known that most TiO_2 nanoparticles show the anatase form, which exhibits generally a substantially higher photocatalytic activity than that of rutile TiO_2 (110) [1]. In last decades numerous Infrared (IR) investigations of metal oxide powders, including the different modifications of TiO_2, have been reported, however an unambiguous assignment of the features in the complex IR spectra recorded for molecules bound to the oxide powders is quite complicate. Otherwise, it could be possible on the basis of data recorded for well-defined reference systems, e.g. surfaces of single crystals, but, unfortunately, studies on oxide single crystals are extremely scarce due to the fact that the sensitivity of reflection IR-spectroscopy for molecular adsorbates is two orders of magnitude lower for oxides than for metal single-crystals.

Here, the interaction of formic acid with anatase TiO_2(101) has been monitored by infrared reflection absorption spectroscopy (IRRAS) using a novel ultrahigh vacuum (UHV) system[2]. It was found that the formic acid molecules do not adsorb intact on TiO_2(101), as proposed previously, but dissociate yielding different formate species. The IR-bands observed in the IRRAS-data indicate the presence of a mono- and a bidentate species. It is proposed that the formation of the bidentate form could be present only with of oxygen vacancies[3].

[1] a)L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, H. J. Scheel, J. Am. Chem. Soc. 1996, 118, 6716; b)T. L. Thompson, J. T. Yates Jr., Chem. Rev. 2006, 106, 4428-4453; c)M. Xu, Y. Gao, E. M. Moreno, M. Kunst, M. Muhler, Y. Wang, H. Idriss, C. Wöll, Phys. Rev. Lett. 2011,106, 138302.
[2] Y. Wang, A. Glenz, M. Muhler, C. Wöll, Rev. Sci. Instrum. 2009,80, 113108-113106.
[3] M. Xu, H. Noei, M. Buchholz, M. Muhler, C. Wöll, Y. Wang, Catalysis Today 2012,182, 12-15.

Influence of (sub)surface O vacancies on the reactivity of TiO_2 anatase (101)

U Diebold, P Scheiber, M Setvin, M Fidler and M Schmid

TU Wien, Austria

Titanium dioxide is a versatile material that finds applications in a wide range of technical fields. While the rutile phase of TiO_2 is well-investigated in surface science, it is the (metastable) anatase phase that is present in most nanomaterial and often considered the technologically more relevant polymorph. Of particular interest have been surface O vacancies (V_0), which form easily on rutile but are not present at anatase (101) [1]. Bombardment with energetic electrons produces such V_0's, which migrate to subsurface sites at temperatures as low as 200 K [2]. We will give an overview how such surface and subsurface defects influence the reactivity of anatase towards small molecules, e.g., H_2O [3], O_2, and CO.

[1] Y. He et al., Phys. Rev. Lett., 102 (10) (2009) 106105.
[2] Ph. Scheiber et al., submitted.
[3] Y. He et al., J. Phys. Chem. C , 13 2009) 10329-10332.

Reduction state of oxide surfaces: oxygen depletion versus hydroxylation

B Meyer

University Erlangen-Nuremberg, Germany

The reducibility of transition metal oxides is often believed to be the essential driving force behind their catalytic activity. Oxide reduction is commonly associated with the loss of oxygen, and therefore oxygen vacancies are conventionally proposed to be the catalytically active sites. However, oxides can also be reduced by the homolytic adsorption of hydrogen. The amount of hydroxylation of the surface, in turn, controls the charge state of the oxygen vacancies. For the examples of ZnO and TiO_2, the competition between oxygen vacancy formation, homolytic and heterolytic hydrogen adsorption has been investigated using density functional theory calculations and thermodynamic modeling in order to determine the most stable configuration of reduced surfaces and the charge state of oxygen vacancies as function of temperature and hydrogen partial pressure. It will be shown that specific limits for the reducibility of the surfaces exist, which depend on the oxide material and surface termination. In the case of ZnO, it is found that metastable hydride anions may be present in oxygen vacancies, which are stabilized by high activation barriers to guarantee long enough lifetimes of the anions so that they might be available for reduction steps in chemical reactions such as, for example, methanol synthesis. Since both, the reduction steps in a chemical reaction as well as homolytic adsorption of hydrogen result in switching oxygen vacancies between different charge states, the two processes are closely coupled, and an understanding of the thermodynamic and kinetic stability of the reduction states of the oxide surfaces is essential for obtaining further insights into underlying reaction mechanisms.

Growth of stoichiometric TiO_2 thin films on Fe(100) by molecular beam epitaxy

A Calloni, A Ferrari, A Brambilla, F Ciccacci and L Duò

Politecnico di Milano, Italy

Titanium dioxide (TiO_2) has been the subject of intense studies in recent years, due to its photoelectric and photochemical properties and its high refractive index and dielectric constant. Thanks to such properties, many applications have highlighted the crucial role played by the TiO_2 surface (see Ref. [1] for a comprehensive review). Most of the interface works on TiO_2 have studied the interactions of different materials with the surface of a TiO_2 substrate. However, these studies can substantially benefit from the use of thin oxide films. The possibility of synthesize new titanium oxide phases at low coverages has been demonstrated [2,3]; additionally, the oxide surface can be electrically and magnetically coupled with the substrate, thus allowing for a more reliable and new characterization by electron spectroscopies and microscopic techniques.

We report on the growth of thin TiO_2 layers on Fe(100) by Ti deposition in a reactive O_2 atmosphere. The oxide growth was investigated both at room and at high (300 °C) temperature. Our experimental results on titanium oxide growth on Au(100) [4] show the presence, together with TiO_2, of reduced Ti-oxide species if growth is performed at low substrate temperature, while high quality films, with the correct 1:2 Ti to O stoichiometry and showing a crystalline rutile TiO_2 surface, were produced at high temperature. Growth on Fe(100) poses substantial challenges due to substrate oxidation and Ti-Fe interdiffusion, activated at high temperature. Preliminary results are presented, where these problems are addressed by the introduction of a thin (1 nm) gold buffer layer on Fe.

Our analysis techniques comprises low energy electron diffraction (LEED) and X-ray photoemission spectroscopy (XPS). Additionally, we employed ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) to study the whole valence and conduction electron states of the grown titanium oxide films.

[1] U. Diebold, Surf. Sci. Rep. 48 (2003) 53.
[2] Finetti et al., Surf. Sci. 602 (2008) 1101.
[3] Papageorgiou et al., J.Phys. Chem. C 111 (2007) 7704.
[4] Calloni et al., Thin solid films 11 (2012) 3922.

Morphological and local electronic properties of Ti and TiO_x nanoislands on Au(111)

P Carrozzo, C S Casari, M Passoni, C E Bottani and A L Bassi

Politecnico di Milano, Italy

Deposition of titanium atoms on the Au(111) herringbone reconstructed surface is known to lead to nucleation of nanoisland arrays at preferential sites [1]. Subsequent oxidation followed by annealing in vacuum results in the formation of nanocrystalline TiO_2 islands with a triangular or hexagonal geometry and rutile phase [2]. Nevertheless, studies of the local electronic properties of Ti and TiO_x nanoislands and a detailed investigation of their growth mechanism are still lacking.

Here we present a Scanning Tunneling Microscopy and Spectroscopy (STM-STS) investigation of the growth mechanisms and local electronic properties of titanium and titanium oxide nanoislands on the Au(111) surface. We deposited Ti on Au(111) in UHV by e-beam evaporation at different coverages in the 0.1 ML to 1.5 ML range. STM images show that above 0.3 ML titanium islands start to nucleate outside the Au(111) elbows of the herringbone reconstruction. Differently to what observed for other metals on Au(111), such as Fe [3], negligible island coalescence is observed between 0.5 ML and 1 ML and a second layer starts to grow on top of some islands. Analysis of STM images permits to follow the trend of island average size as a function of coverage (from 5 nm^2 at 0.1 ML to 20 nm^2 at 1 ML) and the evolution of their shape. By means of STS measurements we characterized the Local Density of electron States (LDOS) around Fermi level. Low temperature (100 K) dI/dV local measurements and differential conductivity maps at low coverage indicate the presence of three peaks at about -0.4 eV, +0.25 eV and +0.7 eV. We then investigated how the electronic properties evolve with increasing Ti coverage.

For different initial coverages, we exposed the system to ~500 L of O_2 and then annealed in vacuum at 850 K to achieve oxidation of Ti islands. We observed a reduction of the coverage of ~25% compared to the system before oxidation. Moreover, the herringbone reconstruction of the Au(111) surface presents some irregularity, as already reported in [2], and islands are now characterized by a more regular shape (hexagonal or triangular) with a flat-top surface. Finally, low temperature STS measurements indicate the presence of a gap around Fermi level, thus confirming the oxidation of nanoislands.

[1] J. Biener et al., J. Chem. Phys. 123, 094705 (2005).
[2] D.V. Potapenko et al., Nano Lett. 9, 2378 (2009).
[3] F. Donati, et al., Surf. Sci. 606, 702–710 (2012).

Controlling the CVD growth of nanodimensional TiO_x phases on Au(111)

D Ragazzon[1], A Schaefer[2], L E Walle[3], M H Farstad[3], P Uvdal[4], A Borg[3] and A Sandell[1]

[1]Uppsala University, Sweden, [2]Bremen University, Germany, [3]Norwegian University of Science and Technology, Norway, [4]Lund University, Sweden

The combination gold-titania is an intriguing system with respect to catalytic properties since both titania-supported Au nanoclusters and gold-supported TiO_2 islands show remarkable activities [1-4]. This points to a unique synergy between the two materials, motivating studies of the Au-TiO_2 boundary.

In this contribution we address the chemical vapor deposition (CVD) of TiO_x ($1<x<2$) nanostructures partially covering a Au(111) surface. In this coverage regime, the structures formed exhibit characteristics that differ from the typical bulk structures. Recent work, utilizing physical vapor deposition, demonstrates that these phases can be atomically well ordered [5]. We have found that these phases and also additional structures can be produced by CVD.

The TiO_x nanostructures were grown on Au(111) by CVD using titanium tetraisopropoxide (TTIP) as precursor. The aim of the present study was to obtain insight in the CVD process as such. Therefore, film growth series were conducted at different temperatures, stepwise characterized by Low-Energy Electron Diffraction (LEED) and Photoelectron Spectroscopy (PES). Independent Scanning Tunneling Microscopy (STM) images have been used to complement the analysis.

The results give clear indications that some structures are metastable. Thus, the exact preparation route highly influence the resulting structure, the morphology and the free gold area, and hence the combined properties of the titania-gold surface.

[1] T. T. Magkoev Surf. Sci. 601 (2007) 3143.

[2] I. Nakamura, H. Mantoku, T. Furukawa, T. Fujitani J. Phys. Chem. C 115 (2011) 16074.
[3] K. Lauwaet, K. Schouteden, E. Janssen, C. Van Haesendonck, P. Lievens Phys. Rev. B 83 (2011) 155433.
[4] J. A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, M. Pérez Science 318 (2007) 1757.
[5] C. Wu, M. S. J. Marshall, M. Castell J. Phys. Chem. C 115 (2011) 8643.

Organic layers and polymers 2

Site specific adsorption and rocking of fullerenes on rare-earth porphyrin double-decker complexes

D Ecija[1], S Vijayaraghavan[1], WAuwärter[1], S Joshi[1], K Seufert[1], A P Seitsonen[2], K Tashiro[3] and J V Barth[1]

[1]TU München, Germany, [2]University of Zurich, Switzerland, [3]International Center for Materials Nanoarchitectonics, NIMS, Japan

Molecular donor-acceptor dyads stabilized by van der Waals interactions are important in the field of 2D and 3D molecular nanoarchitectures and in the realization of functional supramolecular host-guest systems. In particular, a thorough characterization of such dyads at a single molecule level is necessary for the implementation of potential applications like organic light emitting diodes and photovoltaic devices [1].

Here, we report the direct investigation with scanning tunneling microscopy (STM) and spectroscopy (STS), characterizing the bonding and dynamics C_{60} molecules on $Ce(TPP)_2$ double-decker arrays on a Ag(111) substrate in exquisite detail. The $Ce(TPP)_2$ complexes were directly sublimated onto the Ag(111) substrate where they adapt a non-planar macrocycle geometry. The double-deckers self-assemble into dense-packed islands with a square unit cell exhibiting an intermolecular distance of 13.9 ± 0.5 Å [2]. At low coverage and temperature, C_{60} adsorbs right at the center of top porphyrins in the $Ce(TPP)_2$ arrays, thus forming porphyrin-C_{60} dyads stabilized by van der Waals interactions. Complementary density functional theory (DFT) calculations reveal a slightly distorted geometry of the $Ce(TPP)_2$ complex favoring the C_{60} attachment. The STS measurements indicate a weak coupling of the C_{60} to the Ag substrate, as evidenced by a large HOMO-LUMO gap and a negative differential resistance regime. High-resolution STM data resolve three distinct orientations of the C_{60} on $Ce(TPP)_2$. By applying a current pulse with the STM tip, it is possible to switch individual fullerene cages between these three configurations without changing the lateral registry. A plot of tunneling current vs. time reveals three levels of conductance indicating a tri-stable and reversible switch. Each level of the switch corresponds to one of the distinct C_{60} orientations and thus represents a specific intra-dyad coupling.

[1] Guldi, D. M. Fullerene-porphyrin architectures; photosynthetic antenna and reaction center models. Chem. Soc. Rev. 31, 22-36 (2002).

[2] Écija, D. et al. Assembly and manipulation of rotatable cerium porphyrinato sandwich complexes on a surface. Angew. Chem. Int. Ed. 50, 3872-3877 (2011).

Structure and electronic properties of self-assembled transition metal phthalocyanines (M=Fe,Co,Ni,Cu,Zn) on the Au(110) surface

S Fortuna[1], A Calzolari[2] and S Fabris[1]

[1]CNR-IOM DEMOCRITOS, Italy, [2]CNR-NANO, Italy

The relative strengths interplay between intermolecular and molecule–substrate interactions generally controls the pattern formed by surface-adsorbed self-organised molecules. However, when the substrate can easily reconstructs upon molecular adsorption, a self-templating effect on the metallic support can be observed. This is the case for Fe-phthalocyanine (FePc) molecules adsorbed on the Au(110) surface. STM imaging and low energy electron diffraction patterns show how FePc molecules can self-organize into ordered chains along the $[1\bar{1}0]$ direction driving the formation of reconstructed channels on the underlying Au substrate [1]. Density functional theory calculations reveal the energetic origins of the molecule-driven substrate reconstruction, showing that a larger molecular binding is achieved by first reorganizing the metal surface underneath the molecule. The molecule-substrate interaction process further induces a rehybridization of the electronic states localized on the central metal atom. By DFT calculations we clarify the effect and role of the surface, acting as a fifth ligand on the FePc metallorganic states [2].

In addition, we perform a systematic analysis on the first row transition metal MPc (M=Co,Ni,Cu,Zn) on the same substrate, revealing the individual electronic features and the common trends. Since the function of molecular overlayers at surfaces is strongly correlated to their structure, these results have implications in the design of new metal/molecular interfaces.

[1] S.Fortuna, P.Gargiani, M.G.Betti, C.Mariani, A.Calzolari, S.Modesti, and S.Fabris, J.Phys.Chem.C,2012,116(10),6251–6258.
[2] M.G.Betti, P.Gargiani, C.Mariani, S.Turchini, N.Zema, S.Fortuna, A. Calzolari, and S.Fabris, J.Phys.Chem.C,2012, in press.

In-situ STM investigation of self-organized Porphyrin layers on an iodide-modified Au(100) surface

T Kosmala, M Schneider and K Wandelt

University Bonn, Germany

The spontaneous self-assembly of organic molecules is considered a promising “bottom-up” approach in nanotechnology to create surface patterns and molecular electronic devices. Porphyrins, for example, are important organic compounds for potential applications as catalysts, sensors and solar energy storage devices.

In this work we have studied the self-organization of Tetra(4-trimethylammoniophenyl) porphyrin molecules (TTMAPP) on an iodide-modified Au(100) electrode surface using Cyclic Voltametry (CV) and in-situ Electrochemical Scanning Tunneling Microscopy (EC-STM). The CV measurements indicate the various single-electron reduction/oxidation steps. Concomitant changes in the molecular structure of the TTMAPP layers as a function of electrode potential are revealed by in situ STM images with submolecular resolution. These results enable the construction of detailed structure models and their dependence on the nature of the substrate and the applied potential.

Moreover, by continuously changing the electrode potential during scanning STM images we were able to record the dynamical behaviour of individual TTMAPP molecules and the time-dependence of phase transitions on iodine-modified Au(100) surface (movie will be presented).

Interface properties between CuPc:C_{60} blend films and graphene

L Lozzi[1], R Totani[2] and S Santucci[2]

[1]University of L'Aquila, Italy, [2]Department of Physics, University of L'Aquila, Italy

Recently in the realization of organic-based photovoltaic cells graphene is being used as transparent and metallic contact. In this work we will report the spectroscopic results on the interface electronic states between organic blend films and a monolyer graphene sheet deposited on SiO_2. Very thin CuPc:C_{60} blend films have been deposited onto graphene by ultra high vacuum evaporation. The interface properties have been followed by means of ultraviolet and X-ray photoemission spectroscopies. The valence band structures, in particular the HOMO molecular states, shows a shift depending on the film thickness. The shifts are different for CuPc and C_{60} HOMO states. These data have been used to determine the effects of the blend-substrate interface on the film ionization energy. The core levels also present a shift depending on the film thickness, while their line shapes do not depend on the thickness.

Formation of a spatially extended intermolecular band for TCNQ molecules on graphene/Ru(0001) studied by means of scanning tunneling spectroscopy

A vazquez de parga[1], M Garnica[1], D Stradi[1], S Barja[1], C Diaz[1], M Alcami[1], N Martin[2], F Martin[1] and R Miranda[3]

[1]Universidad Autonoma de Madrid, Spain, [2]Universidad Complutense de Madrid, Spain, [3]IMDEA Nanociencia, Spain

The adsorption of molecules on graphene is attracting a great deal of attention for several reasons. First, appropriate molecular doping can be used to tailor the electronic properties of graphene. Another reason is the interest in developing a chemistry of graphene and, finally, because the graphene monolayer could efficiently isolate the molecules from the strongly interacting metallic substrates.

In this communication, we show that graphene grown on Ru(0001) electronically decouples 7,7',8,8'-tetracyano-p-quinodimethane (TCNQ) molecules from the Ru(0001). Graphene on Ru(0001) presents a moiré pattern with a periodic chemical interaction between carbon atoms and the ruthenium, leading to a modulation in the electronic structure and surface potential. Our scanning tunneling spectroscopy (STS) measurements and Density Functional Theory (DFT) calculations show that molecules are negative charge due to a charge transfer from the substrate to the TCNQ molecules. The energy position and spatial distribution of the molecular frontier orbitals for a single molecule are measured by STS maps at 4.6 K in ultrahigh vacuum. The character of the orbitals is determined comparing the experimental data with DFT calculations. The shape of the orbitals calculated and observed is very similar to that calculated for gas phase TCNQ molecules. When the molecular coverage is increased the molecules begin to form chains that finally cover completely the graphene surface. The STS measurements and DFT calculations show that the interaction between the TCNQ molecules is via a saturated C≡N···H-C bonds. STM images show the formation of a tube like structures connecting the TCNQ molecules.

Investigation of the 2D phase behavior of a bimolecular porphyrin system at the solid-vacuum interface

N Wintjes[1], S Nowakowska[1], J Lobo-Checa[1], J Hornung[2], T Samuley[2], T Ivas[1], F Diederich[2] and T A Jung[3]

[1]University of Basel, Switzerland, [2]Laboratorium für Organische Chemie, ETH Zürich, Switzerland, [3]Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, Switzerland

In detailed Scanning Tunelling Microscopy (STM) studies the two-dimensional (2D) phase behavior of a bimolecular porphyrin system on the Cu (111) surface in ultra high vacuum has been investigated in the sub-monolayer regime. The observed self-assemblies were systematically analyzed by their dependence on the total coverage and on the ratio of the two components resulting in the 2D phase diagram. In a small region within the parameter space, a mixed surface layer was observed, while in the complete range a large number of phases was found.

Our studies demonstrate that directional bonding motifs, specifically the CN• • •CN and the CN• • • H, motifs can be complemented by mobile, 'anti-bonding' elements i.e. entropically mobile alkoxy chains. In combination of such motifs, entropy-enthalpy conversion depends on external parameters and allows for the tailoring of bimolecular layers. We also discuss the characteristics of 2D phase behavior in general at the solid vacuum interface with respect to the better established case of the solid-liquid interface which stems from the missing desorption/readsorption thermodynamics and the hindered mass transport at high coverages.

[1] N. Wintjes, J. Lobo-Checa, J. Hornung, T. Samuely, F. Diederich, T. A. Jung, Two-Dimensional Phase Behavior of a Bimolecular Porphyrin System at the Solid−Vacuum Interface, J. Am. Chem. Soc. 132, 7306–7311 (2010).

Nanoaggregates from squaraine dyes

M Schiek[1], F Balzer[2], J Jensen[2], A Osadnik[3], L Beverina[4], A Lützen[3] and H-G Rubahn[2]

[1]Hanse-Wissenschaftskolleg, Germany, [2]University of Southern Denmark, Denmark, [3]University of Bonn, Germany, [4]University of Milano-Bicocca, Italy

Squaraine dyes are useful for various electronic and photonic applications such as two-photon absorbing materials, NIR emitting fluorescent probes, sensitizers for photodynamic therapy, photodetectors and solar cells. Here, nanostructured thin films from various symmetric amino-substituted bisphenyl-squaraine dyes are investigated. The thin films are either solution casted or vacuum sublimed onto substrates such as muscovite mica, which are known to promote self-assembly into oriented, fiberlike, crystalline nanoaggregates. Local characterization is performed via polarized optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) to evaluate their potential for opto-electronic applications such as solar cells.

Orbital-resolved charge transfer in novel donor-acceptor complexes studied by NEXAFS and HAXPES

K Medjanik[1], D Kutnyakhov[1], S Nepijko[1], G Schoenhense[1], A Gloskovskii[1], D Chercka[2], M Baumgarten[2], K Muellen[2]

[1]Johannes Gutenberg-Universität Mainz, Germany, [2]Max Planck-Institut für Polymerforschung, Germany

The mixed phases of the classical acceptor tetracyanoquinodimethane (TCNQ) with novel donors tetra- and hexamethoxyprene (TMP and HMP) are grown via co-crystallization from solution and co-evaporation in UHV. X-ray analysis reveals mixed-stack geometries. NEXAFS (Near Edge X-ray Absorption Fine Structure) and HAXPES (Hard X-ray photoemission spectroscopy) have been performed at ANKA, Karlsruhe (WERA beamline) and PETRA III, Hamburg (beamline P09). Large probing depths (5nm and 15-20nm, respectively) allow the study of as-prepared co-crystals. O1s and N1s are fingerprints of the methoxy-group of donors and cyano-group of acceptor. Marked changes in the intensities of pre-edge resonances in K-edge NEXAFS spectra reveal the participation of specific orbitals in the functional groups of donors and acceptors [1].

The complexes shows two O1s lines shifted by 1.4 (0.9) eV and 2.6 (2.3) eV with respect to the position of the single O1s line of pure HMP(TMP). N 1s shows two peaks as well shifted in opposite direction to the O 1s signals by 0.9 eV and 2.0 eV with respect to the leading line of pure TCNQ. These shifts are much larger than the shifts observed in UPS valence spectra [2]. Peak-area analysis reveals a degree of charge transfer of about 0.6 for microcrystals and thin films of HMP(TMP)-TCNQ. This value lies close to the charge transfer of 2/3 for TTF-TCNQ estimated by analysis of the sulphur 2p spectra and for similar CT compounds such as NMP-TCNQ [3].

[1] K.Medjanik et al., J. Am. Chem. Soc. 134 (10) (2012) 4694–4699.
[2] K.Medjanik et al., PRB 82 (2010) 245419.
[3] J.P.Pouget et al., PRB 21(1980) 486.

Adsorption geometry of Pi-conjugated organic molecules on noble metal surfaces studied by X-Ray standing wave and complementary techniques

A Gerlach[1], C Bürker[1], S Duhm[2], J Niederhausen[3], T Hosokai[4], J Zegenhagen[5], N Koch[3] and F Schreiber[1]

[1]Universitaet Tuebingen, Germany, [2]Chiba University, Japan, [3]Humboldt-Universität zu Berlin, Germany, [4]Iwate University, Japan, [5]European Synchrotron Radiation Facility, France

In order to study the interaction between large π-conjugated molecules with noble metal surfaces we have performed X-ray standing wave (XSW) measurements, photoelectron spectroscopy and Density Functional Theory (DFT) based calculations [1-4].

The XSW technique is an element specific analysis which allows to measure bonding distances with a precision of < 0.05 Å. Adsorption induced distortion of molecules is a common phenomena which influences the electronic structure of the adsorbate. Using ultraviolet photoelectron spectroscopy and ab-initio calculations as complementary techniques we try to establish a comprehensive picture of the adsorption process.

We present a selction of planar and non-planar molecules on Cu(111), Ag(111) and Au(111) with different interaction strength resulting in different bonding distances which range for the carbon core of the molecule from 2.35 Å (pentacene on Cu(111)) to 3.15 Å (diindenoperylene on Au(111)). These different values originate from a complex interplay of covalent bonding, electron transfer processes and van der Waals forces.

[1] A. Gerlach et al., Phys. Rev. B 75 (2007) 045401.
[2] N. Koch et al., J. Am. Chem. Soc. 130 (2008) 7300.
[3] S. Duhm et al., Organic Electronics 9 (2008) 111.
[4] A. Gerlach et al., Phys. Rev. Lett. 106 (2011) 156102.

First-principles study of redox-molecular switch above a polar thinfilm: a van der Waals + U description

J Sharp, F Hanke, I Scivetti and M Persson

University of Liverpool, UK

A redox-type molecular switch functions by coupling the charging and discharging of a molecule to an obvious change in conformation. Such a switch was recently demonstrated experimentally, by investigating the molecule bis-dibenzoylmethanato-copper(II) ($Cu(dbm)_2$) adsorbed on an ultra-thin insulating layer above a Cu substrate[1]. Here we aim to understand the molecular adsorption and switching properties using a first principles density functional approach to investigate the electronic structure of the complex. This investigation is challenging due to the van der Waals dominated adsorption and the presence of highly-correlated d-electrons in $Cu(dbm)_2$. Here we use a van der Waals density functional [2] and a 'GGA+U' term to properly address these issues. Crystal field splitting of thed-orbitals underlies the conformational change that occurs upon charging, and the magnitude of the splitting is affected by the value of 'U' used. The experimentally observed changes in conformation upon charging the adsorbate are only reproduced with a self-consistently determined value of U. Moreover without inclusion of the U term a spontaneous charging of the adsorbate is observed even for the experimentally neutral configuration. Finally, we present scanning tunnelling microscopy simulations and compare the results with the experimentally available data.

[1] PRL 106 216103 (2011); [2] PRB 83 195131 (2011).

Carbon, graphene 4

(invited) Carbon nanotube resonators coupled to charge and flux

G Steele

TU-Delft, The Netherlands

We study the motion of carbon nanotube resonators coupled to single electron charges, and to magnetic flux. Using a single electron transistor embedded in the nanotube to read out the motion of the high quality factor resonator (Q $\sim 10^5$), we observe the static force exerted on the nanotube by a single electron, and frequency dips from a "single-electron spring". Using a suspended carbon nanotube SQUID, we couple magnetic flux to the nanotube motion. We find a record-high critical current of 24 nA and supercurrents that persist to magnetic fields greater than 3T. The magnetic flux in the SQUID is tuned by a DC gate voltage, allowing us to directly observe static displacements of the nanotube with a responsivity of up to 0.4 mF_0/pm.

Electron transport in semiconducting zigzag carbon nanotubes

K Thiagarajan and U Lindefelt

Mid Sweden University, Sweden

Recent advances in scientific technology have enabled researchers to develop carbon nanotube (CNT) based electronic devices. Theoretical modeling should play a key role in optimizing and predicting the performance of CNT based devices. The Monte Carlo (MC) technique has been the preferred theoretical tool to study the charge transport in semiconductors, especially at high electric fields. To understand the transport properties of semiconducting zigzag carbon nanotubes (CNT), we have developed a bulk single-electron MC simulator that employs standard MC techniques.

Here, we report on the MC calculations done on semiconducting nanotubes (10,0) and (13,0) at different lattice temperatures, and for several electric field strengths. Investigating the dependence of the steady-state drift velocity and mobility on the lattice temperature and on the concentration of vacancies forms the main theme of this work. The electronic structure is derived from that of graphene, and the phonon spectrum is calculated using a fourth nearest-neighbour force constant model. The principal scattering mechanisms considered are due to electron-phonon interactions and electron-vacancy interactions. The scattering rates describing the electron-phonon interaction and the electron-vacancy interaction are calculated within the tight-binding formalism.

Electronic transport in intermediate sized multiwalled carbon nanotubes

M Ahlskog[1], D Mtsuko[1], A Koshio[2], M Yudasaka[2] and S Iijima[3]

[1]University of Jyväskylä, Finland, [2]NEC Research Center, Japan, [3]Meijo University, Japan

We have measured the low temperature transport properties of single multiwalled carbon nanotubes (MWNT) of diameters (D) in the range 2-10 nm. Almost all previous work on MWNT's has been on tubes with diameters above 10 nm. In nearly all samples in this work, with D < 10 nm, the gate dependent conductance exhibits a gap whose size increases with the inverse tube diameter and increasing electrode separation. This so called transport gap is attributed, based on the experimental findings, on a combination of localization effects and narrow diameter induced gaps in the electronic band structure.

These results have significant similarities to the current research on graphene nanoribbons (GRN). As graphene does not intrinsically possess a bandgap, GNR's are fabricated, where a gap is created via quantum confinement

due to the narrow width of the channel/nanoribbon. The size of the gap is then roughly in a similar inverse relation with the width of the constriction as in the case of the diameter dependence of the MWNT's in our work.
The transport gap has not generally been observed in the previous works on MWNT's because of the large diameters of the tubes in these. Our work, of which some early results were published previously [1], complements and bridges previous works on both single walled nanotubes and MWNT's, and also to the field of GNR's.

Graphene nanoribbon heterojunctions: from atomistic simulations to synthesis

S Blankenburg[1], J Cai[1], P Ruffieux[1], R Jaafar[1], D Passerone[1], X Feng[2], K Muellen[2], R Fasel[1] and C Pignedoli[1]

[1]EMPA, Switzerland, [2]Max Planck Institute for Polymer Research, Germany

Graphene nanoribbons (GNRs) – semiconducting quasi-one-dimensional graphene structures – have great potential for the realization of novel electronic devices. Standard fabrication techniques are not suitable for the synthesis of ribbons narrower than ~5 nm and do not allow to control the width and edge structure of a specific device with atomic precision.

A bottom-up approach based on surface-assisted cyclodehydrogenation reactions has recently emerged as a promising route to the synthesis of nanoribbons and nanographenes [1,2]. The key step of this bottom-up GNR fabrication method [1] is the thermally induced cyclodehydrogenation of linear polyphenylenes on Au(111) templates. Here, we rationalize the mechanism responsible for the surface-assisted cyclodehydrogenation of polyanthrylene oligomers into armchair graphene nanoribbons (AGNR) by means of a combined experimental and computational approach [3]. We identify a rather generic reaction mechanism that we expect to be relevant to other comparable surface-assisted synthesis processes.

We explain why a careful control of annealing temperature and duration allows to fabricate junctions formed by segments exhibiting the 7-AGNR structure and of one-side-only dehydrogenated segments. The latter correspond to N=5 AGNRs with additional benzene rings ortho-fused to the naphthalene units (5^+-AGNR). These atomically precise 7-AGNR/5^+-AGNR/7-AGNR nanostructures are a first realization of intra-ribbon heterostructures, with properties potentially very similar to the ones predicted by Prezzi and coworkers [4]. Finally, we also demonstrate the ability to selectively modify the nanoribbon heterojunctions via STM tip-induced cyclodehydrogenation, which suggests that the large scale fabrication of nanoribbon heterojunctions by electron beam "writing" might become technologically feasible.

[1] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, M., et al. Nature 466, 470 (2010).
[2] M. Treier, M., C.A. Pignedoli, T. Laino, R. Rieger, et al. Nat. Chem. 3 61 (2011).
[3] S. Blankenburg, J. Cai, P. Ruffieux, R. Jaafar, et al. ACS Nano 6, 2020 (2012).
[4] D. Prezzi, D. Varsano, A. Ruini, E. Molinari Phys. Rev. B 4, 041401(2011).

Nitrogen doping of Single-Wall Carbon Nanotubes by low flux ion irradiation

S Alluqmani[1], R Little[2], L Šiller[2] and M R C Hunt[1]

[1]Durham University, UK, [2]University of Newcastle upon Tyne, UK

Nitrogen atoms are an ideal candidate for substitutional doping of single-wall carbon nanotubes (SWCNTs) and can be incorporated into a carbon nanotube without necessarily causing structural disruption. It has been shown that N-doping creates local regions of enhanced reactivity which may be used as a starting point for further modification or for catalysis [1,2]. Ion irradiation offers an attractive post-growth route to nitrogen doping. We report the functionalization of SWCNTs with nitrogen by exposure of Ar^+ irradiated nanotubes to an appropriate ambient and directly by N^+ irradiation. X-ray photoelectron spectroscopy (XPS) shows that N ion implantation produces nitrogen in a substitutional sp^2 site, linked to two carbon atoms in a sp^2 configuration, and connected to three or four sp^3 hybridised carbon atoms. We find that use of a low nitrogen flux significantly reduces the fraction of sp^3 bound nitrogen. In addition, we address a controversy regarding the assignment of N1s photoemission lines. Measurements have also been carried out on samples annealed at elevated temperatures to explore the thermal stability of the chemically bound nitrogen.

[1] K Gong et al. Science 323 (2009) 760.
[2] A. Nevidomskyy et al. Physical Review Letters 91 (2003) 105502.

Atmospheric pressure dielectric barrier discharge for hybrid materials synthesis: functionalization of carbon nanotubes with platinum nanoclusters

J Guillot, R Mauchauffé, A Mansour and H-N Migeon

CRP-Gabriel Lippmann, Luxembourg

The functionalization of Carbon Nanotubes (CNTs) by inorganic particles or by chemical groups has numerous possible applications in the fields of heterogeneous catalysis, nanoelectronic, sensors, energy…This work focuses on the random functionalization of MW-CNTs with platinum nanoclusters and the characterization of the obtained hybrid materials. The method described here is a “one pot” strategy to simultaneously activate CNT surface, to form and to graft Pt clusters using a cold plasma discharge (Dielectric Barrier Discharge system) working at atmospheric pressure and using an organometallic compound as precursor.

HR-TEM and XPS have been mainly used to characterize these hybrid materials (size and distribution of Pt clusters, concentration of Pt deposited on the CNTs, amount of metallic and oxide contributions in the clusters).

The influence of some deposition parameters as the discharge power, the treatment duration and the composition of the plasma mixture (He or He+O_2) have been studied in order to tune the deposits. Whatever the deposition parameters, the average diameter of the nanoclusters is rather constant and around 2 nm even if the size dispersion, with clusters up to 7 nm, rises with the plasma power. The total Pt concentration depends on two main factors: the longer the deposition duration is the higher the Pt amount; the addition of O_2 (up to 10 vol.%) in the He plasma increases the number of Pt clusters too. At last, the cluster chemical state, i.e. the Pt_{metal}/Pt_{oxide} ratio, can be modified with the plasma power, the treatment duration and the plasma gas composition, opening numerous application fields.

Extraordinarily long structural relaxation in defective achiral carbon nanotubes

M Hunt and S Clark

Durham University, UK

Defects have a profound impact on the electronic, mechanical, thermal and chemical properties of carbon nanotubes due to their quasi one-dimensional structure and high surface-to-volume ratio. The defect formation energy is key in determining the ease by which defects may arise in nanotubes during growth and subsequent treatment. It is therefore highly important to determine accurate structural information for these nanoscale systems. Here we employ *ab initio* calculations using density functional theory (GGA-PBE) to consider the simplest form of vacancy defect in a single wall carbon nanotube (SWCNT) - the isolated monovacancy [1]. We find that the structural relaxation associated with monovacancy reconstruction is extraordinarily long-ranged and can only be captured by using open boundary conditions and exceptionally large supercells (around 1,000 atoms). Our results imply that calculated values for the energies (and hence the derived properties) of reconstructed monovacancies in the existing literature (e.g., [2-5]) are in error and that formation energies of a wide spectrum of other defect types in nanoscale carbon systems need careful (re-) evaluation.

[1] Ajayan P., Ravikumar V. & Charlier J.-C., Physical Review Letters 81 (1998) 1437–1440.
[2] Lu A. & Pan B., Physical Review Letters 92, (2004)105504 .
[3] Krasheninnikov, A., *et al.*, Chemical Physics Letters 418, (2006) 132-136.
[4] Ma, Y., et al., New Journal of Physics 6 (2004) 68 .
[5] Wang, C. & Wang, C.Y., The European Physical Journal B 54 (2006) 243-247.

Surfactant self-assembly to strengthen nanotubes networks

D Müter[1], P Angelikopoulos[2] and H Bock[1]

[1]Heriot-Watt University, UK, [2]Swiss Federal Institute of Technology Zürich, Switzerland

Using computer simulations we show that in a random network of nanotubes, surfactant self-assembling on the tube crossings improve the materials stiffness without compromising its porosity. This is important for applications ranging from scaffolds to electrodes to composites.

Individual carbon nanotubes are promising candidates for a range of applications due to their bespoke record properties, such as high strength and stiffness. Yet, for a network of nanotubes these values drop by several orders of magnitude because the forces between the nanotubes are rather low. We propose that surfactant micelles can act as “glue” holding the tubes together and thereby stabilizing the whole network. In this presentation we demonstrate this using computer simulations.

At small tube/tube separations a surfactant aggregate self-assembles at the crossing and encapsulates the junction. This produces a net attraction between the tubes. While the magnitude of the force depends on the angle between the tubes it is generally attractive.

Reactions on surfaces 2

(invited) How far can we push first principles predictions today? Accuracy, large-scale surface reconstructions and graphene on SiC

V Blum

Fritz Haber Institute, Germany

Electronic structure theory has developed into a powerful tool to understand materials or molecular phenomena from the atomic scale on upwards, and into a predictive tool for "new" materials properties on its own. Using large-scale reconstructed surfaces as an example, this talk illustrates some current capabilities and limits in two respects: Computational requirements where a large-scale, direct first-principles treatment of structures is desirable, and the accuracy of the method itself, where subtle energetic and/or electronic structure contributions must be accounted for. For the reconstructed surfaces of Au(100) and Pt(100), traditional density functional approximations (LDA and GGAs) capture the reconstruction energetics accurately if the necessary structure sizes (up to approx. 1000 atoms) can be accounted for [1]. In contrast, epitaxial grown graphene films on SiC require not just large structure sizes (approx. 2000 atoms) to be free of strain, but also a reliable handling of van der Waals effects and charge transfer at the surface. Such systems are now amenable to accurate all-electron treatments, here using the FHI-aims code [2], in their actual, experimental geometries. For instance, the surface phase diagram for SiC suggests that a single monolayer of graphene should be an equilibrium phase on this substrate when grown at the right temperature and Si background pressure.

[1] P. Havu et al., Phys. Rev. B 82, 161418 (2010).
[2] V. Blum et al., Comp. Phys. Commun. 180, 2175 (2009).

Raman analysis of surfaces of various materials using silica-covered silver and gold nano-resonators

A Kudelski and S Wojtysiak

University of Warsaw, Poland

In this contribution applications of silica-protected silver and gold electromagnetic resonators for Raman analysis of various surfaces will be discussed. Silica-protected silver and gold nano-resonators have been synthesized by coating of respective nanoparticles with ultrathin (ca. 5 nm) layer of silica. Ag@SiO_2 and Au@SiO_2 nanoparticles significantly enhance the electric field of incident electromagnetic radiation of certain wavelengths, hence leading to a very large increase of the Raman signal from species being in the close proximity to them. Layers of Ag@SiO_2 and Au@SiO_2 nanoparticles have been spread over model surfaces that were further probed using Raman spectroscopy. Spreading the silica-covered electromagnetic nano-resonators over the analyzed surfaces allows for identification of well visible contributions in the measured spectra from very small amount of species present on the surface, even though the contribution from these compounds could not be observed in the standard Raman spectra of analyzed samples. We showed that Ag@SiO_2 nano-resonators allows for significantly easier combination of the SHINERS (shell-isolated nanoparticle-enhanced Raman spectroscopy) with the standard resonance Raman effect than previously used Au@SiO_2 nanoparticles. Since silver provides stronger plasmons resonance than gold, sensitivity of SHINERS analysis with Ag@SiO_2 nanoparticles is higher than whenusing Au@SiO_2 nanoparticles. The problem of diffusion of the molecules of the analyte via the silica layer will be also discussed.

Integration of a MEMS z-scanner in a Scanning Tunneling Microscope

F Tabak[1], H Borsboom[1], P van der Tuijn[1], J Frenken[1], M van Spengen[2]

[1]LION - Leiden University, Netherlands, [2]3ME - Technical University of Delft, Netherlands

STM (scanning tunneling microscopy) is a useful tool that enables imaging of surface processes with atomic resolution. Unfortunately, the visualization of surface processes is often limited by the low acquisition rate of STM systems. Many research groups have worked on the development of fast piezo-based STM or AFM, including fast image acquisition and fast feedback. Imaging rates of 20 frames / s are routinely achieved in some dedicated systems and has become commercially available [1]. However, piezo-based STM is limited by the resonance frequency of the scanning piezo element. In general, this resonance frequency will not exceed 200kHz for reasonable scan ranges. We present a new MEMS (micro-electro mechanical system) device which can function as STM z-scanner.

MEMS STM z-scanners can be designed to have a fundamental resonance frequency up to 1 MHz and a scan range that is reasonable for STM (300 to 600 nm). For functional use in STM systems, several issues need to be addressed. The small size of a typical MEMS scanner (40 μm x 40 μm, on a 1 mm wafer) adds new complexities to an STM setup. The three main issues are tip deposition, scanner-sample alignment and capacitive coupling. We handle each of these complications and present preliminary results obtained by using a MEMS STM z-scanner as an add-on in a piezo-based system. In addition, we discuss what improvements should be made and what the critical points are in using MEMS z-scanners.

[1] T. Ando et al., Progress in surface science 83 (2008) 337-437.

SixS (Surfaces Interfaces X-ray Scattering): a new beamline for surface X-ray scattering

A Coati, Y Garreau, A Vlad, M Sauvage-Simkin, B Voisin, M Ribbens and T Moreno

Synchrotron SOLEIL, France

The SixS (Surface Interface X-ray Scattering) beamline at Synchrotron Soleil is now open to external users. SixS is devoted to the studies of surfaces and interfaces of hard and soft condensed matter in the hard X-ray energy range (5-20 keV). SixS is optimized to perform experiments under grazing incidence geometries (Grazing Incidence X-ray Diffraction – GIXD, Grazing Incidence Small Angle X-ray Scattering – GISAXS, …), which lead to an enhanced sensitivity to the first surface layers. X ray reflectivity measurements are also possible. The experiments that can be carried out on SixS mainly concern in-situ growth, fabrication and evolution of nano-objects and surfaces under ultra-high vacuum (UHV) or in various conditions (reactive atmosphere, electrochemistry, liquid interfaces…). The SixS setup allows to obtain several information about the studied sample; in particular, one should be able to determine the shape, the atomic structure, the morphology, the periodicity… of nano-objects at surfaces and follow the evolution of these properties as a function of thermal treatments, gas exposure etc… Moreover, SixS exploits the coherence of the X-ray beam, this capability will allow to study the properties of a single nano-object and to compare them to the averaged properties obtained by standard GIXD/GISAXS measurements.

The beamline is equipped with two experimental stations:

- ‘UHV’. A set of chambers is dedicated to the preparation, the study and X-ray scattering measurements of samples under UHV conditions. A diffractometer coupled with these chambers allows to collect X-ray scattered by the studied sample. The chambers will be equipped with standard UHV tools and specific instruments (STM, LEED, AES).
- ‘MED’. A “Multi Environment Diffractometer” (MED) can be coupled with different experimental setups (reactivity chambers, electrochemical cells, Langmuir trough…) to perform GIXD, GISAXS and reflectivity measurements of surfaces, interfaces and nano-objects under different conditions.

In this presentation the beamline capabilities will be presented, as well as the first experimental results obtained on soft and hard matter samples.

(invited) Acoustic surface plasmon: from Be (0001) to noble metals

L Vattuone

Università degli Studi di Genova, Italy

Acoustic surface plasmons are relevant for electronics and for catalysis, since their energy vanishes for vanishing wavevector, $q_{||}$, and their group velocity is constant. Such characteristics allow, at least in the low wavelength limit, for a non negligible probability of thermal excitation forbidden for conventional optical plasmons having energies in the eV range. The independence of group velocity on $q_{||}$ is interesting for applications since if conversion of an optical signal into the ASP were possible, the latter would propagate without distortion. The ASP has been firstly predicted theoretically [1] and then observed experimentally firstly on Be(0001) [2] and later on Cu(111) [3] and on Au(111) [4]. Its existence is connected with the presence of a 2-dimensional electron gas oscillating in counterphase with the electrons of the underlying 3D substrate. The ASP is a relatively robust excitation since it survives to some extent to surface nanostructuring [5], while it is killed e.g. by O_2 adsorption which destroys the Shockley surface state. The dispersion curves on different substrates will be presented and compared to theoretical predictions.

[1] J.M. Pitarke et al., Rep. Prog. Phys. 70, 1 (2007).
[2] B. Diaconescu, K. Pohl, L. Vattuone et al.,Nature 448, 67 (2007).
[3] K. Pohl et al., Europhys. Lett. 90, 57006 (2010).
[4] S. J. Park and R. E. Palmer, Phys. Rev. Lett. 105, 016801 (2010).
[5] L. Vattuone et al., Plasmonics DOI:10.1007/s11468-011-9310-8.

GaAs phase transitions monitored in real-time by in-situ helium grazing incidence fast atom diffraction

P Atkinson[1], V Etgens[1], M Eddrief[1], H Khemliche[2], A Momeni[2], M Mulier[2] and P Roncin[2]

[1]UPMC - CNRS, France, [2]CNRS-Université Paris-sud, France

Grazing Incidence Fast Atom Diffraction (GIFAD) is a relatively recent technique where low energy (< 1keV) neutral atoms such as Helium, impinging on a crystalline surface at low incidence angle (< 2° typically) gives rise to a diffraction pattern that can be interpreted in a straightforward manner by separating of the atomic motion into a fast motion parallel to the surface and a slower motion perpendicular to the surface with wavelength of the order of the atomic spacing. The intensity envelope of this diffraction pattern provides detailed information about the surface corrugation perpendicular to the beam direction, in effect providing information by a reciprocal space technique comparable to that provided by real-space techniques such as atomic force microscopy [1].

The grazing incidence geometry of GIFAD, similar to that of RHEED, makes it ideal for crystal growth applications. To demonstrate this, we have installed GIFAD on a commercial molecular beam epitaxy machine modified to allow both GIFAD and RHEED investigations on the same sample. We present here real-time monitoring of the GaAs surface reconstructions under growth conditions. The improved surface sensitivity of GIFAD to RHEED is highlighted by these measurements, in particular the ability to track the gradual evolution of the surface and the long-range ordering of the surface reconstructions will be discussed.

[1] see e.g. H. Khemliche et al, *Appl. Phys. Lett.* 95 151901 (2009), H. Winter and A. Schüller et al, *Progress in Surface Science* 86 169 (2011).

Planar laser-induced fluorescence: a new view on catalysis

S Blomberg[1], J Zetterberg[2], Z W Sun[1], Z S Li[1], J Gustafson[1], P A Carlsson[3], E Lundgren[1] and M Alden[1]

[1]Lund University, Sweden, [2]Division of Combustion Physics, Lund University, Sweden, [3]Competence Centre for Catalysis, Chalmers University of Technology, Sweden

We report the first experiments carried out on a new in situ setup for catalysis, which allows for detection of reactants and products close to a catalyst under realistic reaction conditions by the means of Planar Laser-Induced Fluorescence (PLIF) in the mid-infrared spectral range [1]. We show that by exciting a ro-vibrational transition in the CO_2 gas molecule at ~2.7 μm by an IR laser sheet and detecting the resulting fluorescence light at 4.3 μm from the de-excited molecule by a 2D IR camera, the CO_2 spatial and temporal distribution surrounding the catalyst can be followed in real time. In this contribution, the CO_2 distribution above Rh, Pt and Pd model catalysts during the oxidation of CO is presented. We expect the technique to complement the use of traditional mass spectrometers for reactivity measurements, providing a new view on catalysis for almost any reactant or product.

[1] K. Kohse-Höinghaus and J. B. Jeffries, Applied combustion diagnostics. (Taylor & Francis, New York, 2002).

Magnetism 2

(invited) Carbon cage spin shuttles

T Greber

University of Zurich, Switzerland

Carbon cage Fullerene molecules, like C_{60} may be filled with open shell atomic species that make them spin shuttles, i.e. molecules with a chemically well protected spin (and magnetic) moment. Endofullerenes, like Dy3N@C80 are discussed as examples. With angle scanned x-ray photoelectron diffraction (XPD) it is possible to address the molecular orientation on surfaces and to see the endohedral species. With synchrotron based, resonant photoelectron diffraction (RXPD) at the Dy 3d edge the position of the dysprosium atoms inside the cage are resolved [1]. RXPD with circularly polarized light allows the direct determination of the direction of the magnetization axis, as it was shown for the magnetization of Ni(111) [2]. Since the quantization axes in rare earth single molecule magnets depend on the ligand fields, which are imposed by the chemical structure, XPD should be a perfect way to investigate spin shuttles like Dy3N@C80 on surfaces.

[1] Treier et al. Phys. Rev. B 80 (2009) 081403(R).
[2] Morscher et al. Phys. Rev. B Phys. Rev. B 84 (2011) 140406(R).

Controlling magnetic dimensionality with applied pressure

S Ghannadzadeh[1], P Goddard[1], I Franke[1], J Schlueter[2], J Manson[3], D Graf[4] and S Tozer[4]

[1]University of Oxford, UK, [2]Argonne National Laboratory, USA, [3]Eastern Washington University, USA, [4]National High Magnetic Field Laboratory, Florida State University, USA

Metal-organic coordination polymers are self-assembly materials in which transition metal ions are linked via organic molecules into chain or plane-like structures. Strong hydrogen bonds enable these units to form three-dimensional lattices, while the underlying anisotropy causes low-dimensional magnetism to evolve. Through coordination chemistry we have begun to gain chemical control over these systems, allowing us to modify the exchange ligands or the transition ions, while still maintaining the same basic magnetic network. This gives a good degree of control over properties such as the magnetic anisotropy, making these materials ideal candidates for use in purpose-engineered magnetic systems. Furthermore, exploring the relationship between the structure, physical and magnetic properties of these systems allows us to gain an understanding of the nature of the exchange interactions and the electronic correlations that give rise to the low-dimensional magnetically ordered phases of matter.

One material which we have focused on is $CuF_2(H_2O)_2(pyz)_2$ (pyz=pyrazine, $C_4H_4N_4$) [1]. This is a Cu^{II} co-ordination polymer, in which strong hydrogen bonds exist between the copper pyrazine chains, leading to two-dimensional magnetic properties at ambient pressure. This system has an active Jahn-Taller centre, where the magnetic orbitals are elongated along a particular axis, allowing the magnetic properties to be selectively modified through perturbation of the co-ordination environment. We have recently carried out high pressure measurements up to 20 kbar at the National High Magnetic Field Laboratory, using a modified radio-frequency technique which can be used to extract the absolute magnetisation [2]. Recent structural and low-field susceptibility measurements have suggested that $CuF_2(H_2O)_2(pyz)_2$ undergoes a phase transition with the application of pressure [3]. We will show that pressure can be used to switch the Jahn-Teller axis, and hence modify the orbital orientation and the magnetic properties; leading to a sharp transition from two-dimensional to one-dimensional magnetism at 9.1 kbar.

[1] J. L. Manson, M. M. Conner, J. A. Schlueter, A. C. McConnell, H. I. Southerland, I. Malfant, T. Lancaster, S. J. Blundell, M. L. Brooks, F. L. Pratt, et al., Chemistry of Materials 20, 7408 (2008)

[2] S. Ghannadzadeh, M. Coak, I. Franke, P. A. Goddard, J. Singleton, and J. L. Manson, Review of Scientic Instruments 82, 113902 (2011)

[3] G. J. Halder, K. W. Chapman, J. A. Schlueter, and J. L. Manson, Angewandte Chemie International Edition 50, 419 (2011)

Dimensionality selection in a molecule-based magnet

P Goddard[1], J Manson[2], J Singleton[3], I Franke[1], T Lancaster[4], A Steele[1], S Blundell[1], F Pratt[5], R McDonald[3], O A Valenzuela[3], J Corbey[2], H Southerland[2], P Sengupta[6], J Schlueter[7] and C Baines[8]

[1]University of Oxford, UK, [2]Eastern Washington University, USA, [3]Los Alamos National Laboratory, USA, [4]University of Durham, UK, [5]Rutherford Appleton Laboratory, UK, [6]Nanyang Technological University, Singapore, [7]Argonne National Laboratory, USA, [8]Paul Scherrer Institut, Switzerland

Gaining control of the building blocks of magnetic materials and thereby achieving particular characteristics will make possible the design and growth of bespoke magnetic devices. While progress in the synthesis of molecular materials, and especially coordination polymers, represents a significant step towards this goal, the ability to tune the magnetic interactions within a particular framework remains in its infancy. Here we demonstrate a chemical method which achieves dimensionality selection via preferential inhibition of the magnetic exchange in an $S = 1/2$ antiferromagnet along one crystal direction, switching the system from being quasi-two- to quasi-one-dimensional while effectively maintaining the nearest-neighbour coupling strength [1].

We will first introduce coordination polymers, indicating how their compositions can be adjusted to provide a versatile testbed of the structure/property relationship in low-dimensional magnets. We will then discuss how, after initially designing a material based on planes of Cu(II), we adapt the recipe such that the exchange pathways are broken along specific crystal directions, resulting in a chain-like compound. We show the results of x-ray diffraction, pulsed-magnetic-field magnetization, muon-spin relaxation and electron-spin resonance measurements that confirm the change in structural and magnetic dimensionality. The nearest-neighbour exchange energies of the two materials are found to be equal to each other to within 5%. The difference in numbers of nearest-neighbours, however, means that the strength of the interactions acting on each spin in the quasi-two-dimensional material is twice that of its quasi-one-dimensional cousin.

[1] P. A. Goddard et al. Phys. Rev. Lett. 108, 077208 (2012).

Kondo resonance switching with surface chirality of unsymmetrical double-decker 2,3-Naphthalocyaninato Phthalocyaninato Ln(III) complexes

T Komeda, H Isshiki, J Liu, K Katoh, M Shirakata, B Breedlove and M Yamashita

Tohoku University, Japan

Molecular spintronics devices utilize the freedom of charge as well as the spin of electrons. Using molecules in such devices makes it possible to control precisely the spin distribution via molecule synthesis and/or control of the molecule ordering in films. For instance, much research has gone into the synthesis of molecules linked by non-covalent bonding, and chirality is an important tool for such purposes. When a molecule is adsorbed on a surface, it exhibits surface chirality due to the loss of the freedom of flipping while retaining its inherent chirality. For example, identical planar molecules can adsorb on a surface face up and down, which causes surface chirality.

In this study, we synthesized the heteroleptic double-decker complex TbNPcPc (NPc = naphthalocyanate and Pc = phthalocyanate), in which two different planar ligands sandwich a Tb(III) ion, with a 1/2 spin π radical in the ligands and studied its structure and spin properties by using low-temperature scanning tunneling microscopy (STM). As we reported (Komeda et al., Nature Communications 2, 217 (2011)), this type of double-decker molecule displays a Kondo effect due to the single occupancy of a π orbital. Upon adsorption on a surface, two chiral molecules appear depending on which side contacts the substrate surface. The chirality causes several ordered structures, including straight chains of molecules with the NPc ligands on the vacuum side (NPc-up) and a film in which NPc-up and Pc-up molecules alternate. In dI/dV spectra, a Kondo resonance, which is a good conductance control mechanism originating from interactions between conduction electrons and a localized spin, was detected when the STM tip was over a ligand. The Kondo temperature (T_K) shows drastic changes depending on the extent to which the molecules are segregated by chirality.

On the origin of the anti-phase domain boundaries in crystallographically matched systems: $Fe_3O_4/MgAl_2O_4$

D Gilks[1], L Lari[2], C Kelley[1], O Cespedes[3], Z Cia[4], S Thompson[1], K Ziemer[4] and V Lazarov[1]

[1]University of York, UK, [2]The York JEOL nanocentre, UK, [3]University of Leeds, UK, [4]Northeastern University, USA

The predicted half-metallic properties of bulk Fe_3O_4 have generated interest for spintronic device applications. It is believed that deviation from bulk properties (such as magnetoresistance and high saturation fields) in thin films are a result of structural defects, primarily anti-phase domain boundaries (APBs). APBs are half unit cell translations of Fe sublattice positions within an unaltered higher symmetry fcc O sublattice. These defects are the result of different crystal symmetry between substrate and film allowing multiple incoherent nucleation sites on the substrate e.g. Fe_3O_4 growth on MgO. APBs give rise to strong antiferromagnetic super exchange interactions across the defect boundaries hence destroying the desirable bulk spin ordering. The control of the density and nature of APBs is crucial for device application. We present a systematic study of MBE grown Fe_3O_4 films on $MgAl_2O_4$ as a model system where substrate and film have the same crystal symmetry this film is expected to be free from APBs. The structural, optical and magnetotransport characterisation of the films were studied by aberration corrected (S)TEM, VSM, 4-point contact, Raman and infra-red spectroscopy. All films show deviation from bulk properties suggesting APB presence. The $\sim$3% lattice mismatch between $MgAl_2O_4$ and Fe_3O_4 creates interfacial misfit dislocations. We show that the dislocations do not lead to APBs; instead the films are fully relaxed within the first few atomic planes without breaking the bulk symmetry. However, we still observed APBs suggesting new formation mechanisms, most likely as result of the 3D film growth mediated by growth dislocations.

Growth of ultrathin Mn germanide films on Ge(111)

J Hirvonen-Grytzelius, H Zhang and L Johansson

Karlstad University, Sweden

The interest in transition metal layers on semiconductors has increased over the last years. One reason is their potential use in spintronics applications. We have recently investigated the surface electronic structure of Mn_5Ge_3 on Ge(111) by angle resolved photoemission, and scanning tunnelling microscopy and spectroscopy (STM/STS) [J. Hirvonen Grytzelius et al., Phys. Rev. B 84, 195306 (2011)]. In the present work, we continue our studies of thin manganese germanide films grown on Ge(111) by investigating morphology, structure and magnetic properties. The Mn germanide films were formed by solid phase epitaxy, and were investigated by low energy electron diffraction (LEED), high-resolution photoelectron core-level spectroscopy (CLS), X-ray magnetic circular dichroism (XMCD) and STM. The manganese depositions were done with various substrate coverages from 3 to 32 monolayers (ML). After each deposition the samples were annealed at temperatures ranging from 260° C to 450° C for 20 min. Annealing of as-deposited Mn films above 300° C led to the formation of islands with the well-known Mn_5Ge_3 phase, displaying a $\sqrt{3}\times\sqrt{3}$ LEED pattern. To obtain a surface fully covered with Mn_5Ge_3, 32 ML of Mn was needed.

Annealing at lower temperatures led to a smoother surface with an apparent different structure, as indicated by Ge 3d CLS spectra. The structural, electronic and magnetic properties of the different germanide films will be discussed, based on our STM data, Ge 3d, Mn 2p and Mn 3s CLS data, and our XMCD results.

Modification of magnetic anisotropy of linear chains on Pt(111) by external electric field

T Dasa[1], P Ignatiev and V Stepanyuk

Max-Planck Institute of Microstructure Physics, Germany

Performing the state of the art *ab initio* calculations we study the effect of the electric field on magnetic properties of Co and Co-Pt chains on Pt(111). Our studies give clear evidence that an externally applied electric field could permit one to tailor magnetic anisotropy in chains. It is demonstrated that the physics behind this effect is related to the spin-dependent screening of an external electric field at the chains. A strong enhancement of MAE in mixed Co-Pt chains, compared to pure Co chains, is found. The interplay between atomic structure and the MAE is discussed.

Biotemplated patterns of magnetic nanoparticles

J Galloway, J Bramble, A Rawlings, G Burnell, S Evans and S Staniland

University of Leeds, UK

Magnetic nanoparticles (MNPs) are used in many applications, including electronic data storage when in films on surfaces. These MNPs must have a monodisperse size and shape distribution to ensure their magnetic behaviour is consistent. To achieve consistent MNPs often requires the use of environmentally harsh chemicals, high temperatures and elevated pressure. Also, it has only been possible to study the bulk behaviour of MNPs to date. The biomineralising protein Mms6 from M. magneticum AMB-1 templates the formation of monodisperse cubo-octahedral magnetite in vitro under mild conditions that are akin to those formed by the bacterium in vivo. Here, the recombinant Mms6 protein is used to both template the formation and facilitate immobilisation of the MNPs onto patterned surfaces. A method that allows Mms6 to remain functional after immobilisation allows magnetite nanomagnets to form on a pre-patterned surface in a bottom-up assembly. This enables the magnetic behaviour of MNPs to be studied. The MNPs are imaged by SEM and AFM, and the magnetic behaviour of the particles analysed by VSM and MFM. The bottom up approach may be adapted to immobilise any identified recombinant biomineralising protein or peptide sequence, so that ordered patterns of desired minerals can be formed under ambient conditions on patterned surfaces, and used to create multi-material biotemplated devices.

The role of the interface in the magnetic interaction between M-Phthalocyanine and ferromagnetic film

E Annese[1], F Casolari[2], J Fujii[3] and G Rossi[4]

[1]IOM-CNR and Università di Modena e Reggio Emilia, Italy, [2]Università di Modena e Reggio Emilia, Italy, [3]IOM-CNR, Italy, [4]Università Statale di Milano and IOM-CNR, Italy

The control of organic nanostructures suitable for nano-electronics, spintronics and sensor applications can be achieved by tuning their electronic, optical, catalytic and magnetic properties at organic/inorganic interfaces. The feasibility of incorporating organic materials into spintronics devices requires the comprehension of the electronic and magnetic interaction at organic/ferromagnetic interface [3-5]. Several open aspects still need to be explored at the organic/ferromagnetic interfaces: i) the type of magnetic coupling; ii) the role of the organic molecules and iii) the role of substrate surface magnetism.

With this respect, the choice of the molecules and the substrates are primary parameters. Metal-phthalocyanines ($C_{32}H_{16}N_8$-M, MPc) are large planar molecules showing a high level of flexibility that makes them ideal building blocks for functionalized organic systems [1]. Fe and Co films, epitaxially grown on Cu substrate, show magnetic anisotropy from perpendicular to in plane directly related to the film thickness [2].

In this work, we have investigated the behaviour of MPc films deposited on ferromagnetic Fe (Co) film by X-ray absorption Spectroscopy and X-ray Magnetic Circular Dichroism. We have observed and monitored the magnetic coupling between 3d atoms within MPc and the substrate at room and low (80 K) temperatures. We have analyzed the evolution of the magnetic coupling as a function of MPc thickness. We have found that only MPc molecules at the interface are mainly involved in the coupling with ferromagnetic film.

[1] S.R. Forrest, Nature 428, 911 (2004).
[2] J. Shen et al, Phys. Rev. B. 56, 11134 (1997).
[3] A. L. Rizzini et al, Phys. Rev. Lett. 107, 177205 (2011).
[4] H. Wende et al, Nat. Mat., 6, 516 (2007).
[5] A. Scheybal et al, Chem. Phys. Lett. 411, 214 (2005).

Low temperature physics 2

Common mechanisms for the superconductivity and the Fermi-liquid properties of Nb-doped strontium titanate

D van der Marel[1], S Klimin[2], J Tempere[2] and J T Devreese[2]

[1]Université de Genève, Switzerland, [2]Universiteit Antwerpen, Belgium

The experimentally detected Fermi-liquid behavior of the DC resistivity for the Nb-doped strontium titanate [1] is theoretically investigated involving different scattering channels. It has been established that the total relaxation rate in SrTi$_{1-x}$Nb$_x$O$_3$ is provided by two mechanisms. First, the Baber electron-electron scattering [2] with participation of both Coulomb and phonon-mediated electron-electron interactions provides the T^2-dependence of the resistivity and of the relaxation rate. Second, the scattering on the potential landscape caused by impurities is responsible for the residual relaxation rate which does not vanish at $T = 0$. The calculated relaxation rates are in agreement with the experiment [1]. The aforesaid agreement can be achieved only accounting for all phonon branches in SrTi$_{1-x}$Nb$_x$O$_3$ including the acoustic phonons. It is remarkable that the resulting effective electron-electron attraction can overcome the Coulomb repulsion in strontium titanate. Thus the superconductivity and the Fermi-liquid properties of Nb-doped strontium titanate have the common origin, as suggested in [1].

[1] D. van der Marel, J. L. M. van Mechelen, and I. I. Mazin, Phys. Rev. B 84, 205111 (2011).
[2] W. G. Baber, Proc. R. Soc. A 158, 383 (1937).

Local Lattice Instability induced resonant pairing superconductivity - the Boson Fermion Model

J Ranninger

CNRS, France

Cuprate high temperature superconductors are viewed as emerging out of a phase uncorrelated state of resonating bipolaronic singlet pairs in a Bose glass phase, when the competing local intra-pair and non-local inter-pair phase correlations change as the concentration of doped holes exceeds a certain value. The intra-pair phase correlations show a strong lattice driven isotope effect of T*, which determines the onset of pairing as the pseudogap state stabilizes with decreasing temperature. We describe such a scenario in terms of a phenomenological Boson Fermion model, representing a mixture of itinerant electrons and localized bipolaronic electron pairs in chemical equilibrium with each other and a charge exchange coupling acting between the two. This scenario has in the past predicted the pseudogap state with its remnant Bogoliubov modes and its transient Meissner effect. The spectral properties of its single particle in-gap excitations have been proposed to exhibit branch cut rather than pole singularities. These excitations are quantum superposition of fermionic electrons and bosonic electron pairs, accompanied by electron holes. This Boson Femion duality of the charge carriers is similar to that of the Bogoliubov-Valatin excitations in BCS superconductors, representing a quantum superposition of carriers with positive and negative charges. I review here the salient features of this scenario and evoke propositions for crucial experiments to be done.

Condensation of light local pairs at high temperatures

J H Samson[1], G Sica[2] and S Alexandrov[3]

[1]Loughborough University, UK [2]Loughborough University, UK and Università degli Studi di Salerno, Italy,
[3]Loughborough University, UK and Instituto de Fisica “Gleb Wataghin”, Brazil

Local electron-pairing theories of high-temperature superconductivity face two requirements that are at first sight in conflict: an effective *attraction* between electrons to form mobile inter-site pairs with a high Bose-Einstein condensation (BEC) temperature, and an effective *repulsion* between these pairs to prevent clustering or phase separation. However, it has been recently shown that in highly polarisable lattices the competition between Coulomb and Fröhlich interactions results in a short-range polaronic exchange term that favours the formation of local pairs with aneffective pair-pair repulsion [1]. In the absence of hopping, the highly degenerate ground state consists of local singlet pairs. We determine the pair band structure for finite hopping. In a variety of lattices the pairs have small radius and low effective mass and hence high BEC temperature [2]. We discuss the pseudogap structure and thermodynamic properties of this model.

[1] Alexandrov A S (2011) *Europhys Lett* 95, 27004
[2] Alexandrov A S, Samson J H and Sica G (2012) *Phys Rev B* 85, 104520

Quasicondensation and pseudogap in two-dimensional Fermi gases

S Klimin, J Tempere and J Devreese

Universiteit Antwerpen, Belgium

Within the Gaussian pair fluctuation formalism, which is an improvement of Nozières – Schmitt-Rink approach, the phase diagrams for imbalanced Fermi gas with s-wave pairing are obtained accounting for both phase and amplitude fluctuations. We focus on the pseudogap paired state above the Berezinskii-Kosterlitz-Thouhless transition temperature. The amplitude of the order parameter is other than zero in the pseudogap state, while the phase coherence is absent. The Gaussian pair fluctuation approach yields a convergent fermion density for the paired state in 2D. Owing to the fluctuations, the pairing temperature for the pseudogap state can be substantially lowered with respect to the mean-field critical temperature. This difference is especially drastic in the strong-coupling regime. The obtained pairing temperatures are in agreement with recent experimental data on pseudogap pairing of ultracold fermionic atoms in two dimensions. The obtained results can shed light on the pseudogap state for high-temperature superconductors.

Anisotropic charge dynamics in detwinned iron-pnictide superconductors

L Degiorgi, A Dusza and C Mirri

ETH Zurich, Switzerland

A renewed interest in the study of symmetry-breaking competing states in complex interacting systems followed the discovery of a broken rotational symmetry, due to stripe or nematic order, in the pseudogap phase of the copper oxide superconductors. The most recent playground in which to address the competition between structural, magnetic and superconducting phases is provided by the iron-pnictide superconductors. In these systems, the non-superconducting parent compounds undergo an antiferromagnetic transition into a broken-symmetry ground state at T_N, which is always preceded by or coincident with a tetragonal-to-orthorhombic structural distortion at $T_s \geq T_N$. This latter transition implies a twofold electronic symmetry, which for a range of dopings coexists with superconductivity and long range magnetic order. Understanding the effects of the structural transition on the charge dynamics and the electronic bands by studying the optical properties of the system is an important step in order to develop a comprehensive theoretical description of these materials. We investigate the optical conductivity with light polarized along the in-plane orthorhombic a- and b-axes of $Ba(Fe_{1-x}Co_x)_2As_2$ for x=0, 2.5% and 4.5% (i.e., in the so-called underdoped regime) under uniaxial pressure across their structural and magnetic transitions. We estimate the dichroism, which extends to high frequencies and temperatures. All together, our results on such single domain specimens reveal a nematic susceptibility as well as the electronic nature of the structural transition and particularly allow us to shed light on the counterintuitive anisotropic behavior $\rho_b > \rho_a$ (i.e., along the antiferromagnetic a-axis with respect to the ferromagnetic b-axis) of the dc resistivity.

(invited) Fundamental properties of the superconducting state at the $LaAlO_3$/$SrTiO_3$ interface

H Boschker, C Richter, W Dietsche and J Mannhart

University of Stuttgart, Germany

The $LaAlO_3$/$SrTiO_3$ interface provides an intriguing 2-dimensional electron system in which the coexistence of superconductivity and magnetism has been observed. It remains unclear whether the same electrons are responsible for both superconductivity and magnetism. It has been suggested that the superconductivity and the magnetism are spatially separated: scanning SQUID microscopy measurements showed ferromagnetic domains surrounded by superconducting regions. A separation of the two states between different bands has been proposed as well: the magnetism is due to localized electrons in the d_{xy} derived band, while the superconductivity occurs in the d_{xz} and d_{yz} derived bands. Nevertheless, it is also possible that the groundstate of the $LaAlO_3$/$SrTiO_3$ interface is an unconventional superconductor which is intimately connected to the magnetism. We will present detailed transport measurements of the superconducting state in order to clarify this issue.

Unbinding of giant vortices in states of competing order

C Hooley[1], J Fellows[2], S Carr[3] and J Schmalian[3]

[1]University of St Andrews, UK, [2]University of Birmingham, UK, [3]Karlsruher Institut fur Technologie, Germany

We consider a system with two order parameters, one with O(2) symmetry and one with O(M), near a point in parameter space where they couple to become a single O(2+M) order. While the O(2) sector supports vortex excitations, simple topological considerations tell us that the vortices must somehow disappear as the high symmetry point is approached. We develop a variational argument in the size of the vortex core, which shows that the vortex core size diverges as $\Delta^{-1/2}$ and the Berezinskii-Kosterlitz-Thouless transition temperature of the O(2) order vanishes as $1/\ln(1/\Delta)$, where Δ measures the distance from the high symmetry point. Our physical picture is confirmed by a renormalization group analysis which gives logarithmic corrections, and demonstrates full symmetry restoration within the cores. Possible realisations of this physics in easy-plane magnets and supersolid phases in cold-atom systems are discussed.

Anomalous Meissner effect in cuprate heterostructures

E Morenzoni[1], B Wojek[2], E Koller[3], G Logvenov[4], I Bozovic[4], D Eshchenko[2], A Suter[1], T Prokscha[1], H Keller[5], O Fischer[3], V Malik[6], C Bernhard[6] and M Doebeli[7]

[1]Paul Scherrer Institut, Switzerland, [2]Paul Scherrer Institut and University Zürich, Switzerland, [3]University of Geneva, Switzerland, [4]Brookhaven National Laboratory, USA, [5]University Zürich, Switzerland, [6]University of Fribourg, Switzerland, [7]ETH Zürich, Switzerland

The Meissner effect and associated perfect ‘bulk’ diamagnetism together with zero resistance and gap opening are characteristic features of the superconducting state. In cuprates, unusual diamagnetic signals above T_c and anomalous proximity effects in non superconducting layers have been detected, but a Meissner effect has never been observed.

We present a low-energy muon-spin-rotation study of the magnetic and superconducting properties of $YBa_2Cu_3O_{7-\delta}$/$PrBa_2Cu_3O_{7-\delta}$ trilayer and bilayer heterostructures and of underdoped $La_{1.94}Sr_{0.06}CuO_4$ layer (LSCO) (up to 46 nm thick, critical temperature $T_c' < 5$ K) brought in close contact with two optimally doped $La_{1.84}Sr_{0.16}CuO_4$ layers ($T_c \approx 32$K).

Particularly, by determining the magnetic-field profiles on nm scale throughout these structures, we show that a finite superfluid density can be induced in otherwise semiconducting $PrBa_2Cu_3O_{7-\delta}$ (PBCO) layers when juxtaposed to $YBa_2Cu_3O_{7-\delta}$ “electrodes [1] and in underdoped LSCO layer for temperatures well above T_c’ but below T_c [2]. The effect occurs in layers of thickness much larger than typical c-axis coherence lengths of cuprates or thermal coherence length as determined by conventional proximity theory. Although the physical mechanism of the effects may be different in both cases (related to the electronic structure [3] and its sensitivity to local structural changes for PBCO, or to the unusual nature of the pseudogap state for LSCO [4]), these results appear as a further and more compelling manifestation of long range proximity effects [5] and constrain the theory and our understanding of high temperature superconductors.

[1] B.M. Wojek et al., Phys. Rev B 85, 024505 (2012)
[2] E. Morenzoni et al., Nature Communications 2, 272 (2011)
[3] R. Fehrenbacher and T. M. Rice, Phys. Rev. Lett. 70, 3471 (1993).
[4] D. Marchand et al., Phys. Rev. Lett. 101, 097004 (2008).
[5] I. Bozovic et al., Phys. Rev. Lett. 93, 157002 (2004).

Low doping superconducting state anomalies in the high-Tc cuprates as a signature of spin fluctuation mediated superconductivity

F Onufrieva and P Pfeuty

Laboratoire Leon Brillouin, France

Spin fluctuation (SF) are considered as a good candidate for the mediator of high-Tc superconductivity in the cuprates. This scenario explains naturally the d-symmetry of pairing, the low energy electronic properties such as the nodal kink, peak-dip-hump form of spectral functions etc., and moreover, the characteristic energies extracted from different experimental data (ARPES, STM, optical conductivity) are close to the observed SF energies.

Here we show that the glaring anomalies observed in the low doping superconducting (SC) state and not understood until now, also found a natural explanation within the SF scenario. The results are obtained within a microscopic strong coupling dynamical theory [1]. The key point is that SFs become soft and strong at low doping in approaching the AF instability and that such SFs turn out to be a destroyer of the electron coherence and therefore rather a destroyer than a glue for superconductivity. Namely we show that (i) at low doping electronic quasiparticles remain coherent only within a limited area of the Brillouin zone near the node, (ii) this area shrinks with SF softening, (iii) there are two characteristic gaps, the nodal and antinodal ones, which can behave in a divergent way, the nodal gap being obligatory proportional to the SF characteristic energy and therefore decreasing with underdoping, (iv) that the SC order parameter (OP) scales with the nodal gap and not at all with the maximum gap which can behave in a way opposite to the OP, the properties that explain well the remarkable and still non understood electronic anomalies observed in the low doped cuprates.

[1] F.Onufrieva, P. Pfeuty, Phys.Rev.Lett. 102, 207003 (2009).

Electronic structure and topological insulators 2

(invited) Emergent quantum-size effects at topological insulator surfaces

P King

University of St Andrews, UK

Bismuth-chalchogenides are model examples of three-dimensional topological insulators. Their ideal bulk-truncated surface should host a single spin-helical surface state [1], which is the simplest possible surface electronic structure allowed by their non-trivial band topology. However, we show here that real surfaces of such compounds, even if kept in ultra-high vacuum, rapidly develop a much more complex electronic structure than suggested by idealized theoretical models [2,3]. Subband states of a 2D electron gas emerge in the vicinity of the bulk conduction band, which develop large Rashba-type splittings, while new ladders of M-shaped states are created in the original bulk valence bands. Given their propensity for formation, these must all be considered part of the intrinsic electronic structure of the surface of any realistic topological insulator, for example when exposed to air or interfaced to another material. We demonstrate that a conceptually simple model, implementing a semiconductor-like band bending in a parameter-free tight-binding supercell calculation, can quantitatively explain this entire measured hierarchy of electronic states. In combination with circular dichroism in angle-resolved photoemission experiments, we uncover a rich three-dimensional spin texture of this surface electronic system, resulting from the non-trivial topology of the bulk band structure. Moreover, our study indicates an important interplay of the topological and non-topological states, and reveals how the full surface-bulk connectivity in topological insulators is modified by quantum confinement.

[1] Zhang et al., Nature Phys. 5 (2009) 438.
[2] Bianchi et al., Nature Commun. 1 (2010) 128.
[3] King et al. Phys. Rev. Lett. 107 (2011) 096802.

Spin-polarized metallic surface states induced by spin-orbit interaction on semiconductors without heavy elements

T Aruga[1], S Hatta[1], Y Ohtsubo[1], K Yaji[2] and H Okuyama[1]

[1]Kyoto University, Japan, [2]University of Tokyo, Japan

Recently, spin-polarized semiconductor surface states induced by spin-orbit interaction (SOI) due to the surface inversion asymmetry [1-3] or on topological insulators have been intensively studied, These studies are motivated in part by possible spintronic applications. All the surfaces studied to date contain heavy elements which are in fifth or higher rows of the periodic table such as Tl, Pb, and Bi. This is because the strongest SOI is obtained at the closest proximity to the nuclei of heaviest elements.

Here we report the finding of the novel semiconductor surface states which are composed only of valence orbitals of a light element (Ge) but are significantly spin-polarized. The surface states are observed on the Ge(111) surfaces covered with Br [4], Bi [5], and several other elements. Angle-resolved photoelectron spectroscopy (ARPES) indicates that the surface states disperse along the edges of bulk heavy-hole (HH), light-hole (LH), and spin-orbit split-off (SO) bands, indicating that the surface states are split off from the bulk bands due to the truncation of the periodic potential at the surface. The wavefunctions of the surface states are composed only of Ge 4*sp* and extended over tens of subsurface Ge layers. Spin-resolved ARPES as well as full-potential first principles calculation clearly indicate that the surface states are significantly spin-polarized due to the Rashba SOI.

It is also shown that the spin-split surface states are intrinsically metallic or can be made metallic by hole doping, which suggests that these states provide a new machinary to study spintronic phenomena such as spin transport and spin accumulation at the semiconductor surfaces and interfaces. The result also suggest that similar spin-polarized electronic states are obtained at the surfaces and interfaces of compound semiconductors such as GaAs.

[1] *Large Rashba spin splitting of a metallic surface resonance bands on a semiconductor surface*, S. Hatta *et al.*, Phys. Rev. B 80, 113309 (2009).

[2] *Large Rashba spin splitting of a metallic surface-state band on a semiconductor surface*, K. Yaji *et al.*, Nat. Commun. 1, 17 (2010).

[3] *A metallic surface state with uniaxial spin polarization on Tl/Ge(111)-(1x1)*, Y. Ohtsubo *et al.*, J. Phys.: Condens. Matter 24, 092001 (2012).

[4] *Spin-polarized surface state on Br/Ge(111): surface spin polarization without heavy elements*, Y. Ohtsubo *et al.*, to be published.

[5] *Spin-polarized semiconductor surface states localized in subsurface layers*, Y. Ohtsubo *et al.*, Phys. Rev. B 82, 201307 (R) (2011).

Structural and electronic properties of silicene layers on Ag(111)

P Vogt[1], P De Padova[2], A Resta[3], B Ealet[3] and G LeLay[3]

[1]Technische Universität Berlin, [2]CNR-ISM, Italy, [3]Aix-Marseille University, CINaM-CNRS, France

Over the last years graphene has attracted tremendous attention due to its unique physical properties [1] and the possibility to probe quantum electrodynamics. Another similarly structured 2-dimensional material would be expected to have similar properties as graphene. Such a material could be silicene, the silicon based equivalent of graphene. Free standing silicene has been theoretically predicted and is conjectured to have a buckled honeycomb atomic arrangement of sp3/sp2-like hybridized Si-atoms [2]. Still, silicene would exhibit similar electronic properties as graphene, like e.g. an electronic dispersion resembling that of relativistic Dirac fermions.

We have shown recently that silicene layers can be synthesized by growing Si on the Ag(111) face showing structural and electronic properties very similar to graphene [3].STM images of these sheets give rise to triangular structures which are situated in a honeycomb arrangement with a (4×4) coincidence symmetry with respect to the Ag(111) surface. The structural model derived from STM measurements is in very good agreement with our DFT calculations. Synchrotron-based angular-resolved photoemission data reveal a downward conical dispersion resembling that of relativistic Dirac fermions at the Si K points [3]. We will discuss these results and show that depending on the growth conditions the formation of different 2D silicon arrangements can be observed.

Si deposition at room-temperature leads to the formation of amorphous Si-clusters, whereas the deposition at temperatures up to 180°C leads to the formation of 2D hexagonal Si-based structures which, however, show only weak long-range order. The formation of the (4×4) silicene is observed at growth temperatures around 220°C. Another 2D Si structure could be observed at slightly higher growth temperatures, showing a $(\sqrt{13}\times\sqrt{13})$ periodicity in LEED. This structure exhibit a very regular, wide range ordered Moiré-like surface pattern in STM, which, however, is related to surface areas of well-ordered and less ordered arrangements within the Si sheet. We will discuss the formation of this structure and its relation to silicene.

[1] Geim, A.K., Science, 342 (2009), 1530.

[2] Cahangirov, S. et al., Phys. Rev. Lett., 102 (2009), 236804.

[3] Vogt, P. et al.,Phys. Rev. Lett., (2012) in print.

[4] Chun-Liang, L. et al. Appl. Phys. Express 5, (2012) 045802.

Rashba spins with peculiar scattering processes

K Sakamoto[1], T Kuzumaki[1], B Muller[1], Y Yamamoto[1], J Osiecki[2], R Uhrberg[2], K Miyamoto[3], Y Takeichi[4], A Harasawa[4], J Fujii[5], S Stolwijk[6], A Schmidt[6], M Donath[6] and T Oda[7]

[1]Chiba University, Japan, [2]Linkoping University, Sweden, [3]Hiroshima University, Japan, [4]University of Tokyo, Japan [5]TASC Laboratory, Italy, [6]Munster University, Germany, [7]Kanazawa University, Japan

In this paper, we present a Rashba system with spin-polarized metallic surface bands on a semiconducting substrate, in which the Rashba spins would be scattered in particular directions only. The Rashba effect is a novel exotic low-dimensional solid-state property that produces a spin-polarized two-dimensional electron gas from a combined effect of spin-orbit interaction and structural inversion asymmetry even for nonmagnetic materials, and it is the key factor for operating a spin field-effect transistor that is one of the most prominent semiconductor spintronics devices. In an ordinary Rashba system, however, the Fermi surface shows isotropic vortical spin structures with spin polarization vectors lying in the surface plane, which lead to a high-probability of electron spin backscattering and thus lower the efficiency of the electron spin current. By using direct and inverse spin- and angle-resolved photoelectron spectroscopies, we have measured the Rashba spin bands of an electron-doped Tl/Si(111)-(1x1) surface and a Tl/Si(110)-(1x1) surface. In the former system, spin-polarized electron pockets with upstanding Rashba spins were observed at the K and K' points of the surface Brillouin zone. The opposite spin direction at these points indicates that the electron spin backscattering with a non-magnetic impurity is considerably suppressed in this system. Regarding the latter system, we observed an extraordinary quasi-one dimensional Rashba splitting that would also improve the efficiency of the spin current originating from its peculiar spin structure. We will also discuss the origins of these peculiar spin structures based on the symmetries of the surfaces.

(invited) Topological insulators: A romance between momentum and spin

E Hankiewicz

Universität Würzburg, Germany

Topological insulators (TIs) have a bulk energy gap that separates the highest occupied band from the lowest unoccupied band like in ordinary insulators. However, the edge (for 2D TIs) or the surface (for 3D TIs) of a topological insulator exhibits gapless electronic states that are protected by time reversal symmetry [1]. In this talk I will focus on transport properties of topological insulators when the Fermi energy probes the helical edge states (counter-propagating gapless spin edge states) or gapless surface states where a spin follows ("romances") a momentum. In particular I will discuss how the helical edge states merge to the metal and how they can be detected through the electrical response [2,3]. Later I will discuss the magnetotransport of the helical edge channels and surface states; in particular I will analyze the transition between topological insulator and quantum Hall regimes [4]. Concerning 3D TIs, I will focus on the magnetic field dependence of galvanic responses of the system showing anomalies due to broken time-reversal symmetry of the surface quantum Hall state. Relevant experiments will be discussed.

[1] M. Z. Hasan and C. L. Kane Rev. Mod. Phys. 82, 3045 (2010).
[2] C. Brune, A. Roth, H. Buhmann, E. M. Hankiewicz, L. W. Molenkamp, J. Maciejko, X.-L. Qi and S.-C. Zhang, arXiv:1107.0585, Nature Physics in press (2012).
[3] R. W. Reinthaler and E. M. Hankiewicz Phys. Rev. B 85, 165450 (2012) .
[4] G. Tkachov and E. M. Hankiewicz Phys. Rev. Lett. 104, 166803 (2010).

Theoretical study of Rashba effect based on tight-binding model

T Mii, N Shima and K Makoshi

University of Hyogo, Japan

Both the time reversal and spatial inversion symmetries lead to spin-degenerate electronic states. Usually magnetic fields are used to split off spin degree of freedom, breaking the time reversal symmetry. The alternate way proposed by Rashba and Bychkkov for getting spin split states is breaking the spatial inversion symmetry. Spin splitting due to this mechanism is called Rashba effect. It is conceivable that an array of atoms on surfaces and/or exposed to an electric field is in such a situation. Since the Rashba effect opens a possibility to control electronic spins with electric field instead of magnetic field, it is of importance to understand how the spin-orbit interaction affects electronic states not only from the view point of elementary physics but also technological application.

We discuss the Rashba effect in 1D and 2D systems based on tight-binding approximation. In order to violate the spatial inversion symmetry, an external electric field is applied to the systems and as a result it gives rise to the Rashba spin splitting due to the spin-orbit interaction. We suppose that only s-orbit and spin degree of freedom are taken into account at each atom. Transfer matrix elements come from the spin-orbit interaction are fully considered and allow electronic spins to flip during electronic hopping between atomic sites. Despite this simple model, we show various properties related Rashba effect, such as spin textures around Dirac points and singularities in the density of states, can be discussed.

Quantum well states and quantum size effects in ultrathin Bi films

P Kowalczyk[1], O Mahapatra[2], S Brown[2], Gu Bian[3], X Wang[3] and T Chiang[3]

[1]University of Lodz, Poland, [2]University of Canterbury, UK, [3]University of Illinois at Urbana–Champaign, USA

Bismuth is a semimetal located in the 15th group of the periodic table. In the bulk it has low concentration of charge carriers, small effective mass, large de Broglie wavelength and long mean free path. The surfaces of Bi crystals are characterised by the presence of spin orbit split bands making the surface much more metallic than the bulk.

We have previously established techniques to grow ultra thin Bi islands and rods on highly oriented pyrolytic graphite (HOPG) substrates, with the (110) plane parallel to the substrate surface. These structures grow in paired layer fashion on an intermediate ("wetting") layer i.e. with thicknesses 3, 5, 7 ML. For these films we have found formation of spin degenerated quantum well states (QWS) using angle resolved photoemission spectroscopy (ARPES), scanning tunnelling spectroscopy (STS) and density functional theory (DFT). Our ARPES data are characterised by complex bands different from these suggested by calculations using DFT. We explain that discrepancy by coexistence of few Bi domains and different Bi heights influencing ARPES measurements. Our local STS measurements conducted both on islands with different heights and on quantum wedges (Bi islands grown over HOPG step edge characterised by flat surface and at the same time different Bi heights on adjacent terraces). These experimental results allow us to postulate existence of the surface reconstruction or formation of the allotrope for thin Bi films. We will also show other proofs of formation of allotropic structures based on our high resolution transmission electron microscopy results.

Beside vertical quantisation observed using STS and ARPES we will point out possible quantisation in one of lateral directions. We will show our scanning tunnelling microscopy (STM) results suggesting existence of preferred widths of islands. Mechanical coarsening of islands leading to preferred widths will be discussed as well. These observations lead to a conclusion that the lateral growth of thin Bi films is governed by the quantum size effects.

Semi-conductors and their surfaces 2

(invited) Atomic-scale quantum structures in silicon

S Schofield, P Studer, C F Hirjibehedin, N J Curson, G Aeppli and D R Bowler

University College London, UK

Scanning tunnelling microscopes (STMs) can be used to manipulate atoms on surfaces to create quantum structures such as the celebrated quantum corral [1]; such structures scatter electrons confined within quasi 1- and 2-dimensional [1,2] states, producing extended quantum-well bound states. An alternative approach to the formation of quantum bound states on surfaces is to couple individual atomic orbitals to produce quantum states with direct analogy to molecular orbitals. Here we demonstrate the creation of such states on H-terminated Si(001) through the fabrication of interacting dangling bond (DB) orbitals using precisely controlled H atom desorption. We fabricate chains of DBs on next-nearest neighbour lattice sites. We show that these structures support both ground and excited states, and we image the probability distributions of these states using the STM tip bias and tip-sample separation as gates to control what states contribute to the image. The observed ground states are in agreement with previous reports of tunnel coupled DBs [3]. The excited states, in contrast, are entirely new and unexpected and provide insight into in the fundamental nature of semiconductor defects. Our results establish a general model for quantum state engineering through the atomically precise manipulation of chemically passivated surfaces.

[1] M. F. Crommie et al., Science 262, 218 (1993).
[2] K. Sagisaka, et al., Appl. Phys. Lett. 88, 203118 (2006).
[3] T. Hitosugi, et al., Phys. Rev. Lett. 82, 4034 (1999).

Special features of Al atomic chains on Si(100)

I Ostadal[1], M Setvin[2], M Kucera[1], F Rozboril[3], P Kocan[1], P Sobotik[1] and L Jurczyszyn[3]

[1]Charles University in Prague, Czech Republic,[2]Institute of Physics, Academy of Sciences of the Czech Republic, [3]University of Wroclaw, Poland

Aluminum deposited on Si(100) surface forms at low coverage atomic chains like other group III metals – Ga, In. Our scanning tunneling microscopy (STM) experiments showed that behavior of Al adatoms is different than in case of Ga and In.

Surface adsorption of Al at room temperature seems to be not influenced by C-defects, the chains contain “kinks” which do not appear during growth at higher temperature. The number of atoms in chains is always even – the chains or chain segments between kinks are composed from dimers. The chain length distribution was observed monotonous for Ga and In [1, 2] but in case of Al is monomodal - contains a single maximum at an average length.

STM observations at room temperature show different imaging of particular Al dimers in the chains.

The experimental data obtained for aluminum are compared with those reported for indium and gallium. Growth models are discussed with respect of other published experimental [3] and theoretical results [4, 5].

[1] M. A . Albao et al., Phys. Rev. B 72, 035426 (2005); Phys Rev. B74, 037402 (2006).
[2] J. Javorský et al., Phys. Rev. B 79, 165424 (2009).
[3] M. Setvín et al., Phys. Rev. B 85, 081403(R) (2012).
[4] G. Brocks et al., Phys. Rev. Lett. 70, 2786 (1993).
[5] M. A. Albao et al., J. Phys. Condensed Mat. 21, 405002 (2009); M. A. Albao et al., Surf. Sci. 604, 396 (2010).

Electronic properties of dangling-bond nanostructures formed on hydrogen passivated Ge(001) surface by STM tip-induced hydrogen desorption

M Kolmer[1], S Godlewski[1], B Such[1], F Krok[1], H Kawai[2], M Saeys[3], C Joachim[4] and M Szymonski[1]

[1]Jagiellonian University, Poland, [2]Institute of Materials Research and Engineering, Singapore, [3]National University of Singapore, Singapore, [4]Institute of Materials Research and Engineering, Singapore and Nanosciences Group & MANA Satellite, CEMES-CNRS, France

We report on studies concerning preparation of well organized atomic wires and 2D nanopads by scanning tunneling microscope (STM) tip-induced hydrogen desorption from hydrogen passivated Ge(001) surface. A mixed p(2×2)/c(4×2) reconstruction of Ge(001) surface upon exposure to the atomic hydrogen source forms a stable monohydride p(2×1) phase of Ge(001):H. Dangling-bond nanostructures on the passivated surface are then created by cryogenic temperature STM tip-induced atomically precise dimer-by-dimer hydrogen desorption. We present very efficient protocol allowing for at will fabrication of pre-designed DB structures. Their morphological characterization is performed with atomic resolution by means of LT STM. Furthermore, it is demonstrated that I(V) scanning tunneling spectroscopy (STS) characteristics of the fabricated nanostructures could give direct information about the spatial distribution of the density of states, which can be measured successfully with a lateral resolution reaching an individual dangling-bond. Deeper understanding of experimental observations is provided by ab-initio density functional theory (DFT) calculations. The STS results are compared with the transmission spectra, T(E), calculated using the elastic-scattering quantum-chemistry (ESQC) method. Based on the example of short DB wires we discuss the effect of through surface and through space electronic coupling between the created DBs, which results in narrowing of the surface band gap with increasing DB wire length.

What do we ‘see’ during Scanning probe measurements on Silver-Terminated Si(111)?: triskelions, trimers and tips

A Sweetman, A Stannard and P Moriarty

University of Nottingham, UK

The silver-terminated silicon surface, Ag-Si(111)-(√3x√3)R30 (Ag-√3) has been extensively investigated by scanning probe techniques. Although it is now accepted that the ground state of the surface is best described by the inequivalent trimer (IET) model, the contrast mechanism in SPM remains controversial due to the strong influence of the tip state in both STM [1] and NC-AFM [2-3]. In particular theoretical studies have failed to accurately reproduce the observed setpoint dependence (triskelions to trimers) in NC-AFM studies of Ag-√3 at room temperature [4].

By operating a Omicron qPlus NC-AFM/STM in constant frequency shift feedback and acquiring tunnel current simultaneously, we are able to unambiguously determine the origin of the features in NC-AFM by comparing the proposed STM and AFM contrast mechanisms. We show that both the Si-Ag bonds and Ag atoms are imaged depending on tip termination. We also demonstrate that NC-AFM successfully resolves the IET structure at low temperature, and uniquely, can determine the absolute chirality of the surface.

[1] H. M. Zhang et al Phys. Rev. B 74, 201304(R) (2006).
[2] K Yokoyama et al, Phys. Rev. Lett. 83 p. 5023 (1999).
[3] S Morita and Y Sugawara, Ultramicroscopy 91 p. 89 (2002).
[4] N Sasaki et al, Phys. Rev. Lett. 88 046106. (2002).

Formation of antimony induced clusters on the Si(111)7×7 surface

M Franz, S Appelfeller and M Dähne

Technische Universität Berlin, Germany

Self-assembled surface clusters are on the one hand very interesting because of their zero-dimensional properties, and on the other hand they are promising candidates for the application in future nanodevices or in catalysis. Here, the growth behavior as well as the atomic structure of antimony induced clusters on the Si(111)7×7 surface were studied using scanning tunneling microscopy (STM). The clusters were grown by deposition of submonolayer antimony coverages on substrates at temperatures between 200°C and 500°C. Depending on the growth conditions, different cluster structures were found. Generally we observed a substitution of adatoms of the Si(111)7×7 surface by antimony atoms. At low antimony coverage, this leads to the formation of pure silicon clusters, while at higher coverages, antimony containing clusters showing a ringlike appearance in empty state STM images form. These ringlike clusters show a strong preference of occupying the faulted half unit cells of the 7×7 reconstruction. By detailed analysis of the STM images it was found, that the apparent height of different ringlike clusters is varying. For these ringlike clusters we were able to develop an atomic structure model also explaining the variation in their apparent height with different antimony contents.

Modification of atomic and electronic structure of Si(111)5x2-Au surface by single In and Pb atoms

A Stępniak[1,3], M Krawiec[1], P Nita[2], G Zawadzki[1] and M Jałochowski[1]

[1]M. Curie-Skłodowska University, Poland, [2]IMDEA Nanociencia, Spain, [3]Max-Planck-Institut für Mikrostrukturphysik, Germany

Si(111)5×2-Au surface, which is one of various phases of the Au-induced reconstructions, is characterized by spontaneous formation of perfectly ordered, parallel aligned gold atomic chains. The resulting specific anisotropic morphology of the Si(111)5×2-Au reconstruction, and its quasi-one-dimensional electronic structure, may play a crucial role when used as a substrate for production and study of other one-dimensional nanostructures.

In this work we report on the Si(111)5×2-Au surface electronic band structure modification in a controllable fashion by doping with foreign atoms. An effect of adsorption of atoms of different valence, i.e., In and Pb atoms on the surface of Si(111)5×2-Au was studied by scanning tunneling microscopy and spectroscopy (STM/STS) methods. The dopant adatoms settle along the chains with a period equal to $4xa_0$ (where a_0 is the Si lattice constant along the chain). The STM images show that the In atoms adsorb in two almost equivalent sites[1],while Pb – in only one, the same as occupied by Si adatoms[2]. The STS investigations show that the local density of states (LDOS) over the protrusions change from almost symmetrical around the Fermi energy for the undoped Si(111)5×2-Au surface, to highly asymmetrical in the case of the surface with 0.025 ML of In and Pb atoms. The experimental data are compared with results of DFT calculations.

[1] A. Stępniak, P. Nita, M. Krawiec, M.Jałochowski, Phys. Rev. B 80, 125430 (2009).
[2] A. Stępniak, M. Krawiec, G. Zawadzki, M.Jałochowski, J. Phys.: Condens. Matter 24, 095002 (2012).

Direct observation of the electronic structure at the Gd_2O_3/GaAs (100) hetero-interface using scanning tunneling spectroscopy

Y-P Chiu[1], B-C Huang[1], M C Shih[1], J Y Shen[2], P Chang[2], C S Chang[3], M L Huang[2], M-H Tsai[1], M Hong[4] and J Kwo[2]

[1]NSYSU, Taiwan, [2]National Tsing Hua University, Taiwan, [3]Academia Sinica, Taiwain [4]NTU, Singapore

Direct measurements of atomic-scale electronic structure at nm-thick epitaxial Gd_2O_3 gate oxides on GaAshave been performed using cross-sectional scanning tunneling microscopy and spectroscopy. The epitaxial growth of a Gd_2O_3 dielectric film on GaAs(100) has successfully unpinned the Fermi level, and demonstrated the first GaAs metal-oxide semiconductor field-effect transistor (MOSFET). The fundamental mechanism responsible for the striking result mainly occurred at the Gd_2O_3/GaAs interface. As motivated by the significance of this discovery, it is essential to conduct in-depth study to obtain precise structural and electronic information on these epitaxial films and interfaces. These epitaxially grown films are crystalline with low number of defects and interfacial states. Utilizing the capabilities of scanning tunneling microscopy (STM), we have probed the epitaxial interfacial structure of Gd_2O_3 in passivating GaAs. In addition, the local electronic properties with atomic insight are also determined in our present work.

Measuring chemical interactions with dynamic force microscopy on H:Si(100)

S Jarvis[1], P Sharp[1], R Woolley[1], A Sweetman[1], L Kantorovich[2] and P Moriarty[1]

[1]University of Nottingham, UK, [2]King's College London, UK

The Si(100)[1] surface is a particularly attractive system for the study of single atom/molecule chemistry. When terminated with a passivating layer of hydrogen (Si(100):H), isolated chemically reactive sites can be fabricated by removing a single hydrogen atom allowing interactions to be studied within a unique environment. Particularly interesting information can be obtained via the technique of nc-AFM, which allows the forces and energy of interaction to be measured between molecules and surfaces. Although well studied in STM, thus far only a single nc-AFM image of the Si(100):H surface has been published[2].

We will discuss a nc-AFM study of the Si(100):H surface[3] which elucidates the different force interactions responsible for image contrast. In particular, we observe an inverted imaging contrast thought to originate from atomically repulsive force interactions. Force-distance spectroscopy will also be presented and compared with the results of density functional theory simulations. From these comparisons we provide key insights into the characterisation of the tip-sample system, which may have important consequences for molecular imaging as well as for the fabrication of single chemically reactive sites.

[1] Sweetman et al. Phys.Rev.Lett. 106 (2011) 136101.
[2] Yokoyama et al. Jpn. J. Appl. Phys. 39 (2000) L113.
[3] Sharp et al. Appl. Phys. Lett. (In submission).

Nanostructures 2

Imaging fractional incompressible stripes in integer quantum Hall systems

S Heun[1], N Paradiso[1], S Roddaro[1], G Biasiol[2], L Sorba[1], L N Pfeiffer[3], K W West[3] and F Beltram[1]

[1]NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Italy, [2]Istituto Offcina dei Materiali CNR, Laboratorio TASC, Italy, [3]Department of Electrical Engineering, Princeton University, USA

Transport experiments provide conflicting evidence on the possible existence of fractional order within integer quantum Hall systems. In fact, integer edge states sometimes behave as monolithic objects with no inner structure [1,2], while other experiments clearly highlight the role of fractional substructures [3,4]. Recently developed low–temperature scanning probe techniques offer today an opportunity for a deeper–than–ever investigation of spatial features of such edge systems. Here we use scanning gate microscopy (SGM) and demonstrate that fractional features were unambiguously observed in *every* integer quantum Hall constriction studied. The configuration of our samples is similar to that described in [5]. Experiments were performed at bulk filling factor nu=1. We brought two counter–propagating integer–edge channels into proximity by means of a quantum point contact (QPC) and used the biased SGM tip to tune backscattering. Plateaus are observed in source–drain differential conductance maps whenever the tip induces an incompressible phase at the QPC center. We present SGM maps which directly reveal the width of the most relevant fractional incompressible stripes, corresponding to filling factors 1/3 and 2/5, together with their particle–hole conjugates 2/3 and 3/5. Our results compare well with predictions of the edge–reconstruction theory [6] and may open up exciting developments. For instance, the ability to partition an integer edge and partially transmit one of its fractional components may be the key for the implementation of fractional quasi-particle Mach-Zehnder interferometers.

[1] Y. Ji, Y. Chung, D. Sprinzak, M. Heiblum, D. Mahalu, and H. Shtrikman, Nature 422, 585 (2003).
[2] C. Altimiras, H. le Sueur, U. Gennser, A. Cavanna, D. Mailly, and F. Pierre, Nature Phys. 6, 34 (2009).
[3] L. P. Kouwenhoven, B. J. van Wees, N. C. van der Vaart, C. J. P. M. Harmans, C. E. Timmering, and C. T. Foxon, Phys. Rev. Lett. 64, 685 (1990).
[4] S. Roddaro, N. Paradiso, V. Pellegrini, G. Biasiol, L. Sorba, and F. Beltram, Phys. Rev. Lett. 103, 016802 (2009).
[5] N. Paradiso, S. Heun, S. Roddaro, L. N. Pfeiffer, K. W. West, L. Sorba, G. Biasiol, and F. Beltram, Physica E 42, 1038 (2010).
[6] D. B. Chklovskii, B. I. Shklovskii, and L. I. Glazman, Phys. Rev. B 46, 4026 (1992).

Interrelation between charge transport and structural properties of printed metal oxide semiconductors

M Haeming[1], D Walker[2], A Issanin[2], A Klyszcz[1], H von Seggern[2], W Jaegermann[2] and Kl Bonrad[1]

[1]Merck-TUD-Lab for Printed Inorganic Electronics, Germany, [2]TU Darmstadt, Germany

The vision of printing transparent electronic circuits on flexible substrates which outperform a-Si electronics has been driving research on printed metal oxide electronics considerably. We studied systematically the interrelation between the charge carrier mobility μ in printed metal oxide semiconductor field effect transistors (MOSFETs) from In/Zn oximate precursor solutions and the growth of semiconducting Indium-Zinc-Oxide (IZO) thin films. We observed a strong dependence of the carrier mobility μ on the concentration of the precursor solution and the number of deposited layers whereas the total thickness of the IZO film is similar. Further investigations of the film growth with scanning electron microscopy (SEM), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) indicate that the increase in mobility μ is directly related to small but significant changes in morphology of the amorphous IZO thin film.

Moreover, we show that the observed structural differences lead to more than one order of magnitude increase in mobility, in particular from 1 to 15 cm^2/Vs. This demonstrates that a comprehensive and detailed understanding of the interface interaction and the growth mechanism of thin metal oxide films from precursor solutions is crucial for further studies and the development of printed electronics in general, even in case of amorphous thin films. Furthermore, our investigation shows that printed IZO based MOSFETs can yield a significantly higher charge carrier mobility μ than comparable a-Si FETs.

Magneto-electrostatic manipulation of the Josephson current in proximized InGaAs/InAlAs 2DEG quantum rings

M Amado[1], A Fornieri[2], F Carillo[3], L Sorba[3], G Biasiol[4] and F Giazotto[3]

[1]NEST, Istituto Nanoscienze-CNR, Italy, [2]NEST Istituto Nanoscienze. CNR & Università di Pisa, Italy [3]NEST-CNR & Scuola Normale Superiore, Italy, [4]Laboratorio Nazionale TASC INFM-CNR , Italy

Semiconductor quantum rings (QRs) have been proposed as promising structures to study mesoscopic effects such as electron entanglement and electron-phase modulation under the application of an external magneto-electrostatic field. In this work we study the interplay between the electro-magnetostatic Aharonov-Bohm (AB) effect and Andreev reflection in ballistic semiconductor rings coupled to two superconducting leads at miliKelvin temperature.

Superconducting-quantum ring-superconducting (S-QR-S) junctions consist of two Nb leads deposited by sputtering that serve as source-drain and voltage probes and an InGaAs/InAlAs semiconductor two dimensional electron gas (2DEG) tailored by electron beam lithography into a QR geometry. The latter presents a diameter of a micron and is laterally defined by etched side walls. There are also present additional semiconducting in-plane side gates in the system, tailored by reactive ion etching as well, few hundred nms from the ring.

We shall show the temperature evolution of the Josephson current existing in the proximized InGaAs/InAlAs 2DEG and how either the electric, the magnetostatic or a combination of both effects serve us to tune the transmissivity of the QR, and hence to control the magnitude of the supercurrent flowing through the proximized region. Thanks to magneto-electrostatic control of transmissivity such S-QR-S junction is the first step toward electron entanglement and the generation of a controllable Josephson π-junction through an AB interferometer.

Persistent current in a nanoring made of band insulator studied by means of a two-level lattice model

M Moško, J Tobik and A Mošková

Institute of Electrical Engineering, Slovak Academy of Sciences, Slovakia

Persistent current in a conducting ring pierced by magnetic flux is a well known phenomenon. It was predicted theoretically and also measured in superconducting rings as well as in mesoscopic normal metal rings. In a ballistic normal metal ring, the amplitude of the persistent current decays like 1/L, where L is the ring circumference [1]. It has been proposed previously that persistent currents of measurable size can exist also in nanorings made of band insulators [2,3]. In this work, persistent currents in nanorings made of band insulators are analyzed by considering a ring-shaped lattice described by a nearest-neighbor tight-binding model with two levels per lattice site.

These two levels can give rise to two non-crossing electronic energy bands. We leave the upper band empty and fill the lower band completely, thus emulating the band-gap insulator. The persistent current in the ring is obtained by summing all single-electron currents in the fully-filled band. We find that the amplitude of the current decays exponentially with L and we express the decay rate by means of the tight binding parameters.This provides us with a tool for estimating the decay rate in nanorings made of real band insulators. According to our estimates, InAs seems to be a good candidate for experimental demonstration of persistent current of measurable size.

[1] Y. Imry, Introduction to Mesoscopic Physics, (Oxford University Press, Oxford, UK, 2002).
[2] A. Moskova, M. Mosko, and A. Gendiar, Physica E, 1991 (2008).
[3] A. Moskova, M. Mosko, and J. Tobik, arXiv:1001.0496v2.

Carbon nanotube quantum dot transport with spin-orbital coupling and interacting leads

O Ogloblya and G Kuznyetsova

Kyiv National Schevchenko University, Ukraine

The investigations of transport properties of nanotube QDs interacting with contact leads was carried out in this work. We analyzed the effects of a spin voltage as well as a conventionally applied voltage in a QD system with a different number of quantum states in the dot region in the presence of a Coulombic interaction between the quantum dot and two leads. The transport is described within the framework of the Keldysh NEGF framework. We extended the NEGF treatment developed for noninteracting leads onto the case of four quantum states $m = \{\sigma, \lambda\} = \{\pm, \pm\}$ (which is the case for a nanotube QD) interacting with leads. Here $\sigma = \pm$ is the spin and $\lambda = \pm$ is the orbital quantum number which accounts for the existence of an additional orbital degree of freedom in nanotubes. Each electronic state in a QD was assigned an energy of $\varepsilon_m = \varepsilon_0 - \sigma\lambda\Delta_{SO} / 2$. Our derivation is based on the equation-of-motion technique and Langreth's theorem. For a Coulombic repulsion between the contacts and QD we obtain an expression for the current through QD for the four quantum states $m = \{\sigma, \lambda\} = \{\pm, \pm\}$. We calculated the density of electronic states with spin up and down for the case of a single QD without pseudospin states for an infinite Coulomb repulsion, in good agreement with the calculations of Yuan Li, et al. [1]. Our calculation show that the position of the conductance peaks nearest to zero is not affected by the strength of the QD-lead Coulombic interaction parameters. We also demonstrated that this interaction shifts the density of states into the region of higher energies. The interplay between the Kondo effect and the bias is highly temperature-dependent and becomes significant only at low temperatures. Lastly, we found that the existence of four quantum states $m = \{\sigma, \lambda\} = \{\pm, \pm\}$ leads to abrupt changes in the density of states. In this case the values of the current are approximately ten times lower than for QD with only two quantum states $m = \{\sigma\} = \{\pm\}$. However, in the case of a conventional bias the current amplitudes in both cases are approximately the same.

[1] Li Yuan, M.B.A. Jalil, S.G. Tan, "Nonequilibrium Keldysh Formalism for Interacting Leads - Application to Quantum Dot Transport Driven by Spin Bias", *arXiv:1103.4920*, 2011.

(invited) Energy relaxation along the quantum Hall edge channels

F Pierre, C Altimiras, H le Sueur, A Anthore, U Gennser, A Cavanna and D Mailly

CNRS, France

In 1D conductors interactions are enhanced by the confinement, which can have spectacular consequences such as the separation of the spin and charge degrees of freedom. A prototypal ballistic 1D conductors is realized by the edge channels of the integer quantum Hall regime, along which the current propagate without dissipation. However, interactions effects are usually hidden by the robustness of Hall currents. It is only in novel electron quantum optics experiments using edge states (see e.g. the pioneer work [1]) that striking phenomena were attributed to the presence of interactions.

In order to probe interactions, we have driven an edge channel out-of-equilibrium and observed its relaxation toward equilibrium. The energy relaxation is characterized precisely by measuring the energy distribution f(E) of the electronic edge states. This can be done using the discrete electronic levels in a quantum dot as energy filters [2]. We then monitored the deformation of f(E) along the edge path, which results from the energy exchanges taking place. This provides information on the inelastic mechanisms and also on the nature of the electronic edge states.

The experiment was performed at filling factor two, where two adjacent channels propagate along the edge [3]. Whereas there are no discernable energy transfers towards thermalized states, we find an efficient energy redistribution between the two channels, without particle exchanges. The observed short energy relaxation length challenges the usual description of quantum Hall excitations as quasiparticles localized in one edge channel [3,4]. Yet, we found that it is possible to efficiently freeze the energy exchanges rate, and thereby to increase the quantum coherence length, with adequate geometries [5].

[1] Y. Ji et al., Nature 422, 415 (2003).
[2] C. Altimiras et al., Nature phys. 6, 34 (2010).
[3] H. le Sueur et al., Phys. Rev. Lett. 105, 056803 (2010).
[4] P. Degiovanni et al. Phys. Rev. B 81, 121302(R) (2010).
[5] C. Altimiras et al., Phys. Rev. Lett. 105, 226804 (2010).

Transport in inhomogeneous quantum wires

N Sedlmayr[1], J Ohst[1], I Affleck[2], J Sirker[1] and S Eggert[1]

[1]University of Kaiserslautern, Germany, [2]The University of British Columbia, Canada

We consider interacting quantum wires with inhomogeneities in the form of sudden changes in interaction strength and/or velocity. Such a setup is the minimal model for transport through semiconductor wires or carbon nanotubes that are connected to leads. We show that a sudden change, contrary to the well-studied case of an adiabatic change, can be described by effectively local perturbing operators and causes a renormalization of the backscattering with exponents depending on the interaction constants on both sides of the inhomogeneity. The results are relevant for the analysis of the one-dimensional conductance which is characterized by unusual powerlaw exponents in the temperature dependence, if the scattering takes place predominantly in the junctions from lead to wire. The theory is in very good agreement with numerical simulations which can also be used to estimate the size of the effective backscattering. We are able to identify a perfectly conducting fixed point also for large changes, which in the considered model corresponds to a velocity matching condition.

Reduced tunnel-barrier height in Sub-10 nm Au nanoelectrodes

K Curtis and C Ford

University of Cambridge, UK

The electrical study of individual nanocrystals or molecules requires a technique to reproducibly create metallic electrodes with nanoscale separation. This paper presents the development of a selective-etch fabrication process to create vertical sub-10 nanometre metallic gaps and the subsequent characterisation of the gaps by scanning electron microscopy as well as electrical measurements at low temperature.

Before the electrodes are used to study the electrical characteristics of nanocrystals or molecules, the behaviour of the empty gaps must be examined. The *I-V* characteristics of the empty gaps showed a marked reduction of the tunnel barrier height (φ) from the expected value (~5.1 eV, the work function of Au) when the results were fitted to the Simmons tunnelling model for a metal-insulator-metal system. [1] Results indicate that after the barrier height is surpassed, a transition from direct to field-effect (Fowler-Nordheim) tunnelling occurs. The roles of the image potential and surface contamination are discussed.

[1] John G. Simmons J. Appl. Phys 1963, 34, 1793-1803.

Aharonov-Bohm-type oscillations in GaAs/InAs core-shell nanowires

H Lüth, Ö Gül, C Blömers, T Rieger, M I Lepsa, N Demarina, D Grützmacher and T Schäpers

Research Centre Jülich, Germany

For a future low-power nanoelectronics phase-based devices might be of interest. In these devices electron interferences are used for the switching function. Aharonov-Bohm interferences offer interesting prospects for the realisation of such elements. For the study of these electron interferences GaAs/InAs core-shell nanowires are ideally suited. In these structures a well conducting InAs cylinder-like shell covers a highly resistive GaAs core. The shell allows electron transport between two axially arranged contacts with closed loop trajectories around the inner core.

The nanowires were grown in MBE via a self-catalyzed process on GaAs (111)B substrates. For the measurements the as-grown nanowires were harvested from the GaAs substrate and transferred to an n-doped Si (100) substrate covered with a 200 nm thick SiO_2 layer. This layer stack is used as a back gate to vary the carrier density. Ohmic Ti/Au contacts were prepared by electron beam lithography.

Magneto-transport measurements were performed at low temperature with magnetic fields parallel to the wire axis. As a function of the magnetic field periodic Aharonov-Bohm-type oscillations of the conductance with the periodicity of the magnetic flux quantum are observed. As a function of gate voltage the signal exhibits reproducible universal conductance fluctuations. Their correlation length increases with decreasing wire length.

The effects are interpreted in terms of conduction through coherent angular momentum states within the conducting shell cylinder. During their propagation along the wire randomly shaped closed trajectory loops between elastic scattering centres give rise to universal conductance fluctuations as a function of gate voltage.

Oxides and oxide surfaces 2

Dynamic stabilisation of polar oxide growth: the case of MgO(111)

P Hasnip and V Lazarov

The University of York, UK

Intrinsic polar materials are some of the most commonly used materials in electronic, magnetic and chemical applications yet their growth remains challenging. Along the polar direction, these materials consist of oppositely charged ionic planes and this polarity dominates the growth process. Attempts to grow polar oxides in their polar direction often result in surface reconstructions, metallisation or faceting as the system attempts to remove the polarity and prevent a divergent electrostatic dipole.

By using MgO(111) as a model system for polar oxide film growth, we show by ab initio calculations that H can act as a surfactant, stabilising the growth dynamically without disrupting the growth or becoming trapped in the film. The continuous presence of H during the growth of a MgO(111) film efficiently removes the microscopic dipole moment, thus enabling the growth of perfect fcc-ordered MgO(111) films. These theoretical predictions are confirmed experimentally by molecular beam epitaxy single crystal growth of MgO(111) on SiC(0001).

Surface and Interface structure of polar MgO(111) thin films on SiC(0001)

V Lazarov[1], P Hasnip[1], K Ziemer[2] and Z Cai[2]

[1]The University of York, UK, [3]Northeastern University

MgO(111) is a polar oxide surface that has been extensively used as a model surface in order to understand the unique physics of stabilisation mechanisms that take place due to the strong surface polarity. Recent advances in oxide growth provide an opportunity to create atomically sharp polar surfaces and interfaces of polar oxide/oxide and polar oxide/polar semiconductor materials. In this work we present a joint experimental and theoretical study of the MgO(111) surface and MgO(111)/SiC(0001) interface of MgO thin films grown by molecular beam epitaxy on a reconstructed SiC(0001) (R3xR3)R30° surface. Structural surface, interface and film characterisation was done by Reflection High Energy Electron Diffraction, Scanning and Transmission Electron Microscopy ((S)TEM)), X-ray Photoelectron Spectroscopy, and the modelling was done by Density Functional Theory. Aberration corrected (S)TEM shows that the SiC reconstruction is lost during the growth, and that atomic interface structure is determined by Si-Mg bonds with Mg sitting in the tetrahedral T4 site. This interface structure promotes growth of the MgO(111) film that is twinned with respect to the underlying 6h SiC structure. Due to the high surface energy of O-terminated MgO(111), films less than one unit cell thick have a graphitic like structure with a Mg-O (0001) type surface. The film and surface gradually transform above one unit cell to a layered cubic structure with a (111) type of surface. Finally we discuss the role of H for the film surfaces and film structure both below and above one unit cell of thickness.

Tuning the film orientation of CoO/Ir(100) by interface chemistry

F Mittendorfer[1], M Gubo[2], C Ebersperger[2], L Hammer[2], K Heinz[2] and J Redinger[1]

[1]TU Vienna, Austria, [2]University Erlangen, Germany

The crystallographic orientation of a thin oxide film can play a crucial role for the electronic properties and the catalytic activity of the surface. It is commonly assumed that the orientation of an epitaxial film is determined by the surface stress resulting from the deformation of the film.

In this contribution, I present a systematic study of the growth of CoO films on Ir(100) on the basis of density functional theory (DFT) calculations, combined with scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) experiments.We find that the CoO films grow in an (111) orientation on the bare Ir(100) surface, but the orientation can be switched to (100) when an additional Co layer is introduced at the interface between the metal and the oxide film.

With the help of the DFT calculations, we show that this observation is closely related to the formation of a Co3O4 precursor structure, which is only formed at the Co modified Ir interface. This precursor structure is not stabilized by the surface stress, but rather by an enhanced chemical interaction with the substrate. Consequently, the chemical composition of an interface can be used to determine the orientation of an epitaxial film.

Oxidation pathways in ultrathin iron oxide films

J de la Figuera[1], M Monti[1], B Santos[2], A Mascaraque[3], O R de la Fuente[3], T O Mentes[2], A Locatelli[2], K F McCarty[4] and J F Marco[1]

[1]Instituto de Química-Física, Spain, [2]Sincrotrone Trieste S.C.p.A, Italy, [3]Universidad Complutense de Madrid, Spain, [4]Sandia National Laboratories, USA

Binary iron oxides present a range of properties interesting in applications, such as from reasonable conductors to insulators, and from ferrimagnets to antiferromagnets. They differ from one another either in structure (for example, γ-Fe_2O_3 vs α-Fe_2O_3) or composition (Fe_3O_4 vs γ-Fe_2O_3), or both. These differences influence the kind of transformations that take place while reducing or oxidizing them. The study of their transformations, as well as the influence of external parameters on the observed changes is a long standing theme in iron oxide research, with implications in fields as diverse as corrosion, geophysics, catalysis and spintronics.

In the present work we aim at understanding the oxidation mechanisms of iron oxide thin films. The use of thin films allows to limit the amount of iron available. We first grow films on Ru(0001) by O_2-assisted molecular beam epitaxy. Under appropriate conditions either FeO, magnetite or both phases are obtained [1, 2]. By exposing the films to NO_2 at low temperature, the films keep their morphology. We use scanning tunneling microscopy, X-ray photoemission spectroscopy, photoemission microscopy and low-energy electron microscopy to follow the transformation and determine that magnetite is transformed into γ-Fe_2O_3 (maghemite) while FeO is converted to an α-Fe_2O_3-like oxide (hematite). We explain the different oxidation pathways of the thin film oxides by topotactic transformations occurring by the diffusion of iron in octahedral sites to react with oxygen on the film surface.

[1] B. Santos, E. Loginova, A. Mascaraque, A. Schmid, K. F. McCarty and J. de la Figuera, ”Structure and Magnetism in Ultrathin Iron Oxides Characterized by Low Energy Electron Microscopy”, J. Phys.Cond. Mat. 21, 314011 (2009).

[2] M. Monti, B. Santos, A. Mascaraque, O. Rodrıguez de la Fuente, M. A. Niño, T. O. Mentes, A. Locatelli, K. F. McCarty, J. F. Marco and J. de la Figuera, ”Magnetism in Nanometer-Thick Magnetite”, Phys. Rev. B 85, 020404 (2012).

Chromium oxide single layer on Fe(100)

A Picone[1], A Calloni[1], M Riva[1], G Bussetti[1], A Brambilla[1], G Fratesi[2], M I Trioni[3], L Duò[1], F Ciccacci[1], M Finazzi[1]

[1]Politecnico di Milano, Italy, [2]Università Milano Bicocca, Italy, [3]CNR, National Research Council, ISTM, Italy

Low-dimensional oxide nanostructures, supported on well-defined metal surfaces, have been the subject of intensive study because of their relevance both in fundamental physics and in technological applications [1,2]. The ultimate limit of an ultrathin oxide film is a two-dimensional (2-D) oxide monolayer on a metal substrate, consisting of only one unit cell in thickness. However, if the growth of oxide ultra-thin layers is performed on an iron substrates in a background pressure of oxygen (the so-called reactive deposition) the iron oxidation prevents the formation of a sharp interface [3].

In this oral, we show that a sharp interface between a single layer of chromium oxide and the Fe(001) surface can be obtained by growing the Cr on the pre-oxidized Fe(001)-p(1x1)O. Two chromium oxide phases have been detected at different Cr coverages, by using scanning tunnelling microscopy (STM) and low-energy electron diffraction (LEED) techniques. The experimental data are discussed in the light of ab-initio simulations of the electronic, energetic, and geometric properties of the growing film. Our findings demonstrate a potential to fabricate a sharp interface between the iron and transition metal oxides.

[1] F. P., Netzer, F. Allegretti, S. Surnev, J. Vac. Sci.Technol. B 28, 3268503 (2010).
[2] G. Pacchioni and S. Valeri, Oxide Ultrathin Films (WILEY-VCH, Germany, 2012).
[3] M. Finazzi, A. Brambilla, L. Duò, G. Ghiringhelli, M. Portalupi, F. Ciccacci, Phys. Rev. B 70, 235420 (2004).

(invited) Room temperature magnetoelectricity by interface coupling of oxides

J Driscoll, T Fix, E M Choi, A Kursumovic and O J Lee

University of Cambridge, UK

There is much interest in interface coupling the properties of two individual materials systems to create novel emergent properties. Here we study coupling of ferroelectric and ferromagnetic oxides in thin films grown either as multilayers or in self-assembled heteroepitaxial nanocomposite form. In such systems, strain, charge or exchange mediated coupling are all possible functions for achieving magnetoelectricity at room temperature. In this talk we discuss novel optimum materials selection possibilities as well as the nanostructural design which ultimately gives rise to a practical room temperature magnetoelectric.

Preparation strategies for rare earth oxide thin films

A Schaefer[1], S Röhe[1], J Jhang[1], S Lamberti[1], S Gevers[2], W Cartas[3], D Ragazzon[4], A Sandell[4], J Wollschläger[2], J Weaver[3] and M Bäumer[1]

[1]University of Bremen, Germany, [2]University of Osnabrück, Germany, [3]University of Florida, USA, [4]University of Uppsala, Sweden

The oxides of the lanthanides have potentially versatile applications in heterogeneous catalysis. Their versatility is based on the ease of valency changes of rare earth metals (change of f-electron configuration) as compared to, e.g., that of d-block elements. In particular, the possible dioxides in the rare earth oxide (REO) series (ceria, praseodymia and terbia) are highly interesting materials for oxidation catalysis due to their ability to easily give off oxygen and switch to different oxidation states. As lattice oxygen participates directly in the molecule-surface reactions, the selectivity of REO catalysts in oxidation chemistry depends strongly on their oxygen storage/release capabilities. The oxide of samarium for instance, which only forms the sesquioxide Sm_2O_3, seems to be the most effective REO catalyst for partial (selective) oxidation of methane.

Apart from considerable progress in the study of ceria films on metal substrates that has been made, surface science studies of REO films other than ceria are fairly limited. In this context we will present different preparation strategies for epitaxial thin films of various REOs including new routes for adjusting their oxidation state. By means of plasma treatment, e.g., we achieved to obtain even the dioxide of praseodymium (PrO_2), a complex oxide which had not been available for UHV studies up to now. In combination with temperature-programmed desorption of oxygen a whole range of different oxidation states from PrO_2 to Pr_2O_3 can be adjusted and made accessible for model studies. We will further present a more classical approach toward the growth of samaria and terbia on metal substrates by physical vapor deposition, and as an alternative, a facile approach of employing chemical vapor deposition in UHV for REO growth on metal substrates.

The chemical state of the thin films was characterized by photoemission spectroscopy, film structure and morphology were investigated by scanning tunneling microscopy, electron diffraction, and synchrotron radiation-based x-ray diffraction. In combination with studies on surface reactivity performed by adsorbing carbon monoxide and methanol on stepwise reduced surfaces, we can draw clear conclusions on structure-reactivity correlations.

Interfactant-mediated growth of rare-earth oxides on silicon

B Kaemena[1], J I Flege[1], S Gevers[2], J Höcker[1], F Bertram[3], T Schmidt[1], J Wollschläger[2] and J Falta[1]

[1]University of Bremen, Germany [2]University of Osnabrück, Germany, [3]Hamburger Synchrotronstrahlungslabor am Deutschen Elektronensynchrotron, Germany

The growth of high-quality, epitaxial thin oxide films on silicon is a long-standing goal in semiconductor technology. Among other multiple possible applications, rare-earth (RE) oxides are some of the most promising candidates for the realization of "high-k" dielectrics due to their predicted high thermodynamic stability and their almost vanishing lattice mismatch to silicon. However, growth of high-quality ultrathin films has so far been considerably impeded by RE-promoted Si oxidation at the interface, resulting in subsequent silicate and silicon oxide formation. In this contribution, we present an extensive study of epitaxial ceria [1], praseodymia [2] and lanthana films grown on Cl-passivated Si(111) by molecular beam epitaxy.

Truly ultrathin films of a few monolayer thickness were characterized by X-ray photoemission and X-ray standing waves (XSW) using Ce-L_α fluorescence and RE-3d photoelectrons as secondary signal. In all circumstances, the XSW results confirm the improved RE-oxide film quality obtained by Cl preadsorption. Furthermore, the atomic structure and chemical composition of the interface were inferred from chemically-sensitive XSW measurements employing O1s photoelectrons, which allow to separately investigate the atomic structure of the different oxygen species in the interface region. Moreover, monitoring the Cl binding sites with XSW enabled us to draw conclusions on its role in the growth process. Finally, few nanometer thin ceria films were characterized by grazing-incidence X-ray diffraction regarding morphology and interface structure.

[1] J.I. Flege et al., Phys. Rev. B 84, 235418 (2011).
[2] S. Gevers et al., Appl. Phys. Lett. 97, 242901 (2010).

Atomically-resolved stages in the growth of RuO_2(110) epitaxial layers on Ru(0001)

H Over[1], B Herd[1], D Langsdorf[1], J Goritzka[1], A Fraks[1] and O Balmes[2]

[1]Justus Liebig University, Germany, [2]ESRF Grenoble, France

During the past decade the application of Ru-based catalysts has come to play an increasingly important role in chemical industry. The identification of RuO_2 as a stable and efficient oxidation catalyst for HCl oxidation in the Sumitomo-process[1] or in the CO oxidation[2] show the necessity to investigate this system at the atomic scale. The model for this catalyst, a RuO_2 epitaxiallayer on a Ru(0001) single crystal is a well investigated example of a late transition metal oxide. Despite the intense experimental and theoretical work, the oxidation mechanism of Ru to RuO_2 at atomic scale has not yet been properly addressed. In this work we investigate with STM and SXRD the initial oxidation of Ru(0001). For the preparation of the surface oxide the crystal was exposed to molecular oxygen at preset pressure and temperature. STM images show that the oxidation mechanism proceeds via a nucleation and growth mechanism. In the oxide formation small clusters could be identified as nuclei which grow in a first step at the step edges of the Ru-surface. If the cluster has reached a critical size, the oxide begins to grow epitaxially as atomically flat patches out of the clusters. The reduction of the small oxide islands upon CO exposure gives additional information about the structure of the oxide layers and shows that they penetrate exactly one metal layer deep into the Ru(0001) terraces. SXRD measurements indicate that for the nucleation process a critical oxygen pressure is necessary, under which no oxide islands can be formed. Once the oxide islands were formed, their growth becomes independent from the applied oxygen pressure. The size of the oxide islands can be controlled by the experimental conditions (preparation time or the oxygen pressure). Both in the STM and SXRD oxidation experiments the results (induction time, growth) are exactly reproducible.

[1] Iwanaga, K., Seki, K., Hibi, T., Issoh, K., Suzuta, T., Nakada, M., Mori, Y., Abe, T., Kagaku, 2004, I, 1.
[2] Kim, Y.D., Over, H., Krabbes, G., Ertl, G., Top. Catal., 2001, 14, 95.

Tuesday 4 September

Organic layers and polymers 3

Highly ordered self-assembled monolayers of oligophenylene carboxylic acids on silver

H Aitchison[1], H Hamoudi[2], M Zharnikov[3] and M Buck[1]

[1]University of St Andrews, UK, [2]MANA, NIMS, Japan, [3]Universität Heidelberg, Germany

Metal-organic coordination chemistry can be exploited in different ways for the self-assembly of molecules at surfaces as illustrated by two-dimensional metal coordination networks [1], the layer by layer growth of metal-organic frameworks [2] or the formation of self-assembled monolayers (SAMs) [3]. With regard to the latter, aliphatic carboxylic acids have been studied to some extent [3] whereas reports on aromatic systems are very scarce [4].

We present our microscopic and spectroscopic studies of biphenyl and terphenyl mono and 4,4'/4,4''-dicarboxylic acid SAMs formed on a Ag surface by solution based processing. Au films on mica modified by an underpotential deposited Ag bilayer serve as substrates. Near edge X-ray absorption fine structure spectroscopy (NEXAFS) and X-ray photoelectron spectroscopy (XPS) reveal that in all cases well ordered SAMs are formed with molecules standing normal to the surface and being anchored to the substrate by a carboxylate group. Scanning tunneling microscopy (STM) confirms the formation of highly crystalline layers with a dense molecular packing.

The upright orientation, crystallinity and the possibility of functionalisation (e.g. by COOH) make these oligophenylene SAMs an interesting platform for building metal-organic coordination structures into the third dimension.

[1] J. V. Barth, Surf. Sci. 603, 1533 (2009).
[2] O. Shekhah, J. Liu, R. A. Fischer, C. Wöll, Chem. Soc. Rev. 40, 1081 (2011).
[3] S. Jadhav, Centr. Eur. J. Chem. 9, 369 (2011).
[4] C. Shen, I. Cebula, C. Brown, J. Zhao, M. Zharnikov, M. Buck, Chem. Sci, doi: 10.1039/C2SC20087B (2012).

Temperature induced structural phase transitions in a two-dimensional self-assembled network

M Blunt[1], J Adisoejoso[1], W Rżysko[2], P Szabelski[2], K K Tahara[3], Y Tobe[3] and S De Feyter[1]

[1]University of Leuven, Belgium, [2]Maria-Curie Skłodowska University, Poland, [3]Osaka University, Japan

Two-dimensional (2D) self-assembly at solid-liquid interfaces can produce a wide array of molecular networks ranging from closely packed to porous structures. Self-assembly under these conditions is a complex process which depends delicately on the strength of interactions between the different components of the system; network molecules, solvent molecules and the substrate. Environmental conditions such as the concentration of network molecules in solution and temperature[1,2] also play a pivotal role. We report a set of scanning tunnelling microscopy (STM) experiments which study the temperature dependence for the self-assembly for hexadehydrotribenzo[12]annulene (DBA) derivatives at the interface between graphite and organic solvents. Previous work has shown that DBA switches between two different network arrangements by controlling the concentration[2] with lower concentrations favouring a porous structure. We show that a similar reversible transition between the same two structures can also be achieved by varying the temperature, with the porous network favoured at higher temperatures. By measuring the temperature for the transition at different concentrations and applying this data to a thermodynamic model for the transition we derive values associated with the change in enthalpy and entropy when DBA molecules adsorb from solution. These experimental values are then compared to theoretically calculated estimates.

[1] S. Lei, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe, S. De Feyter, Angew. Chem. 2008, 120, 3006-3010.
[2] A. Bellec, C. Arrigoni, G. Schull, L. Douillard, C. Fiorini-Debuisschert, F. Mathevet, D. Kreher, A. J. Attias, F. Charra, J. Chem. Phys., 2011, 13.

Charge transfer at metal-organic interfaces as a means to steer supramolecular self-assembly

G Costantini[1], A Della Pia[1], M Riello[2], D Stassen[3], A Floris[2], D Bonifazi[3] and A De Vita[2]

[1]University of Warwick, UK, [2]King's College London, UK, [3]Universite de Namur, Belgium

Surface engineering through molecular adsorption is emerging as one of the most powerful technologies for the fabrication of advanced nanostructured materials. The real limiting factor for the development and practical use of this technology is the restricted ability to characterise and to control molecular adsorption and organisation. In particular, control over molecular assembly must be extended to length scales where it can be integrated with traditional “top down” nanofabrication techniques.

In this talk the use of long-range interactions generated by charge transfer at metal-organic interfaces will be demonstrated as a novel method for regulating 2D molecular assembly. Specifically designed donor molecules were deposited at various coverages on different metallic substrates and characterised by low temperature scanning tunnelling microscopy (STM). The resulting supramolecular assemblies were analysed by comparing the experimental data with density functional theory (DFT) calculations. Energy level alignment at the metal-organic interface and substrate polarisability appear to regulate the interfacial charge transfer and therefore the development of induced dipoles. These have a profound influence on the supramolecular assembly which is further rationalised by Monte Carlo simulations taking into account the competition between Van der Waals attraction and electrostatic repulsion among the adsorbed molecules. A coherent picture emerges where long-range forces between charged molecules drive the spontaneous formation of a novel classes of supramolecular structures. Conversely, these can be used to obtain crucial information on the electronic properties of metal-organic interfaces.

Chiral induction processes at the liquid-solid interface

S De Feyter

University of Leuven, Belgium

Controlling and inducing two-dimensional (2D) chirality in molecular self-assemblies on solid surfaces is a subject of intense interest. A prochiral molecule can become chiral when confined at a surface. It can self-assemble into mirror domains, while the entire monolayer still consists of an equal number of left- and right-handed molecules, and therefore, remains globally achiral. On the other hand, chiral information at the level of a single molecule can be transmitted into the supramolecular level to produce enantiomorphous monolayers belonging to one of the five chiral plane groups. Moreover, addition of a small amount of a chiral dopant to a molecular network of achiral molecules can change the ratio of left- and right-handed domains, even towards one extreme. This chiral perturbation is the 2D analogue of the so-called 'sergeants-and-soldiers' effect; the ability of a few chiral units (the sergeants) to control a large number of achiral units (the soldiers). The known 2D chiral amplification processes involve recognition of steric interactions between a chiral source and the molecules adjacent to it. Probing the 2D molecular organization on surfaces by scanning tunneling microscopy (STM) has made it possible to identify chirality aspects with submolecular resolution, also at the liquid/solid interface.

Here we discuss several examples of chiral induction in monolayer formation at the liquid-solid interface, based on the sergeant-and-soldier effect or the use of molecular chiral handles. We demonstrate the issue of surface-confined diastereomeric complex formation and enantioselective adsorption, stressing the importance of dynamics at the liquid-solid interface.[1,2,3]

[1] K. Tahara, H. Yamaga, E. Ghijsens, K. Inukai, J. Adisoejoso, M. O. Blunt, S. De Feyter, Y. Tobe, Nat. Chem. 2011, 3, 714-719.

[2] Z. Guo, I. De Cat, B. Van Averbeke, J. Lin, G. Wang, H. Xu, R. Lazzaroni, D. Beljonne, E. W. Meijer, A. P. H. J. Schenning, S. De Feyter, J. Am. Chem. Soc. 2011, 133, 17764–17771.

[3] I. De Cat, Z. Guo, S. J. George, E. W. Meijer, A. P. H. J. Schenning, S. De Feyter, J. Am. Chem. Soc. 2012, 134, 3171−3177.

(invited) Order and disorder in adsorbed molecular arrays

P Beton†

The University of Nottingham, UK

†Work performed in collaboration with M Blunt, A Stannard, M Wieland, J Russell, J Garrahan, N Champness, S Svatek, L Perdigao, A Saywell, J O'Shea, J Sprafke, D Kondratiuk and H Anderson.

The role of disorder in the formation of two-dimensional networks is currently attracting great interest and provides interesting connections between surface science and statistical mechanics. The properties of an entropy-stabilised supramolecular network will be reviewed. These networks map directly onto a rhombus tiling of the plane and support a random tiling phase which has been studied widely by theorists over several decades. The networks are analyzed by treating them as projections of the (111) surface of a simple cubic crystal and are characterized using the height correlations of this virtual surface. It is also shown that topological defects are supported within this array and that broken symmetries lead to phase transitions between ordered and disordered phases[1]. Growth of the networks, which are dynamically-arrested systems, will also be considered. The role of disorder in the formation of covalently bound molecular networks will also be presented including those formed on the surface, and also flexible porphyrin polymers and nanorings deposited using electrospray. For polymeric systems it is possible to define a 2D correlation length and we also discuss distortion, packing and stacking of flexible cyclic polymers.

[1] A. Stannard et.al., Nature Chem 4 112 (2012).

Self-assembly of borazine derivative molecules into 2D molecular networks

N Kalashnyk[1], S K de Meerendré[2], M Riello[3], A Floris[3], T Jones[1], A De Vita[3], D Bonifazi[2] and G Costantini[1]

[1]University of Warwick, UK, [2]University of Namur, Belgium, [3]King's College London, UK

In the last decade, hexagonal boron nitride (h-BN) films have proved to be chemically and thermally stable insulators with potential applications in organic electronics. Ultrahigh vacuum scanning tunnelling microscopy (UHV-STM) recently showed that depending on lattice mismatch and bonding strength between BN and the transition metal surface, the structures of h-BN formed from borazine $(HBNH)_3$ molecules vary from epitaxial monolayers, e.g. on Ni, Pt and Pd (111) surfaces, to more complicated nanomesh nanostructures, e.g. on Rh(111) and Ru(0001) substrates.

The present UHV-STM study focuses on the self-assembly of newly synthesized borazine derivatives in order to build layers stabilised by supramolecular interactions. The two molecules considered are BSK140 consisting of six hydrocarbon groups attached to a central borazine core; and its asymmetric modification, BSK224, where one of the hydrocarbon substituents is exchanged with a hydroxyl group.

We find that BSK140 molecules form highly ordered and widely extended 2D islands with a row tiling pattern on the Cu(111) surface. On the other hand, submonolayer coverages of BSK224 molecules form both regular and irregular small 2D islands on Cu(111). A statistical analysis of the broad island distribution establishes specific “magic” shapes and sizes occurring with a significantly higher frequency.

These results reflect the role of the van der Waals interaction in the formation of complex 2D ordered structures by BSK140 and BSK224 under high vacuum evaporation onto the Cu(111) surface. Furthermore, the physical and chemical properties of these molecules are likely to be preserved upon adsorption because of the lifting of the boron nitride cores from the surface driven by their bulky peripheral groups.

Self-assembly of molecular conformational switches studied by UHV-STM

A Nuermaimaiti, C Bombis, Y Ning, J Cramer, L Ferrighi, B Hammer, K Gothelf, F Besenbacher and T Linderoth

Aarhus University, Denmark

Molecular conformational flexibility is widely recognized to be important for molecular self-assembly, but relatively few studies have addressed this explicitly and systematically [1, 2]. Here, we focus on the degrees of freedom introduced by molecular conformational flexibility in a molecular system that displays a number of distinct conformational states after adsorption on the surface. For this purpose we have synthesized a class of rod-shape molecules that consist of two or three naphthalene (or isoquinoline) units connected by ethynylene spokes and functionalized by systematically varied terminal moieties, including bulky tert-butyl and hydrogen bonding carboxyl groups. Using high-resolution STM measurements to identify molecular conformations on the surface, we investigate adsorption structures formed by UHV thermal deposition on a range of metal surfaces. The adsorption structures are systematically compared focusing on molecular tiling patterns and the distribution of molecular conformations based on careful statistical analysis, allowing us to determine how the conformational degrees of freedom of the single molecules are manifested in the global structures and how intermolecular interactions may lead ordering/selection of molecular conformations. By optimizing the molecular structure, a lamella-type packing is achieved which is suitable for amplification of molecular conformational information. Differences in the distribution of molecular conformations between molecules individually adsorbed and embedded in the adsorption structures show that the growth of ordered structures involves dynamic conformational adaptation. Further investigation by DFT calculations and dynamic STM studies are being performed.

[1[Weigelt, S., et al. Nature Materials, 2006. 5(2): p.112-117.
[2] Matena, M., et al. Chemical Communications, 2009(24): p.3525-3527.

Control of discotic liquid crystals monolayer self-assemblies by molecular engineering

E Lacaze[1], P Sleczkowski[1], N Katsonis[2] and K Uchida[3]

[1]Institut des Nano-Sciences de Paris, France, [2]MESA+ Institute for Nanotechnology, The Netherlands, [3]Ryukoku University, Japan

Discotic molecules consist of rigid polyaromatic cores surrounded by flexible alkyl or alkoxy tails. In bulk, they form columnar mesophases, whith a strong overlapping between p-orbitals in a single column, enabling one-dimensional charge transport [1]. The study of the interfaces of these compounds with substrates is of interest, not only for the control of bulk electronic transport properties, but also because discotic molecules form a fascinating class of molecules which can provide self-assembly even if they are particularly large and complex. We use STM to study disc-like mesogens functionalized with photoswitchable azobenzene units [2].

On Au(111), intramolecular resolution in the self-assemblies demonstrates the occurrence of pairing between azobenzene groups of neighbouring mesogens. Each of the six azobenzene units of one given molecule exhibits similar tendency thus creating symmetrical hexagonal networks, well-defined in large domains. Hexagonal packing of ester-functionalized mesogen is preserved from Au(111) to graphite as substrate. However, when ester group was substituted by an ether linkage, a drastic change in geometry of self-assemblies on graphite was noticed. STM revealed appearance of row like structures, where the equivalent character of interactions with all six neighbouring molecules is lost. Intramolecular resolution reveals formation of dimers in which interactions between azo-benzene units are now favoured thanks to the large flexibility of ether links. In conclusion, presence of azo-benzene groups, but also nature of the linkage play a key role to establish the symmetry of the corresponding 2D assemblies, from hexagonal to row like structures with dimers, both being imposed by strong interactions between azo-benzene groups.

[1] S. Sergeyev, W. Pisula, and Y. H. Geerts, "Discotic Liquid Crystals: a New Generation of Organic Semiconductors", Chem. Soc. Rev., 36, 1902 (2007).
[2] Y. Shimizu, A. Kurobe, H. Monobe, N, Terasawa, K. Kiyohara and K. Uchida, "Calamitic and discotic mesophases formed by kinetically controlled rod-discalternation of molecular shape in a triphenylene-azobenzene mesogen system", Chem. Commun., 14, 1676 (2003).

Carbon, graphene 1

(invited) Surveying Electronic Structure of CVD graphene on polycrystalline copper foils by nano-ARPES

M C Asensio

Synchrotron SOLEIL, France

In today's state-of-the-art ARPES, probed areas are routinely in the range from tens to hundreds of microns. Notwithstanding in advanced materials, length scales from the nano- to the mesoscopic scales dictate and characterize the electronic and other relevant properties. Thus it is not possible access relevant length scales for many complex engineered materials using conventional ARPES. At the Synchrotron SOLEIL, we have recently built a new instrument by combining ARPES principles with scanning microscopy, in which a focused soft x-ray beam is raster-scanned over the samples to create an image one pixel at time while a suitable signal is monitored under computer control. We detect the photoelectron signal with cutting-edge hemispherical photoelectron spectrometer capable of extremely high momentum and energy resolution. This new nano-probe is capable of investigating innovative materials in their earlier stage of synthesis, which often are initially isolated in small crystalline form or in polycrystals constituted by small grains.

During this contribution, we will disclose the latest nano-ARPES results, obtained by our group at SOLEIL, related to the granular structure of monolayer graphene samples grown by chemical vapour deposition (CVD) on polycrystalline copper foils. We have explored the Dirac cone of individual grains as well as we have obtained net images of the distribution of the grains inside and at the copper grain boundaries. The preferential orientation of the graphene grains relative to the copper substrate has also been established. Moreover, the crystalline quality of the copper grains has been evidenced by nano-ARPES images. The doping and the Fermi velocity of individual graphene grains have been unambiguously assessed from the direct determination of the Dirac cone in single graphene grains.

Size-selective carbon nanoclusters as precursors to the growth of epitaxial graphene

R Schaub[1], B Wang[1], M Caffio[1], X Ma[2] and W-X Li[2]

[1]University of St Andrews, UK, [2]Chinese Academy of Sciences Dalian, China

The nucleation and growth mechanisms of epitaxial graphene on a Rh(111) surface will be presented [1]. STM and DFT calculations show that carbon nano-islands form in the initial stages of graphene growth using ethylene as the carbon source, possessing an exclusive size of 7 honeycomb carbon units (hereafter labeled as $7C_6$). These magic-sized clusters adopt a dome-like hexagonal shape indicating that bonding to the substrate is localized on the peripheral C atoms. Smoluchowski ripening is identified as the dominant mechanism leading to the formation of graphene, with the size-selective carbon islands as precursors. Control experiments and calculations, whereby coronene molecules, the hydrogenated analogues of $7C_6$, are deposited on Rh(111), provide an unambiguous structural and chemical identification of the $7C_6$ building blocks.

[1] B. Wang, X.-F. Ma, M. Caffio, R. Schaub, W.-X. Li, Nano Letters, 11 (2011) 424.

Angle resolved studies of sidewall grown graphene nano-ribbons

E Conrad[1], J Hicks[1], C Berger[1], W de Heer[1], F Bertran[2], P Le Fèvre[2], A Taleb-Ibrahimi[2] and A Tejeda[3]

[1]Georgia Tech, USA, [2]CNRS/Synchrotron SOLEIL, France, [3]University de Nancy, France

We will discuss our work on measuring the electronic band structure of graphene nano-ribbons. Recent fabrication advances have allowed us to make extremely narrow graphene ribbons using either e-beam lithography or by sidewall graphitization of SiC trenches. The sidewall ribbons have extremely well ordered edges and can in principle be made with widths approaching 2nm. We have been able to produce large graphene ribbon arrays for both ribbon types, that have either armchair or zig-zag edges orientations. The high degree of ribbon order in these arrays, both in width and straightness, allow area averaged Angle Resolved Photoemission (ARPES) measurements to be carried out. Using ARPES, we have compared the band structure of e-beam patterned with sidewall grown ribbons. We will present our recent results showing that very high quality Dirac cone measurements can be made. These measurements will demonstrate the dominant role of edges on the ribbon's electronic structure and contrast the band picture differences of ribbons made two alternate ways.

SPA-LEED study of strain state of single layer grapheme on IR(111): hysteretic behaviour of lattice parameter and wrinkle formation

C Klein[1], H Hattab[1], A T N'diaye[2], D Wall[2], G Jnawali[1], J Coraux[3], C Busse[4], R van Gastel[5], B Poelsema[5], T Michely[4], F-J Meyer zu Heringdorf[1] and M Horn-von Hoegen[1]

[1]University Duisburg-Essen, Germany, [2]Berkeley National Laboratory Berkeley, USA, [3]Université Joseph Fourier, France, [4]University of Cologne, Germany, [5]University of Twente, The Netherlands

Employing high resolution spot profile analysis low energy electron diffraction (SPA-LEED) the lattice parameter of single layer graphene on Ir(111), prepared by thermal decomposition of ethylene at 1530 K, was studied. We analyzed the strain state and the wrinkle formation kinetics as function of temperature. Using the moiré spot separation as a magnifying mechanism for the difference in the lattice parameters between Ir and graphene, we achieved an unrivalled precision of ±0.1 pm for the graphene lattice parameter. Our data reveals a characteristic hysteresis of the graphene lattice parameter which is explained by the interplay of reversible wrinkle formation and film strain. We show that graphene on Ir(111) always exhibits residual compressive strain at room temperature, that provides important guidelines for strategies to avoid wrinkling. [1]

[1] Hattab et. al.; Interplay of Wrinkles, Strain, and Lattice Parameter in Graphene on Iridium, Nanoletters 12, 678 (2012)

Low temperature growth of graphene on 4H-SiC(0001) flattened by catalyst-assisted etching in HF solution

K Arima, K Nishitani, N Saito, K Kawai, J Uchikoshi, K Yamauchi, Y Sano and M Morita

Osaka University, Japan

Silicon Carbide (SiC) is a substrate to form uniform and wafer-size graphene layers. Because a flat SiC surface is essential to obtain a defect-free graphene film, the SiC substrate is usually treated in H_2 ambient at temperatures higher than 1500 °C before the formation of graphene. However, this H_2 etching induces step bunching, which is the origin of structural defects in graphene. We propose a method to form an atomically-flat 4H-SiC(0001) surface in HF solutions with help of Pt catalysts, which can be an alternative to H_2 etching. The flattened surface is composed of alternating wide and narrow terraces with single-bilayer-height steps, and a clear 1×1 phase is resolved on a terrace by STM [1]. We have also developed a method to remove Si atoms selectively from a SiC surface by plasma oxidation at room temperature. When a SiC surface is exposed to atmospheric pressure plasma with oxygen radicals, a thin SiO_2 film is formed on SiC. Because the plasma treatment is performed at room temperature, carbon species reside at the SiO_2/SiC interface. When the SiO_2 layer is etched in HF solutions, the SiC surface becomes C-rich. By removing Si atoms from surface layers of the flattened 4H-SiC(0001), a graphene film is formed at around 1000 °C, which is much lower than that by a conventional H_2 etching (1500 °C) followed by vacuum anneal at temperatures higher than 1250 °C.

[1] K. Arima et al., J. Phys. Condens. Matter 23 (2011) 394202.

Graphene growth on Cu(111): microscopic angle-resolved photoemission and scanning tunneling microscopy investigations

L Bignardi[1], S Gottardi[1], P Dudin[2], A Barinov[2], M Enache[1], K Müller[1], M Stöhr[1] and P Rudolf[1]

[1]University of Groningen, The Netherlands, [2]Elettra Sinctrotrone Trieste, The Netherlands

Graphene grown on a copper foil by chemical vapor deposition has been widely explored in the last few years. However, only in a very few experiments graphene growth on highly-ordered copper surfaces (i. e. single crystals) has been studied. In these studies, graphene was grown in-situ under ultrahigh vacuum conditions.

Our studies focus on graphene grown on Cu(111) *ex-situ* in a vacuum furnace by chemical vapor deposition of methane. Angle-resolved photoemission spectroscopy with a microscopic photon beam after annealing at 400°C to remove surface contaminants evidenced a clear band structure with a Dirac cone shape. Scanning tunneling microscopy experiments showed that the Cu surface is covered mainly by a single layer of graphene. Different rotational domains were detected, some showing a Moiré pattern. In addition, the role of oxygen on the growth process and its contribution to the modification of the morphology of the graphene was also investigated.

Surface carbide induced changes on graphene/Ni(111)

A Garhofer[1], P Jacobsen[1], B Stöger[1], G S Parkinson[1], M Schmid[1], R Caudillo[2], F Mittendorfer[1], JRedinger[1] and U Diebold[1]

[1]TU Vienna, Austria, [2]Intel Corporation, USA

Graphene with its unique transport properties supported on ferromagnetic materials is a promising candidate for the fabrication of spin-filtering devices. In order to study the growth of graphene on metal surfaces, graphene on Ni(111) is a perfect system from a structural point of view. Usually graphene on Ni(111) is observed only in 1x1 structures. However, in recent studies also moiré patterns are seen. In this study a new growth model for graphene on Ni(111) is presented, where the surface nickel carbide Ni_2C plays a crucial role. The carbide layer is formed on the Ni(111) surface in the first place. Then the graphene layer starts to grow on the carbide with a weak binding so that the graphene layer can be rotated with respect to the Ni(111). After the graphene layer is formed the nickel carbide layer dissolves leaving defective areas and especially nickel vacancies. The moiré patterns are identified as rotated graphene grains.

We studied the systems using the DFT program package VASP with LDA and vdW-DF in the flavor of optB88 to include van der Waals interactions. In our theoretical discussion we analyzed the bonding of graphene and Ni_2C on Ni(111) and graphene on Ni_2C/Ni(111). We calculated the stability of the different phases by means of phase diagrams where the surface free energy vs. chemical potential is plotted. The CVD growth of graphene on Ni(111) was also studied with STM. Results from DFT calculations can explain the experimental findings and provide a new growth model.

Strain-driven Moiré superstructures of epitaxial graphene on transition metal surfaces

A L Pinardi[1], P Merino[2], J Á Martin Gago[3] and M Svec[2]

[1]ICMM, Spain, [2]Centro de Astrobiologia INTA Madrid, Spain, [3]Instituto de Ciencia de Materiales de Madrid, Spain

Epitaxial graphene on transition metal surfaces leads to the formation of coincidence structures (moires) exhibiting different sizes and orientations. We aim to understand how many moires superstructures can be accommodated on a particular metal surface. To this purpose, we have grown submonolayer coverage of multi-domain epitaxial graphene islands on Pt(111) by low-temperature decomposition of large organic precursors (fullerenes).
We present a geometric model that predicts which and how many moires can exist on a metal surface[1]: it was found that graphene can only grow at those angles at which the strain between the graphene and the metal networks is minimized. This model was developed for the case of Pt(111), and successfully applied to other metals and found to work with most substrates.

Finally, we focused on the 2x2G/Pt(111) phase, which was studied by Scanning Tunneling Microscopy and X-ray Photoemission Spectroscopy complemented with ab-initio density functional theory[2]. This moire is different from the others because the large mismatch between the graphene and the Pt(111) surface causes a large stress within the graphene sp^2-bonds, making this structure unstable. Our study indicates that this structure induces a reconstruction on the Pt surface, consisting of an ordered vacancy network formed in the outermost Pt layer and a graphene layer covalently bound to the Pt substrate.[2]

[1] P. Merino, M. Svec, A.L. Pinardi et al., ACS Nano 5 (2011).
[2] G. Otero, C. Gonzalez, A.L. Pinardi et al., PRL 105 (2010).

Electronic structure of epitaxial graphene on Ru(0001)

A vazquez de Parga[1], D Stradi[1], S Barja[1], C Diaz[1], M Garnica[1], D Sanchez-Portal[2], M Alcami[1], A Arnau[3], F Martin[1] and R Miranda[4]

[1]Universidad Autonoma de Madrid, Spain, [2]Material Physics Centre, Spain, [3]Universidad del Pais Vasco, Spain, [4]IMDEA-Nanociencia, Spain

Graphene epitaxially grown on Ru(0001) displays a remarkably ordered pattern of hills and valleys in Scanning Tunneling Microscopy (STM) images. The origin is the difference in lattice parameters between graphene and the Ru(0001) surface that in turn produces a spatial modulation of the interaction between the graphene overlayer and the substrate.

The interpretation of the STM/STS data measured for graphene grown on Ru(0001) is a challenge due to the entanglement between the geometric corrugation of the moiré pattern and its electronic structure. Spatially resolved dI/dV spectra around the Fermi level measured at room temperature on the gr/Ru(0001) show an asymmetry on the LDOS measured on the high and low areas of the moiré pattern. We employ a realistic model for monolayer graphene adsorbed on Ru(0001), based on density functional theory (DFT) including van der Waals interactions, to describe accurately its electronic structure. Our results show that the peaks appearing in STS spectra close to the Fermi level are the result of the periodic modulation in the electronic properties induced by the moiré.
The spectroscopic data measured at high positive bias voltage shows a peak at +3eV in the low areas of the moiré. Our DFT calculations describes accurately the interfacial state that is at the origin of the inversion of contrast observed in the STM topographies for bias voltages higher than +2.6V. At these energies the graphene layer plays an active role in the formation of an interface band strongly localized in the low regions of the moiré.

Reactions on surfaces 3

Light-induced formation of covalent bonds on an insulator

R Lindner, M Kittelmann, P Rahe and A Kühnle

Johannes Gutenberg-Universität Mainz, Germany

The formation of covalently linked networks on surfaces is a key step towards molecular electronics and controlled surface functionalisation. Covalently bonded networks exhibit an increased stability when compared to π-π or van der Waals-interaction as well as the ability to form conjugated double bonds, which is mandatory to provide sufficient electrical conductivity.

Recently, thermally induced covalent bonding on metallic and insulating substrates has been presented [1,2]. The downside of this approach is that the same external stimulus is used for both, molecule deposition and covalent linking. In order to gain more control, photochemical reactions provide an elegant method to separate these two fundamental steps.

In this work, we demonstrate the photopolymerisation of C_{60} fullerene molecules on an insulator. Monolayers of C_{60}, self-assembled onto the calcite (10.4) cleavage plane, were irradiated with a laser to create two-dimensional, polymeric networks. The networks were examined with non-contact atomic force microscopy. The successful reaction was confirmed by a clear change in the C60 superstructure.

[1] Grill, L. Dyer, M. Lafferentz, L. Persson, M. Peters, M. V.; Hecht, S. Nature nanotechnology 2007, 2, 687-691.

[2] Kittelmann, M. Rahe, P. Nimmrich, M. Hauke, C. M. Gourdon, A.; Kühnle, A. ACS Nano 2011,5, 8420–8425.

Imidazolium-based ionic liquids interacting with ordered cerium dioxide surfaces: a synchrotron-radiation photoelectron spectroscopy study

M Laurin[1], Y Lykhach[1], S Schernich[1], N Taccardi[1], V Wagner[1], N Tsud[2], T Skála[3], K Prince[3], V Matolín[2], P Wasserscheid[1] and J Libuda[1]

[1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany, [3]Charles University, Czech Republic, [4]Sincrotrone Trieste SCpA, The Netherlands

In this work we present the first surface science study of an ionic liquid (IL) thin film on a reducible oxide surface. ILs are molten salts liquid below 100°C. They exhibit unusual properties such as an extremely low vapor pressure. This allows them to be handled and studied using standard surface science techniques. Among the applications of ILs, new concepts have been proposed in catalysis, like "solid catalysts with ionic liquid layer" (SCILL), which make use of a thin IL film to tune the properties of supported heterogeneous catalysts. Cerium dioxide (CeO_2) is an active support used in many catalytic processes. Thin CeO_2(111) films epitaxially grown on Cu(111) provide a versatile model of this catalyst support for fundamental studies. The stoichiometric surface can be prepared in vacuo and may be reduced by different methods, including exposure to methanol.[1]

We study the interactions of $[C_6C_1im][Tf_2N]$ with these surfaces. The IL was deposited in situ from a home-built evaporator.[2] Molecular orientations and thermal decomposition of the IL were followed by synchrotron-radiation photoelectron spectroscopy (PES). And the changes in the oxidation state of CeO_2 were probed in parallel by resonant PES. We find that the decomposition mechanism and the thermal stability of the IL film sensitively depend on the oxidation state of the support. Possible interactions and decomposition mechanisms are discussed.

[1] Matolín et al., Surface Science 2009, 603, 1087

[2] Sobota et al., Langmuir 2010, 10, 7199

Pentagonal facets on the leached fivefold Al-Cu-Fe quasicrystalline surface

M Lowe, T Prasad Yadav, R McGrath and H Raj Sharma

University of Liverpool, UK

In the movement to reduce the use of fossil fuels in society, the hydrogen fuel cell has been promoted as a possible alternative to the internal combustion engine. Hydrogen storage and transport is expensive and bulky, especially in mobile applications. For this reason it may be desirable to store hydrogen in the medium of methanol (CH_3OH)[1]. Hydrogen can be produced from methanol through the Steam Reforming of Methanol reaction: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

Currently used Copper based industrial catalysts possess high activity for the Steam Reforming of Methanol. These catalysts suffer from rapid degradation at temperatures close to mobile operating conditions.

Steam Reforming of Methanol has been performed over several quasicrystalline alloys containing catalytically active metals to examine their catalytic activities.[2] Among these icosahedral Al-Cu-Fe quasicrystal powder leached in alkaline solution displayed similar level of activity and selectivity as metal catalysts while remaining stable at high temperatures. The leaching treatments yielded nano-particles of Cu and Fe atop of the quasicrystalline bulk. These nano-particles are believed to be responsible for the catalytic activity. However, the role of underlying quasicrystal is not fully understood yet.

We have studied a simple model system obtained by leaching a well-oriented surface of single grain icosahedral Al-Cu-Fe quasicrystal. The fivefold surface was leached at various times in NaOH solution and subsequently characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, low energy electron diffraction (LEED), X-ray photo electron spectroscopy (XPS) and atomic force microscopy (AFM). The surface composition of the sample was found to change dramatically under leaching and nanoparticles are precipitated on the surface in agreement with the leached powder results. Further to this the appearance of orientated pentagonal facets on the surface and partially revealed dodecahedra were observed and analysed.

[1] Palo, D.R., R.A. Dagle, and J.D. Holladay, Methanol steam reforming for hydrogen production. Chemical Reviews, 2007. 107(10): p. 3992-4021.

[2] Tsai, A.P. and M. Yoshimura, Highly active quasicrystalline Al-Cu-Fe catalyst for steam reforming of methanol. Applied Catalysis A-General, 2001. 214(2): p. 237-241.

Water adsorption on TiO_x thin films on Au(111)

M H Farstad[1], D Ragazzon[2], L E Walle[1], A Schaefer[3], A Borg[1] and A Sandell[2]

[1]NTNU, Norway [2]Uppsala University, Sweden, [3]University of Bremen, Germany

Titania (TiO_2) is a non-toxic, wide band gap semiconductor available in three different crystal structures, rutile, anatase and brookite. It is also possible to deposit TiO_2 particles and grow TiO_x ($x \leq 2$) thin films onto various metal substrates, thereby forming unique structures. Systems based on TiO_2 have a large variety of possible applications, including heterogeneous catalysis, photocatalysis, solar cells for hydrogen and electric energy production and electrochromic devices [1]. Water is an integral part of several of these applications and a solid understanding of the interaction between water and titania is therefore important.

In this contribution we report on water adsorption on thin films of TiO_x deposited on Au(111) by chemical vapor deposition as studied with high-resolution photoelectron spectroscopy (HR-PES). The structure and composition of TiO_x thin films have been characterized with HR-PES, scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Four different ordered phases are distinguished, two 2D phases and two 3D phases. Depending on the phase and surface temperature, different ratios between molecular and dissociated water species are observed at coverages below one monolayer. The presence of OH species on the surfaces indicates that water splitting is taking place. This is similar to observations on the well characterized rutile TiO_2(110) surface [2]. The influence ofhydroxyl groups formed when exposing the TiO_x thin films to atomic hydrogen will also be addressed.

[1] U. Diebold, Surf. Sci. Reports, 48, 53 (2003).
[2] L. E. Walle et al., Phys. Rev. B, 80, 235436 (2009).

CO induced unpinning of Pt clusters from the Ir(111)/graphene moiré

T Gerber[1], J Knudsen[2], P J Feibelman[3], P Stratmann[1], E Grånäs[2], K Schulte[2], J N Andersen[2] and T Michely[1]

[1]Universität zu Köln, Germany, [2]Lund University, Sweden, [3]Sandia National Laboratories, USA

The stability of catalyst particles under reactive conditions is of crucial importance for their performance and durability. Here we report how CO adsorption effects the stability of Pt-cluster superlattices with a periodicity of 25.3 Å on a graphene/Ir(111) moiré.

XPS shows that CO adsorbs atop and preferentially at cluster step edges. Further, a weakened binding of the Pt-clusters to the graphene upon CO adsorption is indicated by a decrease of the C1s graphene feature characteristic for cluster binding. For small clusters with an average size below 14 atoms this unpinning leads to cluster diffusion and cluster coalescence, as observed dynamically through STM image sequences. Larger clusters remain fixed upon room temperature CO adsorption.

An increase of bond length between Pt-atoms and graphene C-atoms as calculated by DFT is consistent with a weakened cluster binding upon CO adsorption.

To prevent cluster coalescence in the early stages of cluster growth and to obtain the most regular Pt-cluster superlattices the CO partial pressure during Pt deposition should be minimal. Otherwise adsorbed CO causes unpinning and subsequent coalescence of small intermediate clusters already during the growth process.

Reaction bifurcation in H-MFI and Faujasite zeolites

D Tranca[1], P Zimmerman[2], J Gomes[2], D Lambrecht[2] and F Keil[1]

[1]Technische Universität Hamburg, Germany, [2]University of California, USA

Passing through a transition state (TS) is a rare event that converts one reactant to a single product. If there is a branching in the potential energy surface, a single unique TS may yield multiple products. When two products result from the same TS, this is called reaction bifurcation and the product distribution depends on the dynamic reaction path following the TS. It will be shown, that bifurcation occurs in n-hexane cracked on ZSM-5 and faujasite zeolites. Although the mechanism for alkane cracking has often been discussed, bifurcation is a new aspect of this reaction that has not been substantially considered.

Quasi-classical trajectories (QCT) are a chemically realistic approach to study reaction bifurcations by sampling reaction dynamics through trajectories begun at TS structures. QCT attempts to model realistic velocities by populating vibrational modes as a function of temperature. This provides quantum mechanical initial conditions on the motion of nuclei in the system, and propagates nuclei classically, resulting in an efficient method for examining reaction paths.

QCT simulations that begin from a TS will sample bifurcating (or more branched) routes that lead to multiple products. Although it is a not our intention to give statistically converged product distributions, QCT provides a useful and computationally tractable tool for determining whether reaction bifurcation is important in a given reaction. Except bifurcation, adsorption thermodynamics and monomolecular cracking of n-hexane on ZSM-5 and faujasite zeolites have been studied within QM/MM method. Thermodynamical properties are influenced by the ueolite structure on which the adsorption occurs. The thermodynamical results obtained are in qualitative and quantitative agreement with the experimental literature.

Adsorption of cyclooctyne on clean and hydrogen precovered Si(001) surfaces

G Mette, M Dürr, R Bartholomäus, U Koert and U Höfer

Philipps-Universität Marburg, Germany

The adsorption of organic molecules on semiconductor surfaces is of special interest with respect to surface functionalisation and its use in molecular electronics. Whereas several alkenes and alkynes form well-ordered monolayers on Si(001), second- and multilayer attachment is still a central challenge towards successful functionalisation [1].

In this context, the adsorption of cyclooctyne on clean and hydrogen precovered Si(001) surfaces was studied by means of scanning tunneling microscopy. Cyclooctyne's high ringstrain due to its stiff triple bond should make it a good candidate for chemoselective cycloadditions in more complex multifunctional compounds.

In our real-space studies, we observe one predominant adsorption geometry at low coverage and very similar adsorption behavior at surface temperatures of 50 K and 300 K. The latter observation indicates a direct adsorption channel of cyclooctyne on Si(001) in contrast to systems like C_2H_4/Si which adsorb via a mobile precursor state. This conclusion is backed by experiments on hydrogen precovered surfaces for which no change in the adsorption behavior was found at distorted dangling-bond configurations. At high surface coverage, cyclooctyne forms a well-ordered first layer on Si(001). This observation of highly ordered surface structures in combination with a direct adsorption channel is of interest for the generation of organic/semiconductor interfaces when implemented in multifunctional adsorbates.

[1] M. A. Filler and S. F. Bent, Progr. Surf. Sci. 73, 1 (2003)

Magnetism 3

(invited) Understanding defects in iron using magnetic tight binding

A Horsfield

Imperial College London, UK

Hydrogen fusion and next generation fission power plants are making demands on steel that are extreme. The radiation creates multiple point defects that need to recover swiftly if the material is to retain its integrity. Understanding the behavior of these, and other, defects is thus a prerequisite if safe structures are to be made. A certain amount can be understood on the basis of elegant electron microscopy, but there is information that is much more readily obtained by computer simulation. However, producing reliable, quantitative results is demanding: a large number of atoms (hundreds or possibly thousands) need to be treated explicitly, while a proper description of magnetism must be retained. Density Functional Theory and Tight Binding are the main contenders. A brief introduction to magnetic Tight Binding will be given, including a discussion of techniques to manage the numerical complexities. This will be followed by results for point and line defects.

Comparing electromagnetic and contact ultrasonic techniques: magnetic phase transitions in single crystal $Gd_{64}Sc_{36}$

O Trsushkevych, R Edwards, Y Fan and R Perry

University of Warwick, UK

The speed and attenuation of ultrasound propagation can be used to determine properties and phase transitions in various materials. Conventional ultrasonic measurements involve piezoelectric transducers to generate and detect ultrasound, which require the use of couplant and a contact with the sample. However, at cryogenic temperatures and with thermal cycling the coupling between the transducer and the sample may quickly deteriorate, and hence non-contact methods are much preferred. Recently, new, reliable non-contact ultrasonic techniques involving electromagnetic generation and detection of ultrasound with electromagnetic acoustic transducers (EMATs) have been developed for use on electrically conductive and/or magnetic materials.

Here we present a detailed study of magnetic phase transitions in a single crystal $Gd_{64}Sc_{36}$ magnetic alloy using both contact and non-contact techniques for two orientations of external magnetic field. We construct phase diagrams based on the measurements of elastic constant C_{33}, the attenuation of the wave, and the efficiency of generation when using EMATs. Our measurements confirm that electromagnetic generation of ultrasound does not lead to any noticeable sample heating and that there are no problems with temperature stability at cryogenic temperatures. We compare the results obtained by the contact and EMAT techniques, discuss the mechanisms involved in electromagnetic generation in $Gd_{64}Sc_{36}$ and show that EMATs are particularly sensitive to magnetic phase transitions.

Exchange and magnetic anisotropic interactions of magnetic ions in antiferromagnetic materials

A N Bazhan

P.L.Kapitza Institute for Physical Problems, RAS, Russia

Investigations of exchange and magnetic anisotropic interactions of magnetic ions in antiferromagnetic materials, based on theory of materials crystallographic and magnetic symmetry, which introduce quadratic forms of thermodynamic potentials, presented in irreducible representations of magnetic moments of interecting magnetic ions and invarianted with respect to operations of magnetic symmetry groups of magnetic materials, are carring out using vector v.s.magnetometer, which can investigate separetely three perpendicular components of the samples magnetic moments. Discussions are presenting in the solvable forms introducing $\frac{1}{2} I^2\chi(1-\chi_{//}/\chi)\ (\gamma H)^2$ terms in thermodynamic potentials, where $\chi_{//}$ - are parallel, $H//\gamma I$, magnetic susceptibilities, χ - are perpendicular magnetic susceptibilities, with $\chi_{//} << \chi$ and vectors γ - are unit antiferromagnetic vectors of interacting magnetic moments. Advantages of vector v.s.magnetometers in investigations of magnetic orderings are indicating in investigations of magnetic field dependencies of three, separate components of samples magnetic moments, that presents magnetic field dependencies of orientations of samples magnetic moments with respect to crystallographic axis and direct information about interactions of magnetic ions, especially magnetic ions with high electrons spin-orbit interactions. Investigations of antiferromagnetic orderings with weak ferromagnetic states, determined by interactions of second and higher orders, which are responceble for weak ferromagnetic moments, at the selected orientations of antiferromagnetic vectors with respect to crystallographic axis and investigations of interactions of magnetic ions in materials of tetragonal and rhombohedral structures, such as, NiF_2 and $NiCO_3$, are discussed as examples. Spin Hamiltonians of second order symmetric, Anderson and antisymmetric, Dzyaloshinskii - Moria exchange interactions of magnetic ions, which are intensevly discussing in investigations of antiferromagnetic matertials, for some rhombohedral structures are presenting by expressions, $H_{ex} = \sum_{ij}J_{ij}(S_iS_j) - \sum_{ij}D_{ij,z}(S_{ix}S_{jy} - S_{iy}S_{jx})$, with $D_{ij,z}$ in absolute values.

Mixed singlet magnetism of the intermetallic PrPtAl

G Abdul-Jabbar[1], D Sokolov[1], C Stock[2], F Demmel[3] and A Huxley[1]

[1]University of Edinburgh, UK, [2]NIST Center for Neutron Research, USA, [3]ISIS Pulsed Neutron Source, UK

Naively magnetism is not expected to occur in systems solely composed of singlet states. The underlying mechanism leading towards magnetic order in these systems can, however, be brought about by mixing singlets through the intersite exchange interaction [1].

The intermetallic PrPtAl with its Pnma space group [2] splits the single ion J=4 multiplet into 9 singlet states. In spite of this PrPtAl realises long range magnetic order at 5.7K. PrPtAl first passes through two helically modulated incommensurate magnetic states at 5.7 K and 5.2 K before ordering feromagnetically at 4.7 K.

In this presentation we will discuss the results of our investigation into the development of magnetic order in PrPtAl. Measurements of the excitations associated with the lowest lying singlet levels using inelastic neutron scattering will be presented alongside magnetic neutron diffraction, thermal and magnetisation measurements.

Our results will be discussed within the framework of an intra-ion singlet mixing model which gives rise to a non-singlet collective ground state. Magnetism is then realised by inter-ion magnetic exchange described using the singlet-singlet excitation model [3].

[1] B. Bleaney , Proc. Roy. Soc. A, 276, 19, (1963).
[2] H. Kitazawa et al, J. Solid State Chem, 140, 233, (1998).
[3] J. Jenson, A. Mackintosh, Rare Earth Magnetism structures and excitations, Clarendon Press,(1991).

The electronic and magnetic structure of I-Mn-V antiferromagnetic semiconductors and semimetals

F Maca[1], J Masek[1], J Zelezny[1] and T Jungwirth[2]

[1]Institute of Physics ASCR, Czech Republic, [2]University of Nottingham, UK

Recent observation of a large magnetoresistance in an antiferromagnet (AFM) based tunnel junction opens the prospect for utilizing AFMs in spintronics [1]. This motivates a search for new materials which may be suitable for spintronics and are room-temperature AFMs. The desired control of devices via electrical fields could be further exploited if the materials involved would be either semiconductors or semimetals with a low density of states at the

Fermi energy [2]. We report on an ab-initio theoretical study of CuMn-V antiferromagnets based on the density functional theory. Previous works showed low-temperature antiferromagnetism and semimetal electronic structure of the semi-Heusler CuMnSb. We show that the transition to a semiconductor-like band structure upon introducing the lighter group-V elements is present in both the metastable semi-Heusler and the stable orthorhombic crystal structures [3]. We also predict a remarkable increase of the Néel temperature and a strong enhancement of magnetocrystalline anisotropy in the layered crystals of CuMnAs. The experimental results indeed indicate that the Néel temperature in CuMnAs is much higher than in CuMnSb. We discuss in detail the ground state of these compounds and the role of defects to stabilize it.

[1] B. G. Park et al, Nature Materials 10, 347 (2011).
[2] T. Jungwirth et al., Phys. Rev. B 83, 035321 (2011).
[3] F. Maca et al, J. Magn. Magn. Mater. 324, 1606 (2012).

Selective Mott mechanism at metamagnetic transition in FeRh

M de Vries[1], M Loving[2], A Mihai[3], L Lewis[2], D Heiman[2] and C Marrows[3]

[1]The University of Edinburgh, UK, [2]Northeastern University, UK, [3]University of Leeds, UK

Iron and Rhodium alloy in any composition but on annealing equiatomic FeRh above 700 C a distinct phase with the CsCl structure is obtained (α'-FeRh). The mechanical, electronic and magnetic properties of this intermetallic compound are distinct from that of the alloys. Most importantly, it is an antiferromagnetic (AF) metal [1,2] in contrast to the Fe-rich alloys which are ferromagnetic (FM) and the Rh-rich alloys which are paramagnetic (PM). It has long been known [1] that α'-FeRh displays a magnetostructural phase transition on heating from an AF to FM magnetic state above ~ 370 K, with a uniform 1% volume expansion, and significant resistivity drop. On further heating to ~ 670 K a (Curie-Weiss) paramagnetic state is obtained.

We have carried out Hall and magnetoresistance measurements on CsCl-ordered FeRh epilayers to characterise this unusual 1st order metamagnetic transition from AF to FM. The data reveal that the sub-metallic density of electron-like majority carriers in the AF phase are attributable to intrinsic doping from Fe/Rh substitution defects, with approximately two electrons per pair of atoms swapped. On heating, the metamagnetic transition is found to coincide with an increase in carrier density of at least an order of magnitude. This is interpreted as an orbital-selective Mott transition [3] of the Fe $3d$ electrons, where upon delocalisation the magnetic exchange between the $3d$ electrons changes sign from antiferromagnetic to ferromagnetic. This is the first observation of a selective Mott transition in an intermetallic compound involving $3d$ electrons.

[1] M. Fallot, Ann. Phys. 10, 291 (1938).
[2] G. Shirane, C. W. Chen, P. A. Flinn, and R. Nathans, Phys. Rev. 131, 183 (1963).
[3] C. Pépin, Phys. Rev. Lett. 98, 206401 (2007).

Characterization and study of new system of ferromagnetic shape memory alloy intermediate of Ni-Mn-X(x = Sn, Sn and In) and Ni-Mn-Al

S Agarwal, P K Mukhopadhyay

S N Bose National Centre for Basic Sciences, India

Off-stoichiometric Ni_2MnX (where X = Sn, Sb and In) Husler alloy with excess Mn are ferromagnetic shape memory alloys (FSMA) which shows many interesting physical properties like giant magnetocaloric effect, large magnetoresistance, field induced structural transformation etc. Most of these properties are outcome of austenitic to martensitic (A →M) structural transformation, which also leads to change in magnetic state of the system, due to change in temperature. These alloys in very narrow range of composition shows these properties near room temperature. To bring A →M transformation temperature towards room temperature we have partially replaced X with Al in above system. These leads to increase in A →M transformation temperature towards room temperature. We have prepared a new system of alloys which has been characterized using X-ray powder diffraction (XRD) measurement and Differential scanning calorimeter (DSC). Magnetic measurement in both ac and dc fields were performed on these alloys. The XRD measurement shows that the system in austenitic state at room temperature. The DSC curve shows that system undergoes A →M and reverse transformation upon cooling and heating (150 K to 400 K). It is also observed that as the Al concentration increases the A →M also increases where as Curie temperature of austenitic state remains almost constant. The dc magnetic measurement at high field shows that this alloys shows field induced shift of transformation temperature like it parent Ni-Mn-Sn alloy. In the dc measurement at low temperature, irreversibility is observed in martensitic state, which shows systematic shift with change in Al concentration. These alloys are thus new system of FSMA.

Metals, alloys and their surfaces 1

Structure of the $Al_{13}Fe_4(010)$ surface using quantitative LEED

A Matilainen[1], K Pussi[1], N Stanisha[2], R Diehl[2], L Sercovic Loli[3], E Gaudry[3], V Fournée[3], J Ledieu[3], P Gille[4] and M Hahne[4]

[1]Lappeenranta University of Technology, Finland, [2]Penn State University, USA, [3]Institut Jean Lamour, France, [4]University of Munich, Germany

Monoclinic $Al_{13}Fe_4$ is a complex metallic alloy that has a unit cell containing 102 atoms. The structure can be described as the stacking along the [010] direction of two types of layers, flat (F) having 17 Al and 8 Fe atoms, and puckered (P), having 22 Al and 4 Fe atoms per unit cell. There are two types of each plane, producing a stacking sequence $F_1P_1F_2P_2$.

We present a quantitative LEED study of the surface structure of the $Al_{13}Fe_4$ CMA using LEED data that were measured at room temperature. The procedure for structure determinations using LEED involves the assumption of a model structure, computation of the intensity spectra for that model structure, and comparison of the calculated spectra to the experimental spectra using a reliability factor (R-factor). These calculations were performed using the SATLEED suite of programs [1].

[1] M. A. Van Hove, software download at: http://www.ap.cityu.edu.hk/personal-website/VanHove.html.

A racemic two chiral kinked surface: a structural study of the Re$(11\bar{2}1)$ surface.

R Bennett[1], H Etman[1], G Held[1] and S Jenkins[2]

[1]University of Reading, UK, [2]University of Cambridge, UK

Intrinsically chiral surface systems are of increasing interest due to the growing demand for optically pure chemicals for feedstocks in drug manufacturing. There is a strong desire to develop enantioselective heterogeneous catalysts which avoid the phase separation problem inherent in today's homogeneous enantioselective processes. A good starting point to understand substrate directed chiral molecular interactions and stereochemistry is to employ an intrinsically chiral surface in which the geometry at the atomic level can be ascertained [1]. To date such studies have either been on mineral surfaces [2] such as quartz or the surfaces of face centred cubic metals cut with three inequivalent nonzero Miller indices [3, 4, 5]. Here we report the first study on a hexagonal close packed chiral metal surface, the Re(112bar1) surface. We show by atomically resolved scanning tunnelling microscopy, quantitative low energy electron diffraction and density functional theory that the surface is globally racemic but locally composed of two terrace types which are either left or right handed and can be interconverted by adding or removing a single atomic layer. The clean surface relaxes with the first three inter-layer separations contracting and a large outward expansion of the fourth interlayer distance. The top layer atom also moves laterally. Excellent agreement is found between experiment and theory. We further discuss strategies for inducing a bias in the system to drive the formation of a globally chiral surface by preferential reduction of one of the chiral terrace populations.

[1] S.J. Jenkins and S.J. Pratt, Surf. Sci. Rep 62 (2007) 373.
[2] R.M. Hazen and D. S. Sholl, Nat. Mat. 2 (2003) 367.
[3] S.R. Puisto, G. Held, V. Ranea, S.J. Jenkins, E.E. Mola and D.A. King, J. Phys. Chem. B 109 (2005) 22456.
[4] G. Jones, M.J. Gladys, J. Ottal, S.J. Jenkins and G. Held, Phys. Rev. B 79 (2009) 165420.
[5] M.L. Clegg, S.M. Driver, M. Blanco-Rey and D.A. King, J. Phys. Chem C 114 (2010) 4114.

LEED intensity analysis of Cu(111)-($\sqrt{3}$ x $\sqrt{3}$)R30◦ - Te

A Chaudhuri[1], K Pussi[1], I McLoed[2], D Hesp[2], E Alice[2], V Dhanak[2], M King[3] and M Kadodwala[3]

[1]Lappeenranta University of Technology, Finland, [2]University of Liverpool, UK, [3]University of Glasgow, UK

The copper-tellurium system has interested researchers for over thirty years. The motivation for early studies was the complexity, and richness, of the alloy phases of the system [1, 2]; and the ability to tune the electronic properties (metallic, semimetallic and semiconductor) of alloys through altering relative compositions [3-5]. The driver for the recent resurgence in interest in the system is its importance in CdTe photovoltaic cells [6]. A critical component of the solar cell is the back contact which is typically CuTe [7-9]. It reduces the contact resistance – thus allowing the device to obtain the cell efficiencies of greater than 15%.

This work describes a study of Te deposited on Cu(111) using low energy electron diffraction (LEED). The first ordered pattern observed by LEED is a (2$\sqrt{3}$ x 2$\sqrt{3}$)R30° structure, with the sharpest pattern occurring at θ_{Te} = 0.18+/-0.02 ML. A ($\sqrt{3}$ x $\sqrt{3}$)R30° LEED structure is observed with further deposition of Te, up to 0.68 ML. The sharpest pattern occurred for θ_{Te} = 0.34 +/-0.02 ML. Increasing deposition of Te causes the degradation in the quality of the ($\sqrt{3}$ x $\sqrt{3}$)R30° LEED structure. The measured surface unit cell for ($\sqrt{3}$ x $\sqrt{3}$)R30°, derived from the LEED pattern, shows that the lattice expands by ~2.8% with respect to the native Cu(111) surface. Presumably, this expansion is a result of the larger Te atom being incorporated in the outermost Cu layer, forming a substituted surface alloy. The structure of ($\sqrt{3}$ x $\sqrt{3}$)R30° phase is analysed by using SATLEED suite of programs [10].

Oxygen adsorption on Ir(100) - Coexistence of extra dense (2×1) phase and O-stabilized surface reconstruction

L Hammer, P Ferstl and M A Schneider

Universität Erlangen-Nürnberg, Germany

Oxygen adsorption on Ir(100) leads to the formation of a (2×1) superstructure, whereby 0.5 ML of oxygen atoms are adsorbed in bridge positions [1,2]. A recent SXRD study [2] found an additional partial occupation of the hollow sites in the centres of the (2×1) cell by oxygen atoms. This finding is now validated by our STM measurements where we could directly image these extra atoms, which, however, are still very mobile at room temperature.

For a reduced oxygen coverage, either due to incomplete adsorption or partial desorption, we do not find a depopulation of the hollow sites but instead sparsely populated stripes perpendicular to the oxygen rows. The mutual spacing of these stripes is rather regular and decreases with coverage eventually leading to a (2×n) superstructure. The occurrence of such a superstructure has been inferred from very early LEED work [3], but its origin remained unclear. We argue that the stripes exhibit an oxygen-stabilized hexagonal reconstruction similar to that of the clean surface, however, without additional Ir atoms incorporated. Both the (2×1) superstructure and the (2×n) stripe phase undergo reversible order-disorder transitions at different temperatures, thus, their coexistence is the equilibrium configuration for the respective coverage.

[1] K. Johnson et al., J. Chem Phys. 112 (2000) 10460.
[2] D. Sander et al., Phys. Rev. B 81 (2010) 153403.
[3] J. Küppers and H. Michel; Appl. Surf. Sci. 3 (1979) 179.

Origin of R(15x3)-C/W(110); Moiré structure of hexagonal α-W_2C on W(110)

J-S Kim[1], J-H Kim[1], G Rojas[2], X Chen[2], A Enders[2] and H Kim[1]

[1]Sook-Myung Women's University, South Korea, [2]University of Nebraska, USA

Carburized W(110) shows reconstructions with large unit cells such as (15 x 12) and (15 x 3), which have been used as templates for the growth of ordered nanoclusters. Their atomic structures are, however, not yet revealed, which has limited the understanding of their physical properties in relation to their atomic structures. Recently, we could obtain atomically resolved images of (15 x 3)-C/W(110) by scanning tunneling microscope. Their unit cell well matches that of hexagonal a-W_2C, indicating that the surface layer is formed of some motif from a-W_2C as predicted by Bauer 45 years ago.[1] We could reproduce the observed height contrast of the image by forming Moiré pattern of a- W_2C with W(110), whose relative orientation is, though, different from the original suggestion of Bauer. Then, we made simulation to reproduce the STM images, employing first principles calculations that is based on density functional theory, and have refined information on the atomic structure of (15x3) reconstructed surface.

[1] E. Bauer, Surf. Sci. 7, 357 (1967).

Surface science of Cs, CsO and CsI layers on Pt(111)

J Drnec[1], D Harrington[2] and R Felici[1]

[1]ESRF, France, [2]University of Victoria, Canada,

Alkali metal layers adsorbed on transition metal surfaces have been widely investigated in the past for their importance in gas phase catalysis and their ability to significantly lower the interfacial work function. In this contribution, cesium adsorption on Pt(111) and its coadsorption with iodine and oxygen is discussed.

The work function during Cs dosing first decreases and at about 3 eV ($\theta_{Cs} = 0.15$) the surface undergoes surface transition between a disordered Cs anomalous state and islands of Pt(111)(2x2)-Cs causing a change in the slope of the work function curve. Cs in the anomalous state desorbs from the surface in a high-temperature TDS peak (> 1000 K). When the lock-in TDS detection technique is used, this peak appears to be phase shifted by 180 degrees when compared to the desorption peak of normally adsorbed Cs ($\theta_{Cs}>0.15$). This phase shift is a consequence of a positive charge of desorbing Cs.

When O_2 is dosed on a Pt(111)-Cs surface, the maximum coverage of oxygen bonded to the surface is significantly increased in comparison to Pt(111). Anomalously adsorbed Cs activates the O_2 bond but does not interact strongly with coadsorbed O. However, when O_2 is dosed on Cs fully covered Pt(111), the oxygen first adsorbs on top of the Cs layer. LEED shows only diffuse scattering while the surface x-ray diffraction shows underlying ordered Cs structure. After annealing to 600K, oxygen adsorbs to a sub-layer site and strongly interacts with Cs. The oxygen in this state is responsible for thermal stabilization of coadsorbed Cs. When iodine is coadsorbed on a Pt(111)-Cs surface, it also strongly interacts with and thermally stabilizes Cs. During the desorption of CsI layers, some Cs and I desorb together in the form of a Cs_xI_y cluster. The surface structures observed by LEED during the coadsorption of Cs, I and O are in good agreement with atomic arrangements predicted for ionic layers.

Formation of single atomic chains of chlorine on Au(111) via elastic interactions: STM and DFT study

K Eltsov[1], B Andryushechkin[1], V Zheltov[1], V Cherkez[1] and B Kierren[2]

[1]A.M. Prokhorov General Physics Institute, Russia, [2]Université H. Poincaré – Nancy, France

In this work, we present a combined low temperature Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) study of chlorine atoms adsorption on Au(111) at low coverages.

STM study of Cl/Au(111) system has shown that at submonolayer coverages ($\theta < 0.1$ ML) chlorine atoms form chain-like structures. In the contrast to the case of $(\sqrt{3}\times\sqrt{3})R30°$ structure (0.33 ML) characterized by the Cl-Cl distance of 5.0 Å, at low coverage, we detected abnormally short distances of 3.8 Å within the chains.

This experimental observation has been supported by the DFT calculations. We've found that one Cl atom occupies fcc position, while the other one appears to be in the bridge position. The formation of the chains has been also tested with DFT. The third chlorine atom was placed in the 14 different positions around the pair of chlorine atoms. According to our calculations, the formation of the compact islands is strongly unfavorable, whereas making the chain is the most energetically favorable scenario for a third atom (at distances of 5.0 Å or 3.8 Å).

In the course of the optimization of atomic coordinates, we've detected a significant perturbation of the upper gold layer. The calculations with frozen positions of the atoms in the gold substrate have not reproduced local minimum at 3.8 Å and the preferable quasi-one dimensional geometry of chlorine chains. In this connection, we believe the interaction between chlorine atoms to be mediated by the elastic substrate distortion.

Thus, chlorine atoms can interact with each other through distortion of the substrate and this indirect elastic interaction is strong enough to affect the arrangement of chlorine atoms in the chain-like structures.

Long range periodicity of S/Au(111) structures at low and intermediate coverages

P Abufager[1], M L Martiarena[2], G Zampieri[2], K Reuter[3] and H F Busnengo[1]

[1]El Instituto de Física Rosario, Argentina, [2]Centro Atómico Bariloche and Instituto Balseiro, Argentina, [3]Technische Universität München, Germany

Sulfur on metals at the sub-monolayer and monolayer levels has attracted considerable attention in the fields of surface science, catalysis, and nanotechnology. In spite of the large amount of work done in this field, many questions remain unanswered. Particularly intriguing is the origin of the rich variety of structures formed by S atoms on Au(111) under different experimental conditions, which suggests a complex picture of the S/Au(111) interaction [1-4].

Through DFT calculations, we have studied the adsorption of S on Au(111) at low and intermediate coverages ($\Theta \leq 1/3$ monolayers, ML). The only stable structure characterized by a short range periodicity is $\sqrt{3}\times\sqrt{3}R30°$, the stability of which, however, seems restricted to a very narrow coverage window: $0.28 \leq \Theta \leq 0.33$ ML. Our calculations predict for the coverage range $\Theta \leq 0.28$ML several structures which are all characterized by a 5x5 periodicity, in line with recent experiments [3,4]. In addition, our results unambiguously reveal a crucial role of S-induced substrate relaxation. The complex coverage dependent scenario described above is dictated by long range substrate mediated S-S interactions which: i) favour 5x5 arrangements due to a slight S-S attraction at ~15 Å, and ii) disfavour large $\sqrt{3}\times\sqrt{3}R30°$ patches because of a strong S-S repulsion at ~10 Å.

[1] Rodríguez et al. J. Am. Chem. Soc. 125 (2003) 277.
[2] Lustemberg et al. J. Phys. Chem. C 112 (2008) 11394.
[3] Yu et al. J. Phys. Chem. C 111 (2007) 10904.
[4] Bienner et al Surf. Sci. 601 (2007) 1659.

Electronic structure and topological insulators 3

Mapping image potential states on graphene nanoflakes

F Craes[1], S Runte[1], J Klinkhammer[1], M Kralj[2], T Michely[1] and C Busse[1]

[1]Universität zu Köln, Germany, [2]Institute of Physics, Croatia

Scattering and spatial confinement of metallic surface states at nanostructures are well known features in Scanning Tunneling Microscopy (STM) [1]. Also for the new material graphene a confinement of occupied states was observed on graphene nanoflakes on Ir(111), leading to characteristic standing wave patterns in Scanning Tunneling Spectroscopy (STS) [2].

In this contribution we describe a closely related behavior for unoccupied free electron states in an STS study of image potential states (IPS) on graphene nanoflakes on Ir(111). IPS are of fundamental interest as they provide access to the local work function and field distribution and thus insight into the interaction of the graphene layer with the metal substrate. IPS are unoccupied surface states energetically residing in an image charge potential between the Fermi and the vacuum level, with a hydrogen-like spectrum. Due to the electric field between the tip and the sample, in STM experiments this series is subject to a Stark shift.

In general, parallel to the surface IPS disperse like free electrons. On a flat metal surface, the peaks in the local density of state (LDOS) point spectra are found always at the same energy and are independent on position. In contrast, on graphene nanoflakes the peak energy depends on the area of the flake and the peak intensity depends on the position inside the flakes. These findings are fingerprints of lateral confinement of the IPS [3]. Further analysis of the substructure of the first resonance by spatial mapping of constant energy LDOS reveals patterns of confined states similar to the findings initially mentioned for confined surface states [1].

[1] J. Li et al., Phys. Rev. Lett., Vol. 80, 15 (1998).
[2] D. Subramaniam et al., Phys. Rev. Lett., 108, 046801 (2012).
[3] R. Fischer, Th. Fauster and W. Steinmann, Phys. Rev. B, Vol. 48, 20 (1993).

STS investigation of europium oxide on graphene

J Klinkhammer, F Craes, S Runte, T Michely and C Busse

Universität zu Köln, Germany

EuO is one of the rare ferromagnetic semiconductors, the bottom of the conduction band is highly spin polarized [1]. Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) as powerful techniques are utilized to investigate the electronic structure of EuO on the atomic scale. The samples magnetism is investigated by means of the Magneto Optical Kerr Effect (MOKE). Ultrathin (3.3 nm) closed films or grains of EuO(100) on graphene on Ir(111) are grown by reactive molecular beam epitaxy [2] and are studied in situ.

STS measurements in the paramagnetic state at 80 K show standing wave patterns of electrons scattered at defects and step edges are oberserved and reveal the existance of a surface state (SS) in EuO(100) which was predicted by calculations [3] in 2001. A dispersion relation of the standing electron wave pattern is manifested by mapping the unoccupied energy space. The dispersion relation of the SS can be fitted with the parabola of an free electron. Below the ferromagnetic transition temperature T_C=70 K, as revealed by MOKE measurements, the SS is spin split by 0.7eV as expressed by a downward shift of one component of the now spin splitted SS by 0.35 eV.

[1] P. G. Steeneken et al., PRL 88, 047201 (2002).
[2] J. Klinkhammer, D. F. Förster, S. Schumacher, C. Busse and T. Michely, in preparation.

[3] R. Schiller and W. Nolting, PRL 86, 3847 (2001).

Effect of martensitic transition on the electronic structure of $Ni_2Mn_{1+x}Sn_{1-x}$ ($0.40 \leq x \leq 0.52$)

S Singh[1], G Adhikary[2], D Biswas[2], K Maitai[2] and C Biswas[1]

[1]S N Bose National Centre for Basic Sciences, India, [2]Tata Institute of Fundamental Research, India

In the recent years disordered Heusler alloys exhibiting martensitic transition has been explored in search of advanced functional material. The off-stoichiometric $Ni_2Mn_{1+x}Sn_{1-x}$ alloys exhibit magnetic field induced shape memory effect, large inverse magnetocaloric effect, and giant magnetoresistance. The various functional properties are due to magnetic field induced reverse phase transition. In the presence of magnetic field martensite phase is unstable. Thus changes in electronic states might be responsible for the unstable martensite which in turn causes magnetic field induced reverse phase transition. The polycrystalline samples of $Ni_2Mn_{1+x}Sn_{1-x}$ ($0.40 \leq x \leq 0.52$) are prepared by arc melting process in pure argon atmosphere. The x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurementsin the austenitic and martensitic phase have been done to understand the relation of electronic structure to the martensitic transition and magnetic field induced reverse phase transition. In the austenitic phase UPS VB exhibits two features at 1.0 eV and 1.6 eV binding energy (BE) similar to that obtained by high energy XPS. The Valence electronic structure modify upon martensitic transition along with the core level shift. The pseudogap in the spectral DOS can be seen at Fermi edge upon the martensitic transition. The depth of pseudogap increases at low temperature within the martensitic phase. Interestingly, within the martensitic phase at low temperature the XPS and UPS spectra are found to be similar as austenitic phase.

Two probe conductance measurements on gold nanostructures assembled at Ge(001) surface

M Wojtaszek, M Kolmer, S Godlewski, B Such, F Krok and M Szymonski

Jagiellonian University, Poland

Recent concepts in nanoscale electronics often invoke molecular circuits which must be connected to the external environment by a set of conductive nanopads (nano-electrodes) and interconnected by a network of atomic and/or molecular wires able to make an Ohmic contact directly with the molecules. Therefore, surface resistance of conductive 2D nanopads and/or nanowires, fabricated on semiconductor surfaces should be known/characterized as a function of the distance down to a nanometer range. One of potentially suitable systems allowing for investigations of its surface conductance properties consist of gold atomic chains assembled on Ge(001) surface. After annealing, gold forms a network of islands surrounded by atomically flat areas covered with well reconstructed conducting wires, hosting a 1D electron liquid [1-3].

In this work, we present results of surface conductance measurements performed for such nanostructures using 2-probe STM tips navigated by a high resolution scanning electron microscope. Surface nanostructures are obtained by deposition of 6 monolayers of gold on the clean, reconstructed Ge(001) surface kept at temperature of 150K. After deposition, the sample is annealed to temperature above 720K causing the formation of desired structures. The conductance dependence on the distance between the probes (in range of 500 nm to 10 mm) confirms its surface 2D character.

[1] C. Blumenstein, J. Schaefer, S. Mietke, S. Meyer, A. Dollinger, M. Lochner, X. Y. Cui, L. Patthey, R. Matzdorf, R. Claessen, Nat. Phys., 7 (2011) 776.
[2] J. Schaefer, C. Blumenstein, S. Meyer, M. Wisniewski, R. Claessen, Phys. Rev. Lett., 101 (2008) 236802.
[3] J. Wang, M. Li, E. Altman, Surf. Sci., 596 (2005) 126.

(invited) Graphene – electronic structure of a model 2-dimensional solid

K Horn[†]

Fritz Haber Institute of the Max Planck Society, Germany

[†] Work performed in close collaboration with A Bostwick, A Walter, J McChesney, T Ohta, T Seyller, and E Rotenberg.

The discovery of graphene, a material that exhibits most unusual properties and promises a wealth of applications, has opened a new chapter in solid state physics, as documented by literally thousands of publications on the material since its experimental realization in the early 2000's. The study of graphene by means of angle-resolved photoemission is particularly fruitful since single-particle as well as many-body aspects of its electronic band structure are revealed in detail. The talk will cover the band structure of single and bilayer/multilayer graphene, with particular emphasis on the shape of the bands at the so-called Dirac point which gives rise to the massless character of charge carriers at the Fermi level. An important aspect in these studies is the possibility to induce ambipolar doping by chemical means, to change the position of the Fermi level over a wide range; this gives access to a multitude of effects, showing a warping of the Fermi surface under strong n-doping, for example. Emphasis will be laid on the analysis of the spectral function of graphene in terms of the coupling of the photohole to elementary excitations such as phonons and plasmons, and the effect of defects on the shape of the Fermi surface and scattering rate. The analysis of such data shows that graphene is ideally suited to study solid state physics in a 2D solid.

Coulomb blockade observed on a nano-sized gold cluster with pendulum AFM

M Langer, M Kisiel, U Gysin and E Meyer

University of Basel, Switzerland

Ultrasensitive cantilevers in the pendulum geometry can be used for probing a wide range of electronic properties of surfaces [1,2]. Due to the high force sensitivity (aN/Sqrt(Hz)) and small internal friction coefficient (10^{-12}Kg/s) we have also access to probe dissipation mechanisms of different materials.

Deposition of nano-sized clusters of gold on 4ML insulating NaCl film grown on Cu(100) results in the formation of Au-Quantum Dots (Au-QDs) coupled to the Cu electron reservoir underneath. System composed of Au-QDs, NaCl tunneling barrier and Cu back electrode is a tunneling junction and an AFM tip positioned on top of the QD is a probing gate electrode coupled capacitively to it. Thus, we are able to investigate the electronic structure of an individual quantum dot.

Results show the change of dissipated power as a function of the bias voltage applied between tip and Cu sample. Observed peaks in the dissipation signal are attributed to charging and de-charging events of a QD. The distance between the observed spikes allows us to calculate the charging energy of the nano-sized Au clusters. Furthermore, constant height energy dissipation images reveal how the energy is dissipated in the space around the Au quantum dot.

[1] M. Kisiel, Suppression of electronic friction on Nb films in the superconducting state, Nature Materials 10,119–122 (2011).

[2] Y. Myahara, Detection of Single-Electron Charging in an Individual InAs Quantum Dot by Noncontact Atomic-Force Microscopy, PRL 94, 056802 (2005).

Effect of photoelectron mean free path on the photoemission cross section of noble metal Shockley states

J Lobo-Checa[1], J E Ortega[2], A Mascaraque[3], E G Michel[4] and E E Krasovskii[5]

[1]ICN2-CFM (CSIC), Spain, [2]Centro de Fisica de Materiales CSIC/UPV-EHU-Materials Physics Center, Spain, [3]Universidad Complutense de Madrid, Spain, [4]Universidad Autonoma de Madrid, Spain, [5]Donostia International Physics Center (DIPC), Spain

Every solid-state material has electrons at its surface with spatial and energetic distributions that depend on both the atomic elements that conforms it and its crystalline structure. These surface electrons can give rise to well defined surface states, such as Shockley states in the case of noble metals. The intensity of these vary with the photon energy as illustrated by its photoemission cross-section [1,2].

By combining angle resolved photoemission (ARPES) experimental data with *ab initio* calculations we are able to understand the complex photoemission cross-section of the Shockley states of (111) terminated noble metals. The generally accepted final-state free-electron band picture based on the nearly-free-electron (NFE) model fails to reproduce the unprecedented fine details observed [3]. Furthermore, the width of the photoemission cross-section curve has no straight relation to the wave function penetration depth, as often believed. Importantly, the differences observed in the photoemission cross-section at the *L* resonance between the two noble metals can be rationalized with the outgoing electron's mean free path, as calculated from the crystal band structure and the optical potential. The present results are particularly relevant for nanostructured systems, for example vicinal surfaces, where the resonant character of their surface states might be investigated through such kind of photoemission cross-section curves—in particular, the question of whether the surface state changes into a surface resonance when increasing the density of steps at the surface, which is still controversial.

[1] S. D. Kevan et al., PRB 36, 5809 (1987).
[2] T.C. Hsieh et al., PRB 35, 3728 (1987).
[3] J. Lobo-Checa et al., PRB 84, 245419 (2011).

Semiconductors and their surfaces 3

(invited) Coherent optical control of excitons and spins in quantum dots

M Fox

The University of Sheffield, UK

Excitons and spins in individual quantum dots are very promising candidates for applications in quantum information processing on account of their long dephasing times compared to semiconductor systems of higher dimensionality. In this presentation, recent progress on the coherent optical control of excitons and spins in self-assembled InGaAs quantum dots will be reviewed. The experiments have been performed by exciting single dots with laser pulses shorter than the coherence time and reading out the outcome by photocurrent spectroscopy. In single-pulse experiments, the state vector of an excitonic qubit can be manipulated on an ultrafast timescale by laser-driven Rabi rotations. Detailed measurements indicate that the dominant dephasing mechanism at high temperatures and high pulse areas is acoustic phonon scattering. [1] The different tunnelling rates of the electrons and holes can be exploited to investigate the dynamics of individual hole spins in charged dots, which are especially interesting on account of their small hyperfine interaction and hence long dephasing time. By using sequences of time-delayed pulses, it has been possible to demonstrate picosceond preparation, full control, and read-out of a single hole spin. [2] These experiments demonstrate the excellent potential of InGaAs quantum dots for ultrafast quantum information processing.

[1] A.J. Ramsay, et al., “Damping of exciton Rabi rotations by acoustic phonons in optically excited InGaAs/GaAs quantum dots”, Phys. Rev. Lett., 104, 017402, 2010; “Phonon-Induced Rabi-Frequency Renormalization of Optically Driven Single InGaAs/GaAs Quantum Dots”, Phys. Rev. Lett., 105, 177402, 2010

[2] T.M. Godden et al, "Coherent optical control of the spin of a single hole in an InAs/GaAs quantum dot," Phys. Rev. Lett., 108, 017402, 2012; “Fast preparation of a single-hole spin in an InAs/GaAs quantum dot in a Voigt-geometry magnetic field,”Phys. Rev. B, 85, 155310, 2012.

Spectroscopy of spin excitations in artificial honeycomb lattice nanofabricated in semiconductor quantum heterostructures

A Gamucci[1], B Karmakar[1], M Polini[1], A Singha[2], A Pinczuk[3], L N Pfeiffer[4], K W West[4] and V Pellegrini[2]

[1]Istituto Nanoscienze-CNR & Scuola Normale Superiore, Italy, [2]Bose Institute, India, [3]Columbia University, USA, [4]Princeton University, USA

The quest to artificially build a honeycomb lattice capable of reproducing the properties of graphene is one of the hottest topics in current condensed-matter experimental research [1,2,3]. Periodic honeycomb patterns nanofabricated on semiconductor quantum wells hosting two-dimensional electron gas (2DEG) open the possibility to study the Mott-Hubbard physics in “artificial graphene” (AG) samples for a wide and custom range of lattice parameters. The formation of Hubbard bands and the occurrence of collective spin-wave and spin-flip modes in an AG sample have been evidenced so far in inelastic light scattering experiment [1]. We report here our recent progresses on the nanofabrication and optical study of AG samples with different lattice constants. The honeycomb patterns with lattice constants in the range of 90 nm-130 nm have been realized by means of state-of-the-art electron beam lithography and dry-etching on GaAs/AlGaAs modulation-doped quantum well hosting 2DEG. We shall discuss inelastic light scattering measurements in magnetic fields that reveal a remarkable impact of Coulomb interaction in the artificial lattice. In particular we report the observation of an anomalous spin-flip mode above the Zeeman gap that appears above a critical magnetic field [1,4]. The results in AG samples with different lattice constants are suggestive for the occurrence of novel spin phases dictated by the geometry of the pattern.

[1] A.Singha *et al.*, Science 332, 1176 (2011).
[2] L.Tarruell *et al.*, Nature 483, 302 (2012).
[3] K.K.Gomes *et al.*, Nature 483, 306 (2012).
[4] A. Gamucci *et al.*, in preparation.

D'yakonov-Perel' spin relaxation in finite-size systems

V Slipko[1] and Y Pershin[2]

[1]V.N. Karazin Kharkiv National University, Ukraine, [2]University of South Carolina, USA

The D'yakonov-Perel' spin relaxation mechanism in two-dimensional (2D) systems has attracted wide attention because of its fundamental importance for the field of spintronics. However, while almost all previous studies of the D'yakonov-Perel' spin relaxation have been focused on infinite semiconductor systems, the influence of the sample boundaries (actually, boundaries exist in any experimental system or device) on spin relaxation has received much less attention. We have found that the sample boundaries can dramatically change the character of spin relaxation [1,2] and result even in an incomplete spin relaxation in 1D case [2].

An exact solution for the problem of D'yakonov-Perel' electron spin relaxation in 2D cirles with Rashba spin-orbit interaction has been found [1]. One may think that in small systems the spin relaxation is incomplete as the spin precession angle across the system is small. However, in such a situation, the different effect plays a role: the noncommutativity of spin rotations. Because of this effect, the electron spin precession angle can largely exceed the maximum rotation angle allowed by naive geometrical considerations. Our analysis shows that the spin relaxation in finite-size regions involves three stages and is described by multiple spin relaxation times. It is important that the longest spin relaxation time increases with the decrease in system radius but always remains finite. Therefore, at long times, the spin polarization in small 2D systems always decays exponentially with a size-dependent rate. This prediction is supported by results of Monte Carlo simulations.

[1] V.A. Slipko and Y.V. Pershin, Phys. Rev. B 84, 075331 (2011).
[2] V.A. Slipko, I. Savran and Y.V. Pershin, Phys. Rev. B 83, 193302 (2011).

(invited) Single atom devices for quantum computing

M Simmons

Australian Research Council Centre of Excellence for Quantum Computation and Communication Technology, Australia

Over the past decade we have developed a radical new strategy for the fabrication of atomic-scale devices in silicon [1-3]. Using this process we have demonstrated that Ohm's Law survives to the atomic-scale [4,5] and the formation of all-epitaxial single electron transistors [6,7] down to the few electron limit. Most recently we have demonstrated a precision single atom transistor [8]. We will present atomic-scale images and electronic characteristics of these atomically precise devices and demonstrate the impact of atomically abrupt vertical and lateral confinement on electron transport. We will also highlight some recent results towards single shot spin read-out of these precisely placed donors and present some of the challenges to achieving truly scalable donor based quantum computing architectures in silicon.

[1] S. R. Schofield et al., Physical Review Letters 91, 136104 (2003).
[2] H.F. Wilson et al., Physical Review Letters 93, 226102 (2004).
[3] F. J. Rueß et al., Nano Letters 4, 1969 (2004).
[4] F. J. Rueß et al., Small 3, 567 (2007); Nanotechnology 18, 044023 (2007).

[5] B. Weber et al., Science 335, 64 (2012).
[6] A. Fuhrer et al., Nano Letters 9, 707 (2009).
[7] M. Fuechsle et al., Nature Nanotechnology 5, 502 (2010).
[8] M. Fuechsle et al., Nature Nanotechnology, DOI: 10.1038/NNANO.2012.21, Published on-line:19 February (2012).

The relationship between minimum gap and success probability in adiabatic quantum computing

J H Samson, M Cullimore, M Ormerod, R Wilson and M Everitt

Loughborough University, UK

Adiabatic Quantum Computing (AQC) is a promising technique for solving optimisation problems: the Hamiltonian of a system is slowly evolved from one with a simple ground state to one whose ground state encodes the solution. We explore the relationship between two figures of merit for an AQC process: the *success probability* and the *minimum gap* between the ground and first excited states [1]. We study a generic adiabatic algorithm and show that a rich structure exists in the distribution of these two important variables. In the case of two qubits, the success probability is to a good approximation a function of the minimum gap, the stage in the evolution at which the minimum occurs and the computation time. This structure persists in examples of larger systems.

[1] Cullimore M *et al*, arXiv:1107.4034.

Zero-frequency noise in adiabatically driven, interacting quantum systems

R Riwar[1], J Splettstoesser[1] and J König[2]

[1]RWTH Aachen University, Germany, [2]Universität Duisburg-Essen, Germany

We investigate the noise created by an adiabatically driven quantum dot pump, subject to Coulomb interaction. In order to calculate the zero-frequency noise including effects of strong Coulomb interaction, we make use of a real-time non-equilibrium diagrammatic approach within a perturbative expansion in the tunnel coupling to the reservoirs. We develop an approach to include a treatment of the explicit slow time dependence of the Hamiltonian to the calculation of the zero-frequency current noise. As a generic example, we consider the case of a single-level quantum dot coupled to two electronic reservoirs, where charge pumping arises by applying two out-of-phase time-dependent parameters, such as the energy levels, the bias or the tunnel couplings.

Apart from the usual thermal and shot noise, we find a pumping contribution which is at the center of our interest. A direct analysis of the different contributions is made possible by expressing the noise in terms of dot quantities, which are local in time, and by their time derivatives. If the leads are at equilibrium at any time, the adiabatic correction of the Fano factor is robust against the choice of the pumping parameters and provides information about the tunnel-coupling and the electron-hole symmetric point. In addition, we find that the noise in zeroth order in the driving frequency is given by a time-averaged fluctuation dissipation relation; however, for the pumping noise we identify a correction term, which is uniquely due to the non-vanishing Coulomb interaction.

In the presence of an additional time-dependent bias voltage, we find that there can be pumping noise even if there is zero pumped charge, which enables us to distinguish different pumping processes. The noise can therefore provide information inaccessible through the pumped charge.

Nanostructures 3

(invited) Frontiers in the atomistic modeling of the excited states of nanostructures

G Bester

Max-Planck-Institut für Festkörperforschung, Germany

Semiconductor nanostructures exhibit a range of interesting properties with potential technological applications. This situation has fueled a large international effort and a rapid progress in different research areas (optics, transport, epitaxial growth, nanochemistry,...). Besides the burning technological interest, these structures also conceal a multiplicity of fundamental questions about "confined matter". I will describe the methodological advanced we have made to properly connect experimental evidence with an ab-initio theory. This involves the calculation of not only ground state properties, but mostly excitations (optics, transport, vibrations) for structures that often contain may thousands of atoms. I will discuss intrinsic effects, such as the atomistic symmetry, spin-orbit interaction, piezoelectric effects and also extrinsic effects, such as the consequence of external pressure or electric fields on electronic and optical properties.

Transforming luminescent silicon nanocrystals into a direct-bandgap semiconductor via surface-capping-induced strain

P Jelinek, K Kůsová, P Hapala and I Pelant

Institute of Physics of the Czech Academy of Science, Czech Republic

We report on combined experimental and theoretical work pointing out the possibility of converting Silicon Nanoparticles (SiNcs) to a luminescing direct-band gap material via the concerted action of the quantum confinement and tensile force induced by proper surface passivation.

The transformation of silicon, originally a very poor light emitter due to its indirect band gap, into a light-emitting medium is a key challenge from the application point of view. One promising way to achieve this goal is through dramatic shrinkage in the size of the crystal down to nanoscale. The observation of an efficient room-temperature luminescence [1] from SiNcs initiated the debate about the nature of their band structure. The most common silicon-oxide-capped SiNcs maintain the indirect bandgap showing long radiative lifetimes (>100 μs) [2].

Beside the size of the nanocrystal, a proper surface passivation (capping) also plays an important role in the light emission. Recently, we have shown that SiNcs sized 3 nm with methyl-based surface passivating layer [3] exhibit luminescence properties (short radiative lifetime ~10 ns and enhanced quatum yield ~20%) analogical to a direct-bandgap semiconductor. This property is further supported by single-nanocrystal luminescence experiments giving emission pattern very similar to that observed in direct-bandgap CdSe nanoparticles [4].

To understand the impact of surface passivation on the electronic structure of SiNcs we performed total energy DFT calculations including up to 1500 atoms and different surface groups (-H,-CH_3,-OH). Our calculations show that the presence of methyl group leads to significant elongation of the Si-Si distances. Further we restore band structure of SiNc mapping real space molecular orbitals into the momentum space [6]. The resotred band structure clearly shows that combination of tensile stress and the quantum confinement strongly modifies dispersion of the conduction band along the Γ-X direction enhancing direct bandgap transition.

[1] L. Canham, App. Phys. Lett. 57, 1046 (1990).
[2] D. Kovalev et al, Phys. Rev. Lett. 81, 2803 (1998).
[3] K. Kůsová et al ACS Nano, 4(8), 4495 (2010).
[4] X. Wang et al Nature 459, 686 (2009).

[5] K. Kůsová et al (submitted).
[6] P. Hapala et al (submitted).

Discretized total angular momentum basis within eight-band k.p theory: application to heteroepitaxial core-shell quantum dots

T Cheche[1], Y-C Chang[2] and V Barna[1]

[1]University of Bucharest, Romania, [2]Academia Sinica, Taiwan

Within the eight-band k.p method and the total angular momentum theory [1], we create a numerical code for computation of the electronic energy structure of heteroepitaxial semiconductor coreshell quantum dots. The modeling takes into account the heteroepitaxial strain, which is introduced by a continuum elasticity model. The leading idea of our discretization algorithm is developing the envelope wave functions in terms of the hard-sphere eigenfunctions. Our method overcomes the limitations of the widely used plan-wave method, which introduces artificial physical interactions when one wishes to study the energy structure of a single quantum dot.

The code is applied to the type II ZnTe/ZnSe semiconductor heterostructure, and the energy structure of the quantum dot for an axial symmetry of the kinetic eight-band k.p Hamiltonian is obtained. Then we calculated the absorption spectra. As result of the spherical symmetry of the quantum dot shape and axial symmetry of the kinetic Hamiltonian, the absorption spectra that we calculated for the left and right circular polarization are identical. The space distributions of the charge carriers (orbitals) are simulated too. We obtain the charges distribute according to the type II ZnTe/ZnSe heterostructure, with the hole inside the core and the electron migrating into the shell with the shell thickness. The orbitals shapes reflect the axial symmetry of the eightband kinetic k.p Hamiltonian we used. A good match is obtained when the orbitals shapes are compared with those predicted by an atomistic approach.

[1] P.C. Sercel and K.J. Vahala, Phys. Rev. B 42, 3690(1990)

Efficient hole surface trapping via inverse Auger cooling in CdSe nanocrystal quantum dots

M Califano[1] and F M Gomez Campos[2]

[1]University of Leeds, UK, [2]Universidad de Granada, Spain

Carrier trapping is one of the main sources of performance degradation in nanocrystal-based devices. Yet very little is known about the specific mechanisms that govern this phenomenon. Recent experimental investigations have shown that, although in principle both electrons and holes can undergo trapping, in the case of a band edge exciton, surface trapping occurs only for the hole but not for the electron.

We present a comprehensive investigation into the efficiency of hole transfer to a variety of trap sites located on the surface of the core or the shell or at the core/shell interface, in CdSe nanocrystals with both organic and inorganic passivation, using LDA-quality wavefunctions within the semiempirical pseudopotential approach.

The results of our investigation show that, as in the case of the electron [1], the hole trapping times are highly dispersed, and range from hundreds of femtoseconds to tens of nanoseconds, in remarkable agreement with the range of decay components identified for the band edge exciton by Knowles et al. [2] (and attributed to different subpopulations of traps characterised by different trapping constants), and with recently observed excited state trapping times [3]. This large variation can be obtained not only for an ensemble but also for a single trap, due to energy diffusion. This finding provides the first quantitative theoretical confirmation of the validity of one of the most successful models explaining blinking ever presented [4,5], which relays heavily on such an assumed (but as yet undemonstrated) large variation for the trapping times as a function of the trap energy.

[1] S. J. Kern, K. Sahu, M. A. Berg, Heterogeneity of the Electron Trapping Kinetics in CdSe Nanoparticles. Nano Lett. 11 3493-3498 (2011).
[2] K. E. Knowles, E. A. McArthur, E. A. Weiss, A Multi-Timescale Map of Radiative and Nonradiative Decay Pathways for Excitons in CdSe Quantum Dots. ACS Nano, 5, 2026 (2011).
[3] P. Kambhampati, Hot Exciton Relaxation Dynamics In Semiconductor Quantum Dots: Radiationless Transitions on the Nanoscale. J. Phys. Chem. C 115, 22089-22109 (2011).
[4] P. A. Frantsuzov, R. A. Marcus, Explanation of Quantum Dot Blinking Without the Long-Lived Trap Hypothesis. Phys. Rev. B 72, 155321 (2005).
[5] P. A. Frantsuzov, M. Kuno, B. Janko, R. A. Marcus, Universal Emission Intermittency in Quantum Dots, Nanorods and Nanowires. Nat. Phys. 4, 519-522 (2008).

(invited) Controlled coupling of co-propagating edge states in the integer quantum Hall effect

F Taddei

NEST, NANO-CNR, Italy

Due to the large electronic phase coherence length, 2DEGs in the integer quant Hall (IQH) regime appear to be specially suited for electronic interferometry, a very stimulating phenomenon both for basic science and for its various possible applications. A breakthrough in this field has been the experimental realization of electronic Mach-Zehnder and Hanbury-Brown and Twiss interferometers. In these experiments electrons in the edge states loop around an annular structure mimicking the optical paths of their photonic counterparts. An alternative theoretical scheme was later proposed which would allow for a concatenation of several Mach-Zehnder interferometers in series. This new opportunity of scalability, which is not topologically possible in the first setups experimentally developed, exploits the interference between adjacent edge channels with the same chirality, coupled by means of some localized potential.

In this talk I will discuss different methods to controllably couple two co-propagating edge states in the IQH regime, which makes use of: i) a movable electrostatic potential induced by a biased atomic force microscope tip - for spin-degenerate edge states; ii) a spatially periodic in-plane magnetic field that is created by an array of Cobalt nanomagnets placed at the boundary of the 2DEG - for spin-resolved edge states. Finally I will describe a proposal for realizing a resonant spin-field-effect transistor for spin-resolved edge states, which exploits the Rashba spin-orbit interaction and employs a periodic array of voltage-controlled top gates that locally modulate such interaction.

An experimental UHV AFM-STM device for characterizing surface nanostructures under stress at variable temperatures

Y Nahas, F Berneau, J Bonneville, C Coupeau, M Drouet, B Lamongie, M Marteau, J Michel, P Tanguy and C Tromas

Institut Pprime, France

An experimental device working under ultrahigh vacuum environment has been developed to follow in-situ at the atomic resolution the evolution by AFM-STM of surfaces under stress at various temperatures. Samples can be deformed at different strain rates ranging from 10^{-6} s^{-1} to 10^{-2} s^{-1}, up to stresses of 500 MPa over a wide range of temperature 80-700 K.

Our attention is currently focused on two research topics: on the one hand, the finding of new ways for surface nanostructurations to provide specific functional properties and, on the other hand, a better understanding of elementary mechanisms of plastic deformation from signatures left at nanometer scale by the emergence process of dislocations.

The first results related to surface nanostructurations concern gold and silicon surfaces, which have significant potential as templates for the growth of nano-objects. In particular, we study the influence of the stress field and temperature on the genesis and evolution of these nanostructures.

Concerning the elementary dislocation mechanisms controlling plasticity, we work on the ordered intermetallic Ni_3Al. The fine slip line structure has been characterized on single crystals at different temperatures. These results are compared and discussed with previous models proposed in the literature to explain the yield stress anomaly of such compounds.

Linear self-assembly of nanoparticles within smectic liquid crystal defect patterns

D Coursault[1], J Grand[2], B Donnio[3], J-L Gallani[3], B Zappone[4], G Lévi[2], N Félidj[2] and E Lacaze[5]

[1]Université Pierre et Marie Curie, France, [2]ITODYS, France, [3]IPCMS, France, [4]LICRYL, Italy, [5]INSP, France

Technical progress offers now various methods to build hybrid and nanostructured materials with new properties. In case of gold nanoparticles (GNPs), the creation of straight chains of single NPs is of great interest due to the induced anisotropic optical properties associated with localized surface plasmon resonance (LSPR). We show that patterns of linearly self organized LC defects in smectic phase [1] can force self-assembly of NPs leading to straight and parallel chains of GNPs and quantum dots, all parallel from each other for one given sample. [2] The LSPR arising from the GNPs becomes polarization dependent: we observe shifts of plasmonic extinction as large as 40 nm when polarization of incident light varies.

The chains have a width comparable to the size of a single NP and can be as long as hundreds of µm. Separation between NPs in a given chain varies from a few µm to 1.5 nm as the concentration increases by 4 orders of magnitude. The minimum distance between particles is related to the thickness of their surfactant layer and appears to be also related to the NPs radius of curvature, which controls the interdigitation of the molecules grafted around NPs. Finally we evidence that nano-rods as well can be preferentially confined within the LC defects which opens the route for a vast number of applications.

[1] E. Lacaze, J.P. Michel, M. Goldmann, M.de Boissieu, M. Gailhanou, M. Alba, Phys. Rev. E,70, (2004).
[2] D. Coursault, J. Grand, H. Ayeb, B. Zappone, G. Lévi, N. Félidj, E. Lacaze, Adv. Mat.,24, (2012).

Hole spin mixing mechanism in semiconductor quantum dots

J Planelles, C Segarra and J-I Climente

Universitat Jaume I, Spain

Valence band mixing greatly influences optical polarization and exciton spin dynamics[1], as well as the performance of qubits based on hole spins.[2] The heavy – light hole (HH-LH) coupling primarily depends on differences on effective masses, leading to a different weight of the diagonal elements of the valence Hamiltonian. Highly desired hole spin purity is present in some quantum dots (QDs), as e.g. GaN/AlN QDs with zinc-blende internal structure. [3] We address the theoretical understanding of this feature as compared to the most commonly fabricated InGaAs/GaAs QDs. [4]

A second relevant factor influencing hole band mixing is the potential shape. [5] We address the differential mixing in QDs and quantum rings (QRs). In addition, we explore the relevance on band mixing of the third order Dresselhaus terms. Recent studies using single-band effective Hamiltonians suggest this term plays a dominant role in the hole spin mixing.[6] Here we assess this claim using an truly multi-band model. Finally, we study the influence on the robustness of theoretical results of assuming or relaxing the axial approximation in the valence Hamiltonian of axially symmetric systems.

[1] H. Tong and M. Wu, Phys. Rev. B 83 (2011) 235323.
[2] D. Brunner et al. Science 325 (2009) 70.
[3] D. Lagarde et al., Phys. Rev. B 77 (2008) 041304(R).
[4] C. Segarra et al., J. Phys. Condens. Matter 24 (2012) 115801.
[5] J. I. Climente and J. Planelles, J. Nanoelectron. Optoelectron. 6 (2011) 81.
[6] D. Bulaev and D. Loss, Phys. Rev. Lett. 95 (2005) 076805; Y.H. Liao et al. Phys. Rev. 83, 165317 (2011).

Surface dynamics 1

The quantum diffusion of H on Ru(0001)

E McIntosh[1], K T Wikfeldt[2], J Aarons[3], J Zhu[4], M Probert[3], A Michaelides[2], W Allison[1] and J Ellis[1]

[1] University of Cambridge, UK, [2]University College London, UK, [3]The University of York, UK

The interaction of hydrogen with transition metal surfaces is important, not only due to practical applications in catalysis, electro-chemistry, and hydrogen fuel cells, but also to compare with theoretical results, as hydrogen atoms are one of the few chemical species with sufficiently low mass for quantum processes to dominate the surface transport at lower temperatures [1-3]. Ab initio methods have previously been used to interpret experimental data [4-5], but no uniform picture to predict the diffusion behaviour and isotopic dependence has emerged.

We present recent Spin-Echo [6] results for the adsorption and diffusion of H/D adsorbed on Ru(0001). Our results indicate a transition to deep quantum tunnelling at relatively high temperatures, in a system with low adsorbate-substrate friction and strong lateral inter-adsorbate interactions.

A variety of methods have been used to analyse and interpret the data, including Path Integral Molecular Dynamics and Monte Carlo simulations, together with proton band-structure calculations.

[1] A. P. Jardine et al, Phys. Rev. Lett. 105 (2010) 136101.
[2] L. Lauhon and W. Ho, Phys. Rev. Lett. 85 (2000) 4566.
[3] X. Zhu et al., Phys. Rev. Lett. 68 (1992) 1862.
[4] T. Mattsson & G. Wahnström, Phys. Rev. B 56 (1997) 14944.
[5] P. G. Sundell & G. Wahnström, Phys. Rev. B 70 (2004) 081403.
[6] A. P. Jardine et al, Prog. Surf. Sci. 84 (2009) 323.

Atomic scale friction: a slippery customer

J Aarons and M Probert

The University of York, UK

Friction is a well known phenomenon, yet its origins on the atomic scale remain unknown. Novel techniques such as Helium-3 Spin Echo Interferometry, allow for the resolution of fast diffusion processes on atomic length-scales [1], yet their interpretation is not straightforward.

Computer simulations may be employed to shed some light on the experimental findings. Unfortunately conventional molecular dynamics (MD) methods severely underestimate diffusion and over-estimate barrier heights (especially for low mass nuclei) due to their neglect of quantum nuclear effects [2].

Path integral molecular dynamics (PIMD) allows for full treatment of quantum mechanical delocalisation of the nuclei including tunnelling and effective barrier lowering. The approach has been adapted so that real-time dynamics are obtained on time-scales commensurate with those seen in experiment [3].

We will present a computational study of atomic scale friction, using hydrogen on a metal surface as a model system. The results of PIMD simulations will be compared with experimentally obtained data from recent Helium-3 Spin Echo Interferometry experiments.

[1] A.P. Jardine *et al*, Prog. Surf. Sci. 84, 11–12 (2009).

[2] D. Marx and M. Parrinello, Z. Phys. B (Rapid Note) 95, 143 (1994).

[3] M.E. Tuckerman *et al*, J. Chem. Phys. 104, 5579 (1996).

How fast is fast? Experimental challenges to Markovian dynamics though a study of pre-diffusive motion

D Ward, W Allison and J Ellis

University of Cambridge, UK

Significant opportunities in the understanding of surface dynamics have arisen through the development of spin echo helium atom scattering[1]. Recent experimental work includes areas such as the quantum diffusion of Hydrogen[2], dynamics on metal-oxides and semiconductor substrates, and the observation of both translational and rotational dynamics in molecular systems[3]. A fundamental tool in the analysis of experimental data is provided by molecular dynamics simulations using a Markovian, Langevin thermostat. The intermediate scattering function (ISF), which describes time correlations, can be calculated for direct comparison with experiment.

In the long time limit, where the motion is diffusive, the ISF is generally well understood[1]. At short times, before the onset of diffusive behaviour, less is known except for very simple systems[4,5]. The pre-diffusive regime is critical to understanding adsorbate-substrate energy transfer and interactions. New, pre-diffusive experimental measurements of atomic adsorbates are presented. Processes that can be studied in this time regime are explored with reference to existing theoretical models[4,5]. The observations show clear deviations from the expectations of Markovian friction on a sinusoidally corrugated substrate.

[1] AP Jardine, H Hedgeland, G Alexandrowicz, W Allison, and J Ellis, Progress in Surface Science84, 323-379 (2009).

[2] AP Jardine, EYM Lee, DJ Ward, G Alexandrowicz, H Hedgeland, W Allison, J Ellis, and E Pollak. *Phys. Rev. Lett.* 105 136101 (2010)

[3] S Paterson, W Allison, H Hedgeland, J Ellis, and AP Jardine. *Phys. Rev. Lett.* 106 256101 (2011)

[4] R Martínez-Casado, JL Vega, AS Sanz, and S Miret-Artés, *Journal of Physics: Condensed Matter* 19, 305002 (2007).

[5] R Martínez-Casado, JL Vega, AS Sanz, and S Miret-Artés, *Journal of Physics: Condensed Matter* 19, 176006 (2007).

H_2 diffraction from a strained pseudomorphic monolayer of Cu deposited on Ru(0001)

C Díaz[1], F Madrid[1], G-J Kroes[2], M Minniti[1], D Farías[1] and R Miranda[1]

[1]Universidad Autónoma de Madrid, Spain, [2]University of Leiden, The Netherlands

Diffraction of atoms (H, He) and light molecules (H_2, D_2) from surfaces has been proposed as a very useful tool to characterize the potential energy surface (PES) of these systems [1], because diffracted atoms and molecules are very sensitive to the PES characteristics [2]. Here, we have studied diffraction of H_2 from a strained pseudomorphic monolayer of Cu deposited on Ru(0001) (H_2/Cu/Ru(0001)), both experimentally and theoretically. Our experimental measurements show a remarkable diffraction probability, both in-plane and out-of-plane. In particular, we observe for the first time third-order diffraction peaks. These striking experimental results have been analyzed by performing theoretical simulations, using both quantum and quasi-classical dynamics methods. Taking into account the relationship between diffraction (quantum phenomenon) and reflection (classical observable), we have performed a classical analysis on a meaningful set of classical trajectories. This analysis reveals that for H_2/Cu/Ru(0001), diffracted molecules practically explore the whole PES, thus favoring high order diffraction. We have also compared H_2/Cu/Ru(0001) diffraction results with those obtained for H_2/Cu(111) [3] and H_2/Ru(0001)

[4]. This comparison have allowed us to investigate the possible relationship between diffraction and dissociative adsorption.

[1] D. Farías and R. Miranda, Prog. Surf. Sci. 86, 222 (2011).
[2] D. Halstead and S. Holloway, J. Chem. Phys. 88, 7197 (1988).
[3] C. Díaz et al J. Phys. Chem. C 114, 11192 (2010).
[4] P. Nieto, et al, Phys. Chem. Chem. Phys. 13, 8583 (2011).

On the relation between fluctuations in STM currents and diffusion coefficients of molecules on surfaces

S Hahne[1], J Ikonomov[2], M Sokolowski[2] and P Maass[1]

[1]University of Osnabrück, Germany, [2]University of Bonn, Germany

Most common experimental methods for determining diffusion coefficients of molecules on surfaces involve particle tracking or a measuring of island densities. Both these techniques are quite extensive and restricted in their adaptability. Particle tracking is limited to sufficiently small mobilities and the measurement of island densities needs to be performed on large defect-free areas in order to allow for a reliable theoretical interpretation. An alternative approach is the recording of signal fluctuations from a locally fixed probe. The challenge is to relate the information entailed in these fluctuations to the diffusion coefficient. We present a refinement of methods based on the auto-correlation function of the signal and the residence time distribution of molecules under the probe. In addition we develop a further new method that relies on the distribution of interpeak times in the signal. This method has the advantage that it is not affected by probe-molecule interactions. We apply all three methods to STM current fluctuations caused by copper phthalocyanine (CuPc) diffusion on Ag(100) and critically discuss their strengths and weaknesses.

1-D vs 2-D diffusion of Cu tetraners on Cu(111) studied by molecular dynamics simulations

J J de Miguel[1], J Ferrón[2] and R Miranda[1]

[1]Universidad Autónoma de Madrid, Spain, [2]Universidad Nacional del Litoral, Argentina

The surface diffusion of Cu tetramers on Cu(111) has been studied by means of Molecular Dynamics simulations using Embedded Atom interatomic potentials [1]. It is found that the Cu clusters diffuse by a concerted hopping mechanism. The topology of the Cu(111) surface introduces an anisotropy in the shape of the Cu tetramers that in turn results in highly anisotropic diffusion. We show how the diffusive movement of the Cu clusters crossover from practically one-dimensional to nearly isotropical two-dimensional with increasing substrate temperature, and analyze the changes in the hopping mechanisms of the individual atoms and in the tetramer morphology that are responsible for this behaviour.

[1] J. Ferrón, R. Miranda and J. J. de Miguel, Phys. Rev. B 79, 245407 (2009).

Does rotational melting make molecular crystal surfaces more slippery?

A Benassi[1], C Pignedoli[1], D Passerone[1] and E Tosatti[2]

[1]EMPA Materials Science & Technology, Switzerland, [2]SISSA - Scuola Internazionale Superiore di Studi Avanzati, Italy

Nanoscale sliding friction shows an interesting non-monotonic behavior at the critical point of model structural phase transitions, and a pronounced dependence on the order parameter value below the critical temperature (Benassi 2011). It has been recently suggested to exploit this sensitivity as a mean to control friction of AFM tips and nano objects. To this aim, a practical structural phase transition to look at, is the rotational melting occurring in C_{60} molecular crystals (fullerite): a first order phase transition leading from an orientationally ordered structure, at low temperatures, with locked fullerene molecules to a disordered one at high temperatures, with freely rotating fullerenes (Laforge 2001). Common sense would lead to think that the unlocking of the fullerene molecules should make the fullerite surface more slippery, thus lowering the friction coefficient, on the other hand the activation of C_{60} rotational degrees of freedom enables new energy dissipation channels leading to an increase in the friction force. To solve this puzzle we simulated the dynamics of a sliding AFM tip driven on top of a fullerite surface across the rotational melting transition. We suggest novel appropriate experiments for exploiting this effect to control nanofriction.

Mechanisms of anisotropic edge retraction during solid-state dewetting of ultra-thin silicon films

F Cheynis, F Leroy, T Passanante and P Müller

CINaM, France

Metastable thin solid films, when annealed, can agglomerate into an assembly of nanocrystals [1]. This dewetting process is a limit for the fabrication of advanced devices in microelectronics but conversely, is also a common method to produce self-organized nanocrystals. As such, a fundamental understanding of the mechanisms governing solid state dewetting is of particular relevance.

Most of the experiments on solid state dewetting concern spontaneous dewetting of continuous thin films [2,3]. However, recent models [4] highlight several crystalline effects (*e.g.* the anisotropy of the dewetting velocity) that cannot be accurately studied through heterogeneous dewetting. Our purpose is to study the anisotropy of solid state dewetting of straight fronts obtained by Electron-Beam Lithography. Our model system is Si(001) thin films on SiO_2 substrate (Silicon-On-Insulator, SOI) with typical thickness in the 20 nm-range. SOI Dewetting experiments have been performed in real time and in-situ using Low-Energy Electron Microscopy. This surface microscopy technique simultaneously gives access to the micrometer-scale structure of the dewetting front and the nanoscale motion of surface atomic-steps.

We show that <110>-oriented edges retract uniformly with a remarkable stability as $h \sim t^{0.4}$ accompanied by a rim-thickening $h \sim t^{0.4}$ (t being time) while <100>-oriented edges are highly unstable. Void fingers are formed perpendicularly to the edges and propagate with $x \sim t$ and $dh/dt=0$. A simple analytical model in which the local front velocity involving the surface free-energy change (*i.e.* the dewetting driving force) and a surface diffusion based mobility nicely reproduces the experimental features.

[1] E. Jiran, C. Thompson, J. Electron. Mater. 19 (1990) 1153.
[2] E. Bussmann, F. Cheynis, F. Leroy, P. Müller, New J. Phys. 13 (2011) 043017.
[3] F. Cheynis, E. Bussmann, F. Leroy, T. Passanante, P. Müller, Phys. Rev. B 84 (2011) 245439.
[4] O. Pierre-Louis, A. Chame, Y. Saito, Phys. Rev. Lett. 103 (2009) 195501.

Dynamics of charging/discharging processes as probed by XPS

S Suzer

Bilkent University, Turkey

We present a novel method to determine how charges are sensed at the molecular level on an insulating polymer film surface when a charging event occurs. Poly(methyl methacrylate) (PMMA) is used as the model system due to its relatively well known chemical and physical properties. Static and dynamic charge sensitive x-ray photoelectron spectroscopy (XPS) measurements are conducted on thin PMMA films spin-coated on a conducting Si substrate.

The peak positions directly reflect the presence and the extent of charging of the films. Accordingly, at the onset of measurements, the PMMA films are negatively charged, but photoelectron emission progressively causes the films to be charged positively. The films can be returned to their negatively charged state by exposing them to low energy electrons via a flood-gun. The influence of the state of the charging is observed to be asymmetric at the molecular level, where we observe that the carbonyl and to some extent the methoxy groups charge differently with respect to the backbone atoms. Likewise the effect of charging on oxygen and carbon atoms are different. Experimentally, these changes are probed either in a static or in a time-resolved fashion, by application of d.c. or square-wave potential pulses to the silicon substrate, respectively, while recording the XPS spectra in the snapshot fashion. Applications to blends and copolymers will also be given.

Organic layers and polymers 4

Isomerization reactions controlled by charge-transfer and the self-assembly of organic acceptors on solid surfaces

R Otero[1], C Urban[1], J Rodriguez-Fernandez[1], Y Wang[1], R Garcia[2], M A Herranz[2], M Alcami[1], N Martin[3], F Martin[1], J M Gallego[4] and R Miranda[1]

[1]Universidad Autonoma de Madrid and IMDEA-Nano, Spain, [2]Universidad Complutense de Madrid, Spain, [3]Universidad Complutense de Madrid and IMDEA-Nano, Spain, [4]ICMM-CSIC and IMDEA-Nano, Spain

Cis-trans isomerization reactions have been recently proposed as models for the action of molecular-scale switches. Molecules like azobenzene derivatives have thus been deposited on solid surfaces and the isomerization reaction has been induced by external influences such as the tunneling current of an STM or light irradiation. Although the catalytic action of the surface on such reactions is amply acknowledged in previous works, understanding the exact mechanism of such reactions still requires further studies. Moreover, the effect of temperature on such reaction has only been studied in very few examples. Here we show STM and DFT results on the thermally-controlled isomerization of the DCNQI molecules adsorbed on Cu(100). Depending on the substrate temperature two different molecular arrangements are observed, along with two different appearances of the molecules in STM images. Comparison with DFT calculations shows that whereas the low-temperature phase is consistent with a trans-geometry of the cyano groups with respect to the molecular axis, at higher temperatures such arrangement is formed exclusively with cis-isomers. The transition temperature, -30 °C, is too low for the molecule in the neutral form to undergo such cis-trans isomerization, and thus a catalytic effect of the substrate must exist. Based on our experimental results and theoretical calculations we attribute such catalytic effect to charge-transfer from the metal to the molecule along with a strong bonding between the cyano groups and the copper atoms of the substrate. Charge-transfer lowers the cis-trans isomerization barrier in two synergistic ways. First it aromatizes the quinoid ring into a benzene ring, enabling a freer rotation of the cyano groups with respect to the molecular axis. Second, such easier rotation leads to an enhanced interaction of the cyano groups with the copper atoms of the substrate that brings the two isomeric forms closer to each other than in the gas phase conformation.

Study of the substrate influence on the properties of physisorbed self-assembled molecular layers: Azabenzene 1,3,5-Triazine on graphite and graphene on metals

L Rodrigo, P Pou, A J Martínez-Galera, J M Gómez-Rodríguez and R Pérez

Universidad Autónoma de Madrid, Spain

The properties of molecular overlayers on inorganic substrates depend on a delicate balance between intermolecular and overlayer-substrate interactions[1]. Here we present a combined experimental and theoretical study of azabenzene 1,3,5-Triazine layers grown on both graphite and graphene on Pt(111). VT-STM experiments show large overlayer islands with Moiré structures on both substrates[2]. While in both cases the last layer is graphene, the atomic arrangements, the measured molecule diffusion barriers and the growing properties are different[2]. This system is, therefore, a perfect model for the study of the properties of physisorbed self-assembled molecular layers[1]. We have carried out ab initio DFT calculations (using VASP) with two approaches for the van der Waals interactions (the semiclassical DFT+D2[3] and a new flavour of the DFT-DF[3]) to fully characterize the intermolecular (H bonds and vdW) and molecule-substrate (vdW attraction and Pauli repulsion) interactions. We have found that the graphene layer, even for these physisorbed molecules, modifies the intermolecular interactions respect to an isolate layer but not significant differences are found between graphite and graphene on Pt substrates. However, the influence of the Pt on the graphene layer results on a small change of the potential surface energy seen by the Triazine, giving origin to the different properties observed in the two substrates.

[1] Forrest, Chem Rev, 97, 1793 (1997), Hooks et al, Adv Mat, 13, 227 (2001).

[2] Martinez-Galera et al, J Phys Chem C, 115, 11089 (2011); J Phys Chem C, 115, 23036 (2011).
[3] S. Grimme, J Comp Chem 27 (2006) 1787; Klimes et al, J Phys: Condens Matter 22, 022201 (2010).

Chiral clusters of functionalized helicenes on Ag(111) surface

<u>B Such</u>[1], R Pawlak[2], T Glatzel[2], S Kawai[2], S Koch[2], E Meyer[2], J Míšek[3], J V Chocholoušová[3], J Vacek[3], I Starý[3], I G Stará[3] and M Szymonski[1]

[1]Jagiellonian University, Poland, [2]University of Basel, Switzerland, [3]Academy of Sciences of the Czech Republic, Czech Republic

In the presentation the adsorption [6]helicene and their functionalized derivatives and the structure of chiral clusters formed by those molecules on Ag(111) surface are investigated at 5K by scanning tunneling microscopy (STM). The functionalization comprises of the replacement of one of the carbon atoms in a terminal aromatic ring by a nitrogen atom, forming (+)-(R)-1-aza[6]helicene and (+)-(R)-2-aza[6]helicene molecules. For all the molecules the clusters are stabilized by the subtle equilibrium between electrostatic interactions, hydrogen bonding and steric repulsion. The chirality of the molecules induce chiral structure of the clusters, however, the position of the nitrogen atom leads to a drastic change of both the adsorption geometry of molecules and the structure of the clusters. The nitrogen atom in the position '2' makes all the molecules adsorb with the pyridine group facing the substrate while in the case of the molecules with the nitrogen in the position '1' both orientations are equally probable. That leads to much larger variety of the cluster morphology of (+)-(R)-1-aza[6]helicenes in contrast to the case of (+)-(R)-2-aza[6]helicene molecules where the regular, six-molecule clusters are dominant.

Herringbone, rhombus tiling and one-dimensional rows of tetracarboxylic acids on metals and graphene surfaces

<u>I Cebula</u>[1], G Eder[2], S Yang[1], M del Carmen Gimenez-Lopez[1], N Taleb[1], M Schröder[1], N R Champness[1] and P H Beton[1]

[1]University of Nottingham, UK, [2]TUM School of Education and Center for NanoScience (CeNS), Germany,

Carboxylic acids play a very important role as ligands in coordination chemistry. There has recently been growing interest in the growth of metal organic frameworks on surfaces [1-2] and this has motivated an investigation of a number of tetracarboxylic acids: QPTC, TPTC and BPTC, which are known to be good candidates for high capacity hydrogen storage materials [3]. These molecules are known support a range of novel packing phases on graphite including random tiling [4]

We now present results of a solution based study of molecular ordering on Au(111) and graphene terminated copper surfaces. Molecules were adsorbed from aqueous solution and imaged after drying and also at liquid-solid interface using alkanoic acids as solvents. Different packing arrangements were observed depending on molecule, substrate and solvent used.

On Au(111) we observe a herringbone-like arrangement stabilised by hydrogen bonding for QPTC and TPTC, but for the smaller BPTC rows are formed. The surface structures observed for graphene terminated copper are similar to those observed for graphite. In particular we observed a random tiling phase.

Theoretical models for experimentally observed structures were calculated. Scanning tunnelling microscopy data and DFT calculations results are discussed.

[1] O. Shekhah, J. Liu, R. A. Fischer, Ch. Wöll, Chem. Soc. Rev., 40, 1081–1106 (2011).
[2] A. Betard and R. A. Fischer, Chem. Rev., 112, 1055–1083 (2012).
[3] X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey, M. Schröder, Angew. Chem. 118, 7518 –7524 (2006).

[4] M. O. Blunt, J. C. Russell, M. del Carmen Giménez-López, J. P. Garrahan, X. Lin, M. Schröder, N. R. Champness, P. H. Beton, Science 322, 1077–1081 (2008).

How chiral solvents affect molecular self-assembly at the liquid-solid interface

I Destoop[1], E Ghijsens[1], K Tahara[2], Y Yobe[2] and S De Feyter[1]

[1]KU Leuven, Belgium, [2]Osaka University, Japan

The unique handedness of chiral molecules affects chemical, physical and biological phenomena. While observed in solution for helical polymers and self-assembled stacks of molecules, transmission of chiral information is particularly selective at ordered interfaces as a result of geometrical restrictions introduced by two-dimensional (2-D) confinement. Chiral amplification of enantiomerically enriched mixtures has been demonstrated either via chemical reactions at the air-water interface, or upon self-assembly on solid surfaces. Homochirality in achiral enantiomorphous monolayers can be realized by merging chiral modifiers in the monolayer or by exposing monolayers to magnetic fields.

Alternatively, the potential role of solvents in amplification of chirality and emergence of homochirality at surfaces remains unexplored yet.[1] Here we show in real time how solvent-induced macroscopic chirality emerges within self-assemblies of achiral molecules on achiral surfaces. We report a set of scanning tunnelling microscopy (STM) experiments which study the self-assembly for hexadehydrotribenzo[1,2]annulene (DBA) derivatives at the interface between graphite and a series of chiral organic solvents. Previous work has shown that DBA switches between two different network arrangements by controlling the concentration with lower concentrations favouring a porous structure.[2] The porous structure is chiral.[3]Being composed of achiral molecules, the overall surface chirality remains achiral. Here, we provide detailed insight in the chiral induction mechanism of chiral solvents by probing the relation between the efficiency of the chiral induction as a function of chiral solvent size and pore size.

[1] N. Katsonis, H. Xu, R. M. Haak, T. Kudernac, Z. Tomovic, S. George, M. Van der Auweraer, A. P. H. J. Schenning, E. W. Meijer, B. L. Feringa, S. De Feyter, Angew. Chem. Int. Ed. 2008, 47, 4997-5001

[2] S. Lei, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe, S. De Feyter, Angew. Chem. 2008, 120, 3006-3010.

[3] K. Tahara, H. Yamaga, E. Ghijsens, K. Inukai, J. Adisoejoso, M. O. Blunt, S. De Feyter, Y. Tobe, Nat. Chem. 2011, 3, 714-719.

Self-assembly of solute molecules controlled by solvent polarity and concentration at the solid-liquid interface

N T N Ha[1], T G Gopakumar[2], M Mehring[1] and M Hietschold[1]

[1]Chemnitz University of Technology, Germany, [2]Universität Kiel, Germany

Concentration of solute and polarity of solvent are suitable parameters in controlling self-assembled structure formation of molecules adsorbed at the solid-liquid interfaces. Here we study polymorphs of trimesic acid (TMA) and benzene triphosphonic acid (BTP) obtained from different solvents as well as different concentrations at solution-graphite interfaces. Solvents with different polarity as phenyloctane, fatty acids and fatty alcohols are applied here. From solvents with non-polar groups (as phenyloctane) TMA forms only a high-density structure[1], however, from solvents with moderate polar functional groups (as octanoic acid) there appear concentration-induced polymorphs[2]. From solvents containing strong polar groups (as undecanol) there appears a mixed structure consisting of TMA and solvent molecules coadsorbed due to strong inter-molecular interaction. The concentration of all solutions is controlled by the time of sonication during preparation of the solute-solvent mixture. BTP molecule similary shows different adsorption structures from different solvents with different polarities as a 3-dimensional ladder-like structure of BTP molecules in octanoic acid solvent, or a co-adsorption of BTP and undecanol molecules.

[1] Nguyen T.N.Ha et al. J. Phys. Chem. C 2010, 114, 3531–3536.

[2] Nguyen T.N.Ha et al. .J. Phys. Chem. C 2011, 115, 21743 –21749.

Atomic-scale friction of molecular adsorbates during diffusion

B A J Lechner[1], A S de Wijn[2], H Hedgeland[1], J Ellis[1] and W Allison[1]

[1] University of Cambridge, UK, [2]Stockholm University, Sweden

Frictional forces and dissipation control the rate of self-organisation in adsorbate systems. We present a combined experimental and theoretical study on the friction experienced by single organic molecules as they move across a surface.

Helium spin-echo (HeSE) spectroscopy is uniquely capable of measuring surface diffusion, thus giving insight into the friction experienced by adsorbates. HeSE studies show that atomic and diatomic species, such as alkali metals or carbon monoxide, tend to have lower friction coefficients than molecular species, such as benzene [1]. Theoretical calculations for benzene/graphite show that the chaotic internal degrees of freedom of the molecular adsorbate can explain its increased friction coefficient [2, 3].

In order to investigate the mechanism of frictional dissipation, we study a series of five-membered aromatic molecular adsorbates, cyclopentadienyl (Cp) [4], pyrrole and thiophene on a copper surface. While Cp and pyrrole adsorb in a flat-lying geometry, thiophene is adsorbed at an angle to the substrate, bonded through the sulfur atom. We find that all three adsorbates exhibit a 'high' friction coefficient, despite their different adsorption geometry, giving strong support to the model of increased friction through chaotic internal degrees of freedom.

[1] A. P. Jardine, H. Hedgeland, G. Alexandrowicz, W. Allison, and J. Ellis, Progress in Surface Science 84, 323-379 (2009).

[2] A. S. de Wijn, A. Fasolino, J. Phys.: Condens. Matter 21, 264002 (2009).

[3] A. S. de Wijn, Phys. Rev. E 84, 011610 (2011).

[4] H. Hedgeland, B. A. J. Lechner, F. E. Tuddenham, A. P. Jardine, W. Allison, J. Ellis, M. Sacchi, S. J. Jenkins, B. J Hinch, Phys. Rev. Lett.106, 186101 (2011).

Modifying the bonding of PTCDA on Ag(110) through surface substitution

S Tautz[1], G Mercurio[1], O Bauer[2], M Willenbockel[1], T Sueyoshi[1], C Weiss[1], R Temirov[1], S Soubatch[1] and M Sokolowski[2]

[1]Forschungszentrum Jülich, Germany, [2]Universität Bonn, Germany

Tailoring the structural and electronic properties of organic/metal interfaces is currently the subject of an intense research effort. Functional organic molecules support multiple chemical interactions (or bonding channels) with the metal surface. To modify the interface properties at will, a good understanding of not only the individual bonding channels but also of the their interdependence is essential.

We have investigated 3,4,9,10-perylenetetracarboxylic acid dianhydride (PTCDA) on the Ag(110) upon potassium deposition and annealing. The K/PTCDA/Ag(110) interface is studied by a combination of high resolution electron diffraction and low temperature (5 – 10 K) scanning tunneling microscopy (STM) for lateral structure determination, normal incidence x-ray standing waves (NIXSW) for vertical structures, x-ray photoelectron spectroscopy (XPS) for chemical analysis, and (angle resolved) ultraviolet photoelectron spectroscopy ((AR)UPS) for work function and electronic structure measurements.

We find that potassium atoms induce a missing row reconstruction and are located in the top-most Ag layer near the oxygen atoms of PTCDA, leaving the surface region beneath the core of the molecule unchanged. As a result, the bond of the functional groups (O=C-O-C=O) to the substrate is modified drastically. Hence, the local modification of the Ag(110) surface enables the selective manipulation of the Ag-O bonding channel of PTCDA. This allows to study the coupling of this bonding channel to the second bonding channel of the PTCDA/Ag(110) interface, namely the interaction between the perylene core and the silver substrate which involves metal-molecule hybridisation and charge transfer. We present a discussion of this coupling in the light of a comprehensive bonding model for PTCDA on silver surfaces.

High-resolution core-level spectroscopy of molecular switches at surfaces

D Przyrembel[1], D Brete[1], C Gahl[1], W Freyer[2], R Carley[1], M Å Petersen[3], A Hebert[3], K Rück-Braun[3] and M Weinelt[1]

[1]Freie Universität Berlin, Germany, [2]Max-Born-Institut für Nichtlineare Optik, Germany, [3]Technische Universität Berlin, Germany

We present results of high-resolution X-ray photoelectron spectroscopy (XPS) measurements, carried out on two different systems, functionalised self-assembled monolayers (SAMs) of azobenzenes and fulgimides. XPS gives insight into the chemical composition of a sample by measurement of characteristic elemental core-level electron binding energies. In addition, oxidation state and chemical environment of an individual atom lead to specific chemical shifts of its characteristic energies. This allows deducing further properties such as molecular structure or molecular environment. Thus, among others XPS can serve three important purposes in the investigation of SAMs of molecular switches at surfaces: First, in sample preparation XPS is a powerful tool to monitor efficiency and quality. Second, ratios of sample constituents can be determined, which makes it possible, *e.g.*, to investigate the mixing behaviour of two component SAMs. Third, in case that switching a molecule modifies its dipole moment or the state of one or more atoms strongly enough, this can be observed by XPS.

Mixed SAMs of two azobenzene derivatives with different end-groups in *para*-position, anchored on gold via an alkanethiolate, were systematically examined. The change in local potential induced by the concentration dependent variation of the molecular environment of the two SAM constituents allows us to quantify in detail the mixing characteristics. The ratio of adsorbed molecules can be precisely adjusted via the ratio of the components in solution. By simulating the electric dipole-field distribution, the observed continuous core-level shifts are ascribed to a homogeneous mixture of molecules with different end-groups adsorbed on adjacent lattice sites. Additional near-edge X-ray absorption fine structure (NEXAFS) measurements yield structural data on the pure and mixed layers.
The fulgimide SAM was grafted onto a silicon (111) surface in a stepwise reaction, starting with the reduction of Si surface oxides through to the coupling of the fulgimide layer by means of an amidic alkyl linker. The XPS measurements prove the success and completeness of the reactions in each step. Finally, we were able to observe optically induced reversible switching of the surface bound fulgimide molecules.

Donor-to-acceptor core-level shift in a molecular blend

E Ortega[1], A El-Sayed[1], E Goiri[2], P Borghetti[2], C Rogero[3], D de Oteyza[4], J L Cabellos[2], D Mowbray[2], L Floreano[5] and A Rubio[1]

[1]Universidad del País Vasco, Spain, [2]DIPC, Spain, [3]Centro Superior de Investigaciones Científicas, Spain, [4]University of California Berkeley, USA, [5]ELETTRA, Italy

Donor/acceptor multilayer structures and blends deposited on metal surfaces are actively investigated in optoelectronics applications and solar cells, as well as for the exploration of the exotic physics of charge transfer complexes. The organic/metal contact is of key importance, since it defines the energy barrier that determines the ultimate performance of any injection device. In most cases, a two-dimensional donor/acceptor layer segregates from multilayers or blends as the stable phase in direct contact with the metal, thereby defining the relevant organic/metal interface. It is therefore of major importance to investigate the electronic and chemical properties of organic donor/acceptor-on-metal interfaces, and their dependence on the molecular nature and the donor/acceptor composition.

In this contribution, we present a high resolution core-level photoemission analysis of a number of donor/acceptor/metal interfaces The experiments reveal an unexpected but characteristic shift in core-level energies when donor-like monolayers turn acceptor-like, irrespectively of the nature of the molecule or the metal. Moreover, the sign of the shift is contrary to the simple expectation that charge flows "horizontally" from donors (oxidation) to acceptors (reduction) within the molecular layer. Based on both first principles theory and model calculations we show that such donor-to-acceptor core-levels shift is explained by the "vertical" interaction with the substrate, namely by a combined effect of local vacuum level alignment, characteristic of weakly interacting molecules, and the charge variation at interface metallic states.

Carbon, graphene 2

(invited) Transport in graphene nanostructures – achievements and challenges

T Ihn, S Dröscher, D Bischoff, A Jacobsen, C Barraud and K Ensslin

ETH Zürich, Switzerland

Single-or bi-layer graphene sheets host a unique two-dimensional electron gas, which is one hundred times thinner than that in silicon inversion layers, but has superior electronic transport properties. Along with the enormous impact and success of the two-dimensional material in scientific research, and its great potential for applications, the fabrication and investigation of nanostructures has sparked great hopes, but also poses serious technological challenges. The fundamental effects of electronic transport in nanostructures, such as electron tunneling, the Aharonov-Bohm effect, Coulomb blockade, and even conductance quantization have all been demonstrated in graphene. However, the increased surface-to-volume ratio, common to all nanostructures, is driven to the extreme in nanoscale devices made of graphene. The structures are therefore even more sensitive to surface-and edge-related disorder than usual nanostructures. The lack of a band gap adds to the complexity, as it prevents us to confine carriers using electrostatic potentials induced by surface gates. In this talk we will review some recent successes in the investigation of graphene nanostructures, such as ribbons and quantum dots, and we will pinpoint open questions. Particular emphasis will be on the most recent developments on bilayer graphene, where dual gating gives access to an electrically tunable band gap that we have exploited for nanostructure fabrication. The combination of graphene with hexagonal boron nitride as a substrate, and also as a gate insulator is one of the most promising avenues for nanostructure fabrication at present. We will show our results on the electronic transport through nanoribbons fabricated on boron nitride and compare them to structures on a SiO2 substrate.

Interlayer tunnelling in graphene- hBN- graphene devices

J Wallbank and V Falko

Lancaster University, UK

Hexagonal boron nitride (h-BN) is an insulating layered material that is often used as a substrate for graphene. There is a growing interest in the use of monolayer h-BN as a dielectric in multilayer graphene heterostructures (such as in super-capacitors or Field-Effect Tunnelling Transistors) both for fundamental and technological reasons [1].

Starting from a tight binding perspective we investigate the tunnelling of electrons from one layer of graphene to another through an intermediate monolayer of h-BN. The fact that the interlayer separation is greater than both the graphene lattice constant and the Bohr radius drastically simplifies the matrix element for interlayer tunnelling. Both the latices mismatch between graphene and h-BN and the potential misalignment of the three layers results in interesting rules for momentum selection. The resulting tunnelling current is enhanced when the misalignment angles between the layers is small and we hope that such results could be a useful guide to experiments.

[1] L. Britnell, et. al., Science 335, 947 (2012).

Controlled structural variation of bottom-up fabricated graphene nanoribbons

C Pignedoli[1], J Cai[1], P Ruffieux[1], X Feng[2], K Müllen[2] and R Fasel[1]

[1]EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, [2]Max Planck Institute for Polymer Research, Germany

Graphene nanoribbons (GNRs) – narrow stripes of graphene – are predicted to exhibit remarkable properties making them suitable for future electronic applications. Contrary to their two-dimensional parent material graphene, which exhibits semimetallic behavior, GNRs with widths smaller than 10 nm are predicted to be semiconductors due to quantum confinement and edge effects. Despite significant advances in GNR fabrication using chemical, sonochemical and lithographic methods, the production of sub-10 nm GNRs with chemical precision remains a major challenge. Recently we reported a simple GNR fabrication method, which consists in the surface-assisted coupling [1] of suitably designed molecular precursors into linear polyphenylenes and their subsequent cyclodehydrogenation [2]. This surface chemical approach allows for atomically precise GNRs such as N=7 armchair GNRs and chevron-shaped GNRs whose topology, width and edge periphery are defined by the precursor monomers [3]. Here, we demonstrate that similar bottom-up approaches allow for the design of a wide range of GNR-related structures, thus opening the route to control the electronic properties of GNRs. Furthermore, we discuss interesting differences in the surface-assisted cyclodehydrogenation process, which depends on subtle variations of the monomer structure.

[1] M. Bieri et al., J. Am. Chem. Soc., 132 (2010) 16669.
[2] M. Treier et al., Nature Chemistry, 3 (2011) 61.
[3] J. Cai et al., Nature, 466 (2010) 470.

Zero-energy states in graphene waveguides and quantum dots

C Downing[1], R Hartmann[1], D Stone[2], N Robinson[2] and M Portnoi[1]

[1]University of Exeter, UK, [2]University of Oxford, UK

There is a widespread belief that electrostatic confinement of graphene charge carriers (massless Dirac fermions) is impossible as a result of the Klein paradox. We show that full confinement is indeed possible for zero-energy states in pristine graphene. We present exact analytical solutions for the zero-energy modes of two-dimensional massless Dirac fermions confined within a smooth one-dimensional potential given by hyperbolic-secant [1], which provides a reasonable fit for the potential profiles of existing top-gated graphene structures. A simple relationship between the characteristic strength and the number of confined modes within this model potential is found. A numerical method for finding the number of fully confined zero-energy modes in any smooth potential, decaying at large distances faster than the Coulomb potential, has also been developed and used to evaluate the conductivity of a channel formed by a realistic top-gate potential [2]. An experimental setup is proposed for the observation of these modes. Thus, we present a solution to obtaining on/off behavior within graphene, a major obstacle to device realization.

We also show that full confinement is possible for zero-energy states in electrostatically-defined quantum dots. Again, analytic solutions are found for a class of model potentials, [3] which allow us to draw conclusions on general requirements for the potential to support fully confined states, including a critical value of the potential strength and spatial extent. The implications of fully-confined zero-energy states for STM measurements and minimal conductivity in graphene are discussed.

[1] R. R. Hartmann, N. J. Robinson, and M. E. Portnoi, Phys. Rev. B 81, 245431 (2010).
[2] D. A. Stone, C. A. Downing, and M. E. Portnoi, arXiv: 1112.4034 (2011).
[3] C. A. Downing, D. A. Stone, and M. E. Portnoi, Phys. Rev. B 84, 155437 (2011).

(invited) Tuning properties of graphene by controlling its environment

K Bolotin

Vanderbilt University, USA

Every atom of graphene, a monolayer of graphite, belongs to the surface. Therefore, the environment of graphene -- the substrate onto which graphene is deposited and any coating on top of graphene -- intimately affects the properties of graphene. In this talk, we demonstrate that both the mechanical and electrical properties of graphene can be tuned by varying its environment.

First, we discuss the dependence of electrical transport in graphene on the dielectric constant (k) of graphene's environment. For graphene in vacuum (k=1) we observe very strong electron-electron interactions leading to robust fractional quantum Hall effect at temperatures up to 15K. By suspending graphene in liquids, we explore the regime of dielectric constants between ~1.5 and ~30. We observe the dependence of carrier scattering in graphene on k and demonstrate large values for room temperature mobility (>60,000 cm^2/Vs) in ion-free liquids with high k. We also explore the rich interplay between the motion of ions inside liquids and transport of electrons in graphene. We observe signatures due to streaming potentials and Coulomb drag between ions in the liquid and electrons in graphene.

We also briefly address the mechanical properties of graphene and their dependence on graphene's environment. We demonstrate that the built-in strain, the substrate adhesion force and even the thermal expansion coefficient of graphene depend on the substrate supporting graphene.

Strain effects in patterned graphene nanoribbons

J Baldwin and Y Hancock

The University of York, UK

Graphene Nanoribbons (GNRs) are predicted to be important future electronic components with properties that can be engineered via top-down patterning (e-beam lithography)[1]. Graphene is highly flexible and is being exploited in 'stretchable electronics', whereby the electronic properties can be tuned as a function of strain induced by flexible substrates. We have modelled the effect of uniaxial strain on patterned graphene nanoribbons that have random edge disorder using a generalised tight-binding model, which reproduces DFT results[2][3]. An inverse squared (Harrison) relation[4] was used to implement the uniaxial strain, with a Poisson's ratio obtained from DFT calculations. The coherent transport properties of the patterned GNRs were modelled as a function of strain and edge-disorder using the Landauer-Bütticker formalism[5], with the variations in the conductance, transport gap and magnetism showing the potential to be engineered via the type of patterning, amount of strain and strain direction.

[1] X. Jia et al., 2011, Nanoscale 3, 86.
[2] Y. Hancock et al., 2008, J. Low Temp. Phys.153, 393.
[3] Y. Hancock et al., 2010, Phys. Rev. B 81, 245402.
[4] W. Harrison, 1999, Elementary Electronic Structure, World Scientific Pub. Co. Pty. Ltd.
[5] S. Datta, 1997, Electronic Transport in Mesoscopic Systems, Cambridge University Press.

Electron dynamics simulation of laser-assisted field emission from graphene nano-ribbons

K Watanabe, D Utsugi, J Haruyama and C Hu

Tokyo University of Science, Japan

Field emission from metallic tips with nanometer sharpness has been utilized to various devices because of highly bright and coherent electron source. Recent experiments on applying femtosecond laser pulses to such tips have realized a spatially and temporally localized source of ultrafast electron beam, predicting emerging applications such as an ultrafast electron microscopy [1]. So far little is known about the microscopic processes of femtosecond electron emission from nanotips. Since only phenomenological models have been proposed [1,2], first-principles approach that takes account of electron excitation and tunneling dynamics on equal footing is needed toward complete understanding of such highly nonequilibrium phenomena.

Our objectives in the present study are to investigate the femtosecond laser-assited electron emission from graphene nano-ribbons (GNR) using the time-dependent density functional theory calculations [3,4], and to elucidate the emission mechanism consisting of excitation and tunneling. The most important finding in our simulation is that electron emission from GNR abruptly increases when the laser energy approaches the value that corresponds to the energy band gap at gamma point in the first Brillouin zone. The emission channel for the present laser parameters is found to be over-barrier emission instead of photo-field emission and optical field emission. We present the detailed results on the effects of ribbon width, ribbon-edge structures, hydrogen termination and laser parameters on the correlated emission mechanism.

[1] H. Yanagisawa et al., Phys. Rev. Lett. 107, 087601 (2011).
[2] P. Hommelhoff et al., Phys. Rev. Lett. 96, 077401 (2006).
[3] K. Tada and K. Watanabe, Phys. Rev. Lett. 88, 127601 (2002).
[4] J. A. Driscoll et al., Phys. Rev. B 83, 233405 (2011).

Reactions on surfaces 4

Bridging the pressure and materials gap with the ReactorAFM

S Roobol[1], M Cañas-Ventura[1], W Onderwaater[1], K Herbschleb[1], Q Liu[1], V Navarro[1], J Bakker[1], I Taminiau[1], P van der Tuijn[1], M Bergman[1], R Koehler[1], A Ofitserov[2], G van Baarle[2] and J Frenken[1]

[1]Leiden University, The Netherlands, [2]Leiden Probe Microscopy, The Netherlands

The development of new in-situ experimental methods is essential to advance the field of catalysis. We present the ReactorAFM: a novel Atomic Force Microscope (AFM) for operando catalysis studies. The ReactorAFM allows insitu imaging of supported nanoparticle model catalysts at pressures up to 5 bar and temperatures up to 600 K, thereby bridging both the pressure and materials gap.

The scanner of the ReactorAFM is based on a quartz tuning fork and operates in Non Contact (or Frequency Modulation) mode. The scanner is embedded in a high-pressure flow reactor with a volume of 500 µl. This reactor is mounted inside an Ultra High Vacuum (UHV) system that is equipped with several standard tools for sample preparation and characterization. A computer controlled gas flow system feeds the reactor with a wide range of gas mixtures and a mass spectrometer is used for the analysis of the reaction products, enabling direct correlation of catalyst structure with reactivity.

Operando images of a supported nanoparticle model catalyst demonstrate that the ReactorAFM is a unique instrument for unravelling catalytic mechanisms under realistic conditions.

The new instrument for ambient pressure and UHV x-ray photoelectron spectroscopy at MAX-lab

J Schnadt[1], J Knudsen[1], N Johansson[1], A Pietzsch[1], F Hennies[1], J N Andersen[1], H Siegbahn[2] and N Mårtensson[2]

[1]Lund University, Sweden, [2]Uppsala University, Sweden

Ambient pressure x-ray photoelectron spectroscopy (APXPS) dates back to the 1970s and 1980s, but has developed very significant impact first during the past ten years. APXPS allows x-ray photoelectron spectroscopy (XPS) measurements under realistic or close-to realistic conditions, while conventional XPS is limited to vacuum conditions of 10^{-6} mbar or better. APXPS thus contributes to closing the pressure gap of surface science, which has inhibited the understanding of processes, for which the chemical potential of a gas atmosphere plays a decisive role. It also renders possible experiments on liquids and solid samples with a high degasing rate.

Today, there exist a number of APXPS instruments around the world, including a small number at synchrotrons. These instruments perform well at elevated pressures, but none of them is designed to also allow studies under ultrahigh vacuum (UHV) conditions. This complicates the connection to results from UHV studies.

A new instrument for APXPS has been installed at the Swedish synchrotron radiation facility MAX-lab. This instrument, delivered by SPECS GmbH, has been developed with the particular aim of providing a strong link between UHV and ambient pressure experiments. A unique design, based on the use of a retractable (and exchangeable) ambient pressure cell, makes possible the recording of XPS measurements on the same sample in both UHV and ambient pressure. For ambient pressure operation at 10^{-4} to 10 mbar the cell is docked to the electron energy analyser and closed off from the surrounding vacuum so that the vacuum remains intact in the analysis chamber. For measurements at lower pressures down to UHV the cell is retracted into a separate chamber, and the measurements can be performed normally.

The instrument is equipped with a mass spectrometer connected via leak valves to both the in- and outlet of the ambient pressure cell. Reaction and APXPS data can be recorded simultaneously, and a direct link is established between the surface's reactivity and electronic structure.

In this contribution the design and concept of the APXPS instrument at MAX-lab will be discussed. Results will be shown from a number of investigations, including the study of interaction of metal-organic compounds with oxygen and carbon monoxide and catalysis-related studies. Plans for an upgrade of the APXPS beamline will be presented.

CO oxidation over Pt group metals studied by in situ high pressure XPS

J Gustafson[1], S Blomberg[1], N M Martin[1], V Fernandes[2], A Borg[2], R Chang[3], Z Liu[3] and E Lundgren[1]

[1]Lund University, Sweden, [2]Norwegian University of Science and Technology, Norway, [3]Advanced Light Source, USA

Catalytic CO oxidation over Pt group metals has been studied for decades. Although most surface science studies have been performed at conditions close to UHV, some notable exceptions exist. Among these, SXRD studies have found that the catalytic surface is oxidized when the catalyst is active [1-2], while IR spectroscopy finds that the catalytically active phase is metallic [3]. Consequently, there has been a strong debate concerning the active phase of these catalysts during CO oxidation.

While IR spectroscopy probes the adsorbate (CO) and SXRD is sensitive to the surface structure of the substrate, XPS probes both the adsorbate and the substrate, and in the case of High Pressure (HP-) XPS, also the gas phase. Hence, the chemical properties of the surface, the adsorbate, as well as the composition of the gas phase can be studied simultaneously. In this contribution we present in situ HP-XPS results of CO oxidation over Pd(100) and Rh(100).

In agreement with previous reports, our results show that adsorbed CO poisons the reaction, while the oxygen covered surface is catalytically active. The O coverage in the active phase is highly dependent on the total pressure, and under realistic catalytic conditions, the catalyst is expected to be oxidized.

[1] J. Gustafson, et al., J. Phys. Chem. C 114 (2010) 4580.
[2] R. van Rijn, et al., Phys. Chem. Chem. Phys., 13 (2011) 13167.
[3] S. M. McClure, and D. W. Goodman, Chem. Phys. Lett. 469, (2009) 1.

Protonation of alanine on Ni{111} - an ambient-pressure-XPS study

R Nicklin[1], A Shavorskiy[2], F Aksoy[2], A Cornish[1], Z Liu[2], K Schulte[3] and G Held[1]

[1]Reading University, UK, [2]Nigde University, Turkey, [3]Lund University, Sweden

Syntheses of a range of biocompatible products require enantiopure feedstock. Stereocontrol of heterogeneously catalysis has been demonstrated using chiral auxiliaries in hydrogenations. Alanine (Ala) can modify Raney Nickel for enantioselective hydrogenation of methyl acetoacetate (MAA)[1,2]. This system exhibits enantiomeric excess (e.e.) inversion with variation in temperature/pH/solvent. Baddeley et al.[3] demonstrated that for glutamic acid, protonation of the amine coincides with inversion, and the adsorbed state of MAA switches from keto to enol.
As a first step towards probing this reaction by means of Ambient-Pressure-XPS, chemical changes of L-Ala on Ni{111} were studied as a function of temperature and hydrogen pressure. Under UHV conditions alanine chemisorbs in its anionic state around room temperature. At low temperature the molecule forms multilayers which are zwitterionic.The data also suggest that the amine group is protonated at elevated hydrogen pressures. The data show that the chiral modifier is in a different state under reaction conditions than what would be expected from UHV experiments.

[1] Y. Izumi, M. Imaida, H. Fukawa, S. Akabori, Bulletin of the Chemical Society of Japan, 36, 155 (1963).
[2] M. A. Keane, Langmuir, 10, 4560 (1994).
[3] T. E. Jones, C. J. Baddeley, Langmuir, 22, 148 (2006).

Ozone decomposition and nitrate formation on Fe- and Ti-oxide surfaces studied by ambient pressure XPS and NEXAFS

M Lampimäki[1], V Zelenay[1], A Křepelová[1], Z Liu[2], R Chang[2], H Bluhm[2] and M Ammann[1]

[1]Paul Scherrer Institute, Switzerland, [3]Advanced Light Source, USA

Metal oxides, as a part of atmospheric mineral dust, have an important role in the heterogeneous reactions of ozone and nitrogen oxides in the atmosphere [1,2]. However, the mechanism behind these processes is yet not well understood. For instance, the effect of surface hydroxylation or water adsorption in the catalytic decomposition of ozone is still not clear. In the present study we have investigated Fe_3O_4(100) and TiO_2(110) single crystal surfaces during exposure to O_2, O_3, NO and humidity. Ozone concentration was monitored by gas phase measurements and O, Fe, Ti and N core-level XPS-transitions as well as valence band regions were measured in situ at elevated pressures. Additionally, the surface chemical composition was monitored by Near edge X-ray absorption fine structure (NEXAFS) spectroscopy.

Preliminary results for ozone decomposition indicate no significant pressure dependency or inhibition due to water adsorption. The formation of surface nitrogen oxide species after exposure to NO_2 have been previously investigated on TiO_2 and MgO surfaces by ambient pressure XPS [3,4]. In this study we have used O_3 and NO to observe different phases of surface NO_2– and NO_3– formation and thermal decomposition during a sequence of gas exposures.

[1] E. Frinak, et al., J. Phys. Chem. A, 108 (2004) 1560.
[2] C. R. Usher et al., Chem. Rev. 103 (2003) 4883.
[3] D. E. Starr et al., J. Phys. Chem. C, 113 (2009) 7355.
[4] J. Haubrich et al., Langmuir, 26 (2010) 2445.

Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) at Imperial College London

D Payne

Imperial College London, UK

X-ray photoelectron spectroscopy (XPS) is one of the most utilized and interdisciplinary characterization techniques in modern science, with typical XPS experiments taking place in ultra-high vacuum (UHV) conditions (10^{-10} mbar), as a result of needing to minimise the unfavourable collisions of photo-emitted electrons before they enter the energy analyser, and to maintain a clean sample surface for analysis. Whilst a standard XPS measurement provides very useful information on the nature of the surface electronic structure of materials in “perfect” (i.e. UHV) conditions, it does not provide information on the electronic structure of the technologically important materials that operate under normal (i.e. near-ambient or pressurized) atmospheres. It is therefore vital to bridge this so-called “pressure gap” if we are to begin truly understanding the processes occurring at the surfaces of materials as they undergo operation. Recent developments in near-ambient pressure XPS (NAP-XPS), a technique performed under pressures of 10−50 mbar, have now bridged this “pressure gap”. This represents a step-change in the field of XPS, and has the potential to open up new areas of research and deliver previously unobtainable scientific breakthroughs.

Recently the Department of Materials at Imperial College London has been awarded an equipment grant by the EPSRC to design and commission a NAP-XPS instrument (the first system of its kind in the UK), capable of measuring XPS spectra at up to 50 mbar pressures under a variety of different gas (N_2, O_2, H_2, H_2O...etc) atmospheres. This presentation will discuss: (i) the instrument capabilities, (ii) research themes and (iii) routes to access the facility.

Ambient Pressure PES and NEXAFS study of ZnO supported Ni-Co bimetallic model catalyst

Y T Law[1], S Zafeiratos[1], M Hävecker[2] and A Knop-Gericke[2]

[1]LMSPC, France, [2]Fritz-Haber-Institut der MPG, Germany

Supported Ni-Co alloys are promising as catalyst for ethanol steam reforming (ESR) reaction. Understanding the nature of the catalytic active sites and the influence of the support is a crucial step towards optimization of their performance. In this work, the interaction of ZnO support with Ni-Co bimetallic overlayers was studied under reactive environments *in-situ* by synchrotron based surface characterization techniques. The surface oxidation state and the compositionof 1.4ML Ni-Co overlayer vapor-deposited on ZnO single crystal was compared to unsupported Ni-Co nanoparticles under reduction-oxidation and ethanol steam reforming conditions.

In UHV, the Ni-Co overlayers were composed of metallic Ni-Co layer at the outer surface and Ni-Co oxide at the Ni-Co/ZnO interface. Temperature programmed oxidation with *in-situ* real time XPS monitoring reveals that Ni-Co/ZnO forms Ni-Co oxides with oxidation state different to unsupported Ni-Co in 0.3 mbar O_2. At 473 K unsupported Ni-Co was oxidized to Ni^{2+} and Co_3O_4 (Co^{2+} and Co^{3+}), while Ni^{2+} and Co^{2+} are the only species formed for Ni-Co/ZnO. In addition, NEXAFS results show that both octahedral and tetrahedral Co^{2+} ions were formed in O_2 for Ni-Co/ZnO, while only octahedral Co^{2+} was formed on unsupported Ni-Co particles.

By combining online mass spectrometry with ambient pressure photoemission spectroscopy (APPES) and near-edge x-ray absorption spectroscopy (NEXAFS), we could observe the change in the surface state of the model catalyst under reaction condition. In ESR reaction mixture, the tetrahedrally coordinated Ni-Co/ZnO was reduced to metallic state at 523K while the unsupported Ni-Co nanoparticle remains in oxidized form. This shows that by introducing ZnO support, Ni-Co of different coordination could be formed, and could be activated differently under reaction.

Recent trends in photoemission; high energy and high pressure

J Åhlund, H Bergersen and R Moberg

VG Scienta AB, Sweden

The fields of Hard X-ray Photoelectron Spectroscopy (HAXPES) and High Pressure Photoemission (HiPP) are growing fast. There has also been a recent interest of combining them. Here we present instrument development and results within HAXPES and HiPP as well as the merged field of HiPP-HAXPES.

Photoelectron spectroscopy (PES) is an excellent tool in surface science due to the possibility to probe electronic and geometric structure. With higher energies (hard X-rays), in combination with improvements in PES detection techniques, this tool can be extended to bulk materials, forming the field of HAXPES. Here we present instrument development for HAXPES, as well as results obtained using such equipment, with emphasis on the use of 2-D detectors to obtain angularly resolved or spatially resolved spectra.

Experiments done under normal surface science conditions (Ultra High Vacuum) are of limited use in some applications, e.g catalysis, due to the pressure gap problem. This motivates the study of systems at ambient pressures. Here we present a HiPP instrument developed in collaboration with Advanced Light Source (ALS). This instrument allows standard PES measurements as well as spatial and angle resolved spectra at HiPP conditions.

Some recent results include spatially resolved investigations of solid oxide electrochemical cells (SOC:s) and electrochemical properties of junctions.

Finally, we report on recent advances in constructing a new generation of instrumentation combining HiPP and HAXPES. A novel electron analyser, designed for optimal transmission in combination with very efficient differential pumping, will be presented together with preliminary results.

Ambient Pressure Scanning Photoemission Microscopy – a new tool for studying heterogeneous systems with sub-micron resolution and under realistic conditions

A Shavorskiy, H Bluhm, Z Hussain and T Tyliszczak

Lawrence Berkeley National Laboratory, USA

Many systems of interest for physical, chemical, biological, and atmospheric sciences are chemically heterogeneous on the micron- and sub-micron scale. Examples of such systems include industrial and model catalysts, atmospheric aerosols, fuel cells, rocks, solar cells, and other. The chemical properties of such heterogeneous systems cannot always be represented by the superposition of the properties of individual (homogeneous) parts of the system. One of the reasons is the unique properties of the interface between homogeneous parts. Therefore, it is crucial to get fundamental understanding of how such an interface looks and works under real-world conditions.

We present the conceptual design, technical implementation and first results of a newly commissioned ambient pressure scanning photoemission microscope (AP-SPEM) at the Advanced Light Source in Berkeley. The instrument uses Fresnel zone plate to focus X-rays to a spot of < 200 nm, and collect electros emitted from the surface of the solid sample with the commercial differentially-pumped hemispherical electron energy analyzer, which allows measurements at pressure of up to several Torr. First results on insitu studies of electrochemical interfaces will be presented.

Magnetism 4

Spatially modulated tunnel magnetoresistance on the nanoscale

H Oka, K Tao, S Wedekind, G Rodary, V Stepanyuk, D Sander and J Kirschner

Max-Planck-Institute of Microstructure Physics, Germany

Electron tunneling between electrodes is a spin-dependent phenomenon. The tunneling current depends, among other factors, on the relative magnetization direction of the electrodes. This dependence gives rise to the tunnel magnetoresistance (TMR) effect, which is the basis of current magnetic data storage technology. We report a novel venue to tune TMR on the nm scale.

We map the TMR within a single nm small Co island by low-temperature spin-polarized scanning tunneling microscopy in magnetic fields. We measure the tunnel current I between the magnetic tip of the STM and the nm small Co island as a function of the bias voltage V for parallel (P) and anti-parallel (AP) magnetization orientation of tip and island. We find a TMR of 290 MOhm for the AP and 190 MOhm for the P state at -0.27 V at the center of a Co island. This gives a TMR ratio of 50%. The TMR ratio depends on energy and position within the nano-island. We observe a clear spatial modulation of the TMR ratio with an amplitude of 20% and a spacing of 1.3 nm between maxima and minima around the Fermi level. This result can be ascribed to a spatially modulated spin-polarization within the Co island due to spin-dependent quantum interference [1]. Our combined experimental and theoretical study reveals that spin-dependent electron confinement affects all transport properties such as differential conductance, conductance and TMR. We demonstrate that the TMR within a nanostructured magnetic tunnel junction can be controlled on a length scale of 1 nm through spin-dependent quantum interference [2].

[1] H. Oka, et al., Science 327, 843 (2010).
[2] H. Oka, et al., Phys. Rev. Lett. 107, 187201 (2011).

2D reflection-type electron spin filter increasing detection efficiency in spin-resolved spectroscopy by orders of magnitude

G Schoenhense[1], D Kutnyakhov[1], M Kolbe[1], P Lushchyk[1], K Medjanik[1], H-J Elmers[1], C Tusche[2], J Kirschner[2], F Giebels[3], H Gollisch[3] and R Feder[3]

[1]Johannes Gutenberg-Universität Mainz, Germany, [2]Max Planck-Institut für Mikrostrukturphysik, Germany, [3]Universität Duisburg, Theoretische Festkörperphysik, Germany

The novel approach of 2D electron spin filtering[1,2] has recently broken an old paradigm. Since the early work of Mott, spin-resolved spectroscopy was characterized by extremely low detection efficiency, quantified by a figure of merit FoM = $S^2 I/Io$ (S: spin sensitivity, I/Io: reflectivity) of typically 10^{-4}. Electron diffraction from W(001) surfaces in the specular (00) LEED spot facilitates parallel detection of 3800 data points in our imaging spin filter in the column of a photoemission electron microscope[1], and 900 behind a hemispherical energy analyser[2]. Along with an additional increase of S, we achieved a “2D FoM” of 1.7 being four orders of magnitude higher than the FoM of previous designs.

For further optimization we study the spin sensitivity and reflectivity as functions of scattering energy and angular range. Intensities, spin-orbit-coupling induced asymmetries and figures of merit were calculated by means of a relativistic layer KKR SPLEED code[3]. Au(100) surfaces seem very promising because of high FoM and high lifetime of the surface. The superior performance of multichannel spin detection facilitates experiments on highly reactive surfaces like in-situ prepared Heusler films or radiation-sensitive organic layers. Multi-electron detection paves the way to single-shot experiments at ultra bright fs-sources like FELs and to spin-resolved coincidence experiments. The status of the development is reported.

[1] C. Tusche et al., APL 99(2011)032505.
[2] M. Kolbe et al., PRL 107(2011)207601.
[3] R. Feder, Polarized Electrons in Surface Physics (World Scientific, 1985).

(invited) Transition from spin accumulation into interface states to spin injection in the Ge conduction band

M Jamet[1], A Jain[1], J-C Rojas-Sanchez[1], M Cubukcu[1], J Peiro[2], J-C Le Breton[2], C Vergnaud[1], C Portemont[3], C Ducruet[3], L Vila[1], J-P Attané[1], E Augendre[4], S Gambarelli[1], H Jaffrès[2] and J-M George[2]

[1]CEA-Grenoble and UJF, France, [2]UMP CNRS-Thalès, France, [3]CROCUS-Technology, France, [4]CEA-Grenoble, France

Spin injection into semiconductors is crucial for exploring spin physics and new spintronic devices. Unlike GaAs or Si, very few studies have dealt with spin injection in Ge. This material is of great interest for high carrier mobility, long spin diffusion length and large spin-orbit coupling to perform electric field spin manipulation through Rashba interaction. However the exact role of interface states in spin injection mechanism in n-Ge has not been clarified yet and no clear evidence of spin accumulation in the channel has been given. In this paper, we show a clear transition from spin accumulation into interface states to spin injection in the Ge conduction band. For this purpose, we have grown CoFeB/MgO spin injector on GOI. We observe spin signal amplification at low temperature due to spin accumulation into interface states. At 200 K, we observe a clear transition to spin injection in the channel up to room temperature: the spin signal is reduced down to a value compatible with spin diffusion model and more interesting we could demonstrate spin signal modulation applying a back gate voltage and spin-pumping by the ferromagnetic resonance of the CoFeB layer which are clear manifestations of spin accumulation in the Ge channel. Finally by setting a temperature difference between Ge and CoFeB we could thermally induce a spin accumulation in Ge due to the tunnelling spin Seebeck effect.

Half-metal Heuslers: order/disorder effects on spin polarisation in films and interfaces

V Lazarov[1], P J Hasnip[1], J Smith[1], J Sizeland[1], J Sato[2], M Oogane[2], D Gilks[1], A Hirohata[1] and Y Ando[2]

[1]The University of York, UK, [2]Tohoku University, Japan

Half metal materials, which are a 100% spin polarised at the Fermi level, are of great interest in spintronics. Among various materials system predicted to be half metallic Co based full Heuslers alloys have attracted a lot of research attention due to their successful application in device structures such as spin valves and magnetic tunnelling junctions. Half metallic state in Heuslers is very sensitive to the level of atomic/chemical ordering. In this work we present the study of the effect of the ordering on spin polarisation in thin films of full Co_2MnSi and $Co_2(Mn,Fe)Si$ Heuslers and their spintronic heterostructures with metallic spacers. Atomic ordering in the thin films and heterostructure interfaces (grown by UHV sputtering) was studied by aberration corrected scanning transmission electron microscopy. Based on these studies, atomistic models of thin films and interfaces were determined and by using Density Functional Theory their spin polarisation was calculated. In addition we study theoretically systematically the effect of the ordering on the spin polarisation in the bulk Heuslers. We found that Mn(Fe) intermixing with Co does not affect the half-metalicity though the half-metallic band gap decrease for half. The Mn-Si and Si-Co intermixing destroy the half-metalicity; e.g 25% disorder on Mn and Si sublattice decrease the spin polarisation to 50%. These finding correlates well with magnetotransport properties of $Co_2MnFe/Ag/Co_2MnFe$ spin valves. We found direct correlation between the magneto-resistance (80% at low temperatures) and the ordering at the interface at these spin valves.

Epitaxial growth and magnetism of Fe-Ge / Ge / Fe-Ge trilayers

G Garreau, I Maafa, S Hajjar, D Berling, A Mehdaoui and C Pirri

Université de Haute-Alsace, France

The MBE growth of Fe-Ge / Ge / Fe-Ge trilayers on Ge(111) wafers has been investigated versus Fe-Ge stoichiometry, substrate temperature and partial pressure of atomic hydrogen. Morphology and crystal structure have been characterized in situ by means of STM, LEED, XPD and ex situ with HRTEM. Magnetic properties (anisotropies, interlayer coupling and Curie temperature) were investigated by surface Kerr magnetometry. The Ge spacer was deposited on epitaxial ferromagnetic $Fe_{2-x}Ge$ ($0.1<x<0.5$) electrode that adopts the $B8_2$ structure of hexagonal symmetry. This Fe-Ge layer, which is nearly perfectly matched to Ge(111), was synthesized by RT co-deposition and post-annealing at 250°C [1].

We found that Ge epitaxial growth required deposition temperature above 200°C. However the partial H pressure significantly influences the growth mode of the Ge spacer. Without H supply, the surface consists of well separated 3D Ge diamond islands leaving large area of the Fe-Ge uncovered. On the other hand, continuous and flat Ge spacers are obtained for partial H pressure above 10^{-6} mbar. In this last case, the Ge single cristallinity is improved continuously from 200 to 300°C. Whatever the surface morphology, the Ge spacer is rotated by 180° around the [111] growth direction with respect to the Ge wafer. Finally, the top Fe-Ge electrode crystallizes in the same $B8_2$ structure as the bottom electrode.

We will show that the RT-ferromagnetic electrodes can be magnetically decoupled by tuning the in-plane magnetic anisotropy through the adjustment of the deposition geometry for each layer.
These results suggest that these fully epitaxial RT-ferromagnetic Fe-Ge/germanium hybrid heterostructures could be promising candidates for semiconductor spintronics.

[1] R. Jaafar et al., Physical Review B 81, 155423 (2010).

Novel development of high brightness and high spin-polarized SPLEEM and application to spintronics

T Koshikawa[1], M Suzuki[1], T Yasue[1], E Bauer[2], Y Takeda[3] and T Nakanishi[3]

[1]Osaka Electro-Communication University, Japan, [2]Arizona State University, USA, [3]Nagoya University, Japan

Memory size has been tremendously enlarged after the development of GMR. Recently new concept MRAM (magnetic random access memory) has been proposed, in which the magnetic domain wall can be driven with current (current-induced domain wall motion) using perpendicular magnetic anisotropy. $[Co/Nix]_y$ multi-layer nano-wires might be an important candidate, which has strong perpendicular magnetic anisotropy . In order to clarify the detailed magnetic thin film formation and their property, we need more sophisticated magnetic microscopy instrument which gives us high spatial resolution, dynamic observation and so on. Here we will present the results of development of a novel high spin-polarization and high brightness low energy electron microscope (SPLEEM) with new idea; strained super lattice cathodes for high spin-polarization (90%, better than commercial one by factor 3.5), the back side illumination of laser beam to the cathode for very high brightness ($1.3x10^7$ A/cm^2 sr, better than commercial one by over 10,000) and XHV (extreme high vacuum) at the electron source chamber for long life time (over 2 months, better than commercial one by over 200). We have investigated the detailed magnetization process of those multi-layers with newly developed SPLEEM. The magnetic images of $Co/Ni_2/W(110)$ and 1 ML Au on $Co/Ni_2/W(110)$ show that Au ultra-thin film conducts to the strong perpendicular magnetic anisotropy.Additional development has been carried out in order to improve the high quantum efficiency of the photo-cathode with reducing the absorption of the laser light at the GaAs inter-layer and the reflection of the laser beam at the back-side surface, which makes us now improving the factor four. We are also making a compact spin gun with a novel idea in which we can reduce the devices for spin manipulation and rotation from two to one. This novel device can operate the spin direction in 3 dimensional ways.

Metals, alloys and their surfaces 2

(invited) Bimetallic nanoparticles modelling: towards nanoalloys phase diagrams

C Mottet[1], A Lopes[1], J Los[2], F Calvo[3] and G Tréglia[1]

[1]CINaM - CNRS / AMU, France, [2]Johannes Gutenberg University Mainz, Germany, [3]LASIM - CNRS / Université LYON, France

Alloys phase diagrams are essential in the characterization of the equilibrium structure of the bulk alloys at finite temperature. The structural and chemical ordering has been the subject of intensive studies for a long time, notably from a theoretical point of view [1] and especially on metallic systems.

Surface segregation phenomena modify the chemical order inducing a competition or synergy between the surface segregation and the bulk ordering or demixing tendency, giving rise to an important investigation field from alloy surfaces to surface alloys [2].

More recently, nanoparticles have attracted much attention because of their wide variety of structure and morphology. Associated to chemical ordering and surface segregation in case of alloys, nanoalloys lead to complex systems [3]. The characterization of their equilibrium properties in their fundamental state (0K) and at finite temperature is of great importance in order to make the link between their structure and their properties.
We propose a theoretical study of the structure, morphology and order/disorder transition by Monte Carlo simulations using tight binding models of bimetallic nanoparticles with the tendency to ordering in the bulk alloy. Some steps towards the description of size dependent phase diagram of nanoalloys will be shown and the theoretical results will be compared to experimental ones.

[1] F. Ducastelle, Order and Phase Stability in Alloys, ed. De Boer and Pettifor, North-Holland (1991).
[2] G. Tréglia, B. Legrand, F. Ducastelle et al., Computational Materials Science 15, 196 (1999).
[3] R. Ferrando, J. Jellinek, R. Johnston, Chemical Reviews 108, 845 (2008).

Structure and magnetism of ultra-thin hcp Fe layers on Re(0001)

B Santos[1], T O Mentes[1], J I Cerda[2], J M Puerta[2] and A Locatelli[1]

[1]Elettra Synchrotron Light Source, Italy, [3]ICMM, Spain

The epitaxy of fcc metals on bcc and hcp substrates has attracted intense scientific attention because of the unique physical properties of thin films ad overlayers with different crystal structure than that shown at equilibrium in the bulk. Crystal structure affects in particular magnetic properties, which may vary dramatically with thickness depending on the strain induced by the substrate[1]. For example, it has been shown that prototypical ferromagnetic metals such as Fe became antiferromagnetic on W(001) [2] . The morphology of hcp iron films have been extensively studied on Ru(0001) but their magnetic structure is often difficult to interpret, because the non-magnetic, ferromagnetic and antiferromagnetic order on these films are degenerate in energy [3]. The transition between different magnetic orders depends on small changes in their crystal structure. Here we present a complete study of the crystal structure and magnetic properties of hcp Fe monolayers on Re(0001). The growth mode and morphology of the films was studied by LEEM and LEED. The structure of the films was determined by means of LEED-IV analysis. The data obtained in the fits were used in the theoretical calculations to predict the magnetic order of the films, obtaining that 1 and 2 ML thick Fe films do not present any ferromagnetic order. XMCD experiments confirm the theoretical calculations

[1] B.C. Bolding and E.A. Carter, Phys. Rev. B 44, 3251 (1991).

[2] A. Kubetzka, P. Ferriani, M. Bode, et al. Phys. Rev. Letters 94, 087204 (2005).
[3] T. Kraft, M. Methfessel, M. van Schilfgaarde and M. Scheffer, Phys. Rev. B 47, 9862 (1993).

Atomic-scale composition of Ni-Cu bimetallic surfaces: competition between segregation and dissolution

M Peressi, E Vesselli, M Rizzi, S Furlan, C Dri, A Peronio, C Africh, G Comelli and A Baldereschi

University of Trieste, Italy

Bimetallic surfaces can have different local composition depending on how they are obtained (e.g., by metal-by-metal deposition or from bulk alloys) and on surface segregation thermodynamics. They exhibit peculiar electronic and reactivity properties, different from the surfaces of the constituent metals and dependent on their particular composition.

A very attractive example of bimetallic surfaces is the Ni/Cu system. In case of Ni deposited on Cu, at low temperatures Ni stays at the topmost layer; by annealing, a surface alloy is formed; further, a Cu layer pops on-top of the Ni film; finally, Ni diffuses into Cu bulk. We investigate in this work the different steps of the segregation mechanism in Ni-on-Cu(110) at the atomic scale, using in-situ real-time spectroscopy and first principles calculations. We address the question of which are the rate determining steps and the related barriers. We identify and explain the mechanisms of Ni island formation along (1-10) and (111) faceting and of the surface-to-bulk dissolution and bulk-to-surface segregation by increasing the temperature.

Understanding the mechanisms governing the arrangement of the surface atoms at bimetallic surfaces and the composition profile of the first layers opens the way to the possibility of controlling them and hence of tuning their reactivity. For this reason bimetallic surfaces play a decisive role in heterogeneous catalysis. We discuss some examples related to the interaction of bimetallic NiCu alloys with few atoms and small molecules.

The metastable bcc phase of ultra-thin Ni layer on Fe(001) studied by scanning tunneling microscopy

G Bussetti, M Riva, A Picone, A Brambilla, L Duò, M Finazzi and F Ciccacci

Politecnico di Milano, Italy

The interest in magnetic materials has been spurred by the ability to realize metastable phases experimentally through epitaxial growth on single-crystal substrates acting as templates. Examples include face-centered-cubic (fcc) iron and body-centered-cubic (bcc) nickel. Phase diagrams derived from total-energy calculations for these bulk metastable structures predict a stable magnetic state at some lattice constant. In the ultrathin-film region [one to two monolayers (ML)], interesting properties, such an enhanced moments, have also been predicted.

In the past, the structure of the bcc phase of nickel grown epitaxially on Fe(001) substrates has been studied using low-energy electron-diffraction (LEED) and reflection high-energy electron-diffraction (RHEED) techniques. The bcc-fcc Ni transition is interpreted, at the present state-of-art, in terms of a not-continuous Bain's path or equivalent more detailed transformations. It means that, up to about six layers, the nickel is found to grow in a bcc manner, and above this thickness a slight distortion occurs, eventually leading to c(2X2)-like LEED and RHEED patterns. The latter is consistent with a distortion and rotation of the Ni super-structure, respect to the Fe(001) substrate.

In this talk we show, for the first time, the morphology evolution of Ni ultrathin and thin films (up to 40ML) on clean Fe(001) at RT. We used an in-situ scanning tunneling microscopy (STM) to check the surface evolution during each step of Ni growth in our molecular beam epitaxy (MBE) chamber. We observe an intermediate new phase transition between the Ni bcc (1x1) and the fcc c-(2x2). The latter has been interpreted in terms of a Ni surface cell distortion not followed by the rotation.

Our findings can help the current debate about the microscopic changes that occur in the formation of the Ni/Fe interface.

(invited) Isolated Pd sites on low indexed surfaces of intermetallic PdGa catalysts

R Widmer

Empa, Switzerland

With its highest technological and economic importance, catalysis is an extremely active research area, which yields in a great impact on the development of new catalyst systems with the aim to produce more efficient and selective chemical processes. To this point the development and optimization of novel catalysts most commonly proceed via the modification of composition and surface treatment in a trial and error fashion. Surface science methods offer the possibility to change this paradigm by gaining a fundamental understanding of the chemical reaction on a molecular level and determining the relation between catalytic properties and atomic structure of the surface. The obtained insight can then be applied to a knowledge-based development on novel catalysts showing increased activity and/or selectivity.

In this context, intermetallic compounds have been identified as an interesting materials class for novel catalysts with tailored properties [1]. Among these compounds PdGa, with the FeSi type of structure, has attracted considerable attention due to its exceptional selectivity and activity as a heterogeneous catalyst for the semi-hydrogenation of acetylene [2]. These properties were assigned to the separation of catalytic sites on the surface of the intermetallic material [3]. Due to its structure there are non-equivalent surface terminations of the different low indexed surfaces of PdGa [4].

Here, we present a detailed atomic and electronic structure analysis on low Miller indexed PdGa surfaces based on XPD, LEED-I(V), STM, ARPES and DFT based stability calculations. Additionally, TDS and FT-IR investigations were performed to probe the chemisorption behavior of CO. In particular we will address the very different local arrangement of Pd atoms on the different PdGa surface, which qualifies this intermetallic compound as ideal model system to study the role of site separation on the catalytic properties. These insights in the surface structure are essential inputs for the determination of catalytic reaction pathways and theoretical calculations of molecular adsorption energies.

[1] J.A. Rodriguez, Surf. Sci. Rep. 24 (7-8), 225 (1996).
[2] M. Armbrüster, K. Kovnir, M. Behrens, D. Teschner, Y. Grin, R. Schlögl, J. Am. Chem. Soc. 132, 14745 (2010).
[3] K. Kovnir, M. Armbrüster, D. Teschner, T. V. Venkov, F. C. Jentoft, A. Knop-Gericke, Y. Grin, R. Schlögl, Sci. Technol. Adv. Mat. 8, 420 (2007).
[4] D. Rosenthal, R. Widmer, R. Wagner, P. Gille, M. Armbrüster, Y. Grin, R. Schlögl, O. Gröning, submitted

Silicide formation on Ni surfaces

T Fukuda[1] and K Umezawa[2]

[1]Osaka City University, Japan, [2]Osaka Prefecture University, Japan

Metal silicides are one of most studied materials and they are widely utilized in microelectronics. Although formation of silicide thin films on silicon substrates have been extensively studied, reaction of Si and silicide formation on *metal* substrates have not been studied so far with a few exceptions.Here we address initial silicide formation on Ni(111) and Ni(110)surfaces under UHV by employing STM and LEED.We found that Si deposited onto a clean Ni(111) surface tends to aggregate at step edges at very initial stage and two-dimensional dendritic-like growth follows. Unlike ordinary dendrites, Si clusters with about 5 nm in width congregate, but they never touch each other. Silicide reaction begins beyond 373 K particularly at step edges where Si adatom density is highest. By reacting with substrate Ni, original steps meander outward of terraces and silicide is formed at these convex regions at the step edges. 1/3 ML Si deposition induces flat surface with a root-3 by -root-3 reconstruction. We could discriminate two types of $\sqrt{3}$ by $\sqrt{3}$ reconstruction with different atomic geometries depending on annealing temperatures. In addition, a defect structure with two bright lines separated by 5 nm are superimposed on one of the reconstructions for samples annealed at 573 K. When Si deposition is less than 1/3 ML and the surface is annealed beyond 573 K, amorphous phase was stabilized on the surface. In case of Si deposition on a Ni(110) surface, Si/Ni mixing is initiated even at room temperature.

The various forms of Bi islands on the (100) surface of the $Al_{13}Co_4$ complex metallic alloy

V Fournée, S Bobaru, E Gaudry, M-C de Weerd and J Ledieu

Institut Jean Lamour CNRS, France

The growth and stability of Bi thin films on the $Al_{13}Co_4$ (100) complex metallic alloy surface has been investigated from submonolayer to high coverage regime by STM and LEED. Initially, Bi adsorption leads to the formation of a pseudomorphic monolayer, which is followed by the formation of islands of specific heights with increasing coverage. The islands height and morphology as well as their in-plane structure indicate that both pseudo-cubic Bi(110) and hexagonal Bi(111) coexist on the wetting layer. The Bi(111) islands show a moiré structure resulting from the locking into registry with the substrate leading to 4 rotational domains while the Bi(110) islands are randomly oriented. The (110) oriented islands correspond to bilayer stacking (either 2 or 4 ML) while the (111) oriented islands correspond to either 3 or 4 ML. Above 5 ML, the entire film adopt the (111) structure and the growth continues in a layer-by-layer fashion. The fact that Bi islands grow either with (110) or (111) structure simultaneously must be related to a subtle energy balance between these two orientations, allowing both structures to co-exist. The deposition temperature and the flux have a strong influence on which of the two structures dominates. Specific features appear in STS spectra recorded on the various types of islands, which have their own electronic signature. We also tested the chemical reactivity of the various form of Bi grown on this substrate by oxygen dosing. We found that the wetting layer is far more reactive than both the (110) and (111) structures.

Electronic and lattice instability and its relaxation mechanism in Pt-Co interfaces

W-L Yim[1] and Thorsten Kleuner[2]

[1]Institute of High Performance Computing, Singapore, [2]University of Oldenburg, Germany

Lattice instabilities of bimetallic Pt-Co interfaces have been examined within density functional theory. We discovered that the lattice instability and electron instability in momentum space were strongly correlated on bimetallic interfaces. The lattice instability of the Pt-Co interface was illustrated by Fermi surface nesting in two dimensions, and the nesting vector along the (110) direction in electron momentum space has been identified. The predicted reconstruction-induced Pt diffusion trend was in excellent agreement with previously obtained experimental findings.

[1] Wai-Leung Yim and Thorsten Kleuner, Phys. Rev. B, 2012, 85, 035435.

Electronic structure and topological insulators 4

(invited) High resolution photoemission studies of the high T_c superconductors

P D Johnson

Brookhaven National Laboratory, USA

High resolution photoemission is now recognized as one of the most powerful probes of the electronic structure in condensed matter systems. Here we report studies of the high Tc superconductors. In the under-doped or pseudo-gap phase of the cuprate superconductors, a significant portion of the Fermi surface is still gapped at temperatures above the transition temperature T_c. Further instead of a closed Fermi surface, photoemission studies indicate that the low-energy electronic excitations appear to form Fermi arcs separated by gapped regions. Here we report high-resolution photoemission studies of this underdoped regime. We show that the Fermi arcs may in fact be one side of Fermi pockets, consistent with the underlying nature of the spin liquids in these materials and indeed consistent with the fact that these materials are doped Mott insulators. By examining a range of reduced doping levels down into the non-superconducting regime, below the 5% doping level, it appears that the areas of the hole pockets scale with the doping level. A particle-hole asymmetry observed in the nodal region is clear evidence that electron pairing does not originate from the Fermi arcs in the normal state. However in contrast the particle-hole symmetry observed in the anti-nodal region is interpreted as evidence for singlet pairs forming along the copper-oxygen bond directions at temperatures above the superconducting transition temperature T_c. We also report studies of the Fe based superconductors where are we again able to show that strong correlations must play a role in the development of the superconducting state.

Intrinsic spin polarity at the surface of magnetite Fe_3O_4

A Pratt[1], M Kurahashi[2], X Sun[3] and Y Yamauchi[2]

[1]The University of York, UK, [2]National Institute for Materials Science, Japan, [3]University of Science and Technology of China, China

The spin polarization at the surface of Fe_3O_4 is of huge technological and fundamental importance. Predictions of half-metallic ferrimagnetism (HMF) and a Curie temperature that greatly exceeds other candidate materials have led to intensive efforts to incorporate Fe_3O_4 into spintronic devices such as magnetic tunnel junctions [1]. Additionally, at temperatures below ~125 K, Fe_3O_4 undergoes a unique structural transformation known as the Verwey transition [2]. The surface structure of Fe_3O_4 has been well-characterized with a number of techniques. However attempts to use spin-polarized photoemission spectroscopy to measure the Fermi-level spin polarization, $P(E_F)$, predicted to be -100 % in the bulk, have given rise to intense debate as to whether Fe_3O_4 is a HMF at all [3]. Here we report an extensive investigation of the spin polarization at the surface of the Fe_3O_4(001) and Fe_3O_4(111) using a spin-polarized helium beam. For Fe_3O_4(001), we find that $P(E_F)$ is almost zero although a significant recovery of half-metallicity occurs when the surface is terminated with hydrogen [4,5]. For Fe_3O_4(111), we measure a strong positive value for $P(E_F)$ that is insensitive to the adsorption of hydrogen. Density-functional theory calculations confirm these unexpected results which together suggest that the (001) and (111) surfaces of Fe_3O_4 have an intrinsic spin polarity which differs greatly from the bulk. This has important implications for spin injection across Fe_3O_4 interfaces and could explain the poor performance of Fe_3O_4-based devices and previous photoemission data. Furthermore, revealing such drastic changes in the surface electronic structure leads to significant new insight into fundamental phenomena such as the surface Verwey transition and suggests that other ferrimagnetic compound crystal surfaces require investigation.

[1] T. Kado, Appl. Phys. Lett. 92, 092502 (2008).
[2] M. S. Senn, J. P. Wright, and J. P. Attfield, Nature 481, 173 (2012).

[3] M. Fonin, Y. S. Dedkov, R. Pentcheva, U. Rüdiger, and G. Güntherodt, J. Phys.: Condens. Matter 20, 142201 (2008).
[4] M. Kurahashi, X Sun, S. Entani, and Y. Yamauchi, Appl. Phys. Lett. 93, 132505 (2008).
[5] M. Kurahashi, X. Sun, and Y. Yamauchi, Phys. Rev. B 81, 193402 (2010).

STM and ARPES studies of Sn/Si(111):B- 2(√3xr√3)R30°

W Srour[1], A Tejeda[2], M Abuin[3], P Le Fèvre[4], F Bertran[4], Y F Révurat[2], B Kierren[2], D Malterre[2] and A Taleb-Ibrahimi[1]

[1]SOLEIL Synchrotron, France, [2]Institut Jean Lamour -Nancy, France, [3]Universidad Complutense de Madrid, Spain, [4]SOLEIL Synchrotron-Gif sur Yvette, France

Electronic correlations and electron-phonon coupling may promote electronic and structural transitions as Mott or bipolaronic transitions. Sn/Ge(111) [1] and Sn/Si(111) [2] are known to exhibit a Mott transition and alkali/Si:B(111) systems have been intensively studied because of the role of electron-phonon coupling [3]. We have thus tried to obtain a stable reconstruction of Sn on Si(111):B in a seek for exotic electronic properties. The Si:B(111) substrate is highly boron doped and exhibits a (√3x√3)R30° reconstruction under adequate preparation conditions, where Si adatoms are in T_4 and B atoms in S_5 adsorption positions, giving rise to a semiconductor surface. The deposition of 0.5ML of Sn induces a 2(√3x√3)R30° reconstruction as observed by LEED and STM. Photoemission measurements at Cassiopée beamline (SOLEIL synchrotron) show a new surface state associated to Sn at 270 meV below Fermi level. This surface state is weakly dispersive. We will combine the different experimental data with ab-initio calculations to propose a structural model for this reconstruction.

[1] R.Cortés et al., Phy. Rev. Lett. 96, 126103 (2006).
[2] S. Modesti, L. Petacciadesti, G. Ceballos, I. Vobornik, G. Panaccione, G. Rossi, L. Ottaviano, R. Larciprete, S. Lizit and A. Goldoni, Phys. Rev. Lett. 98, 126401 (2007).
[3] L.A. Cardenas et al., Phy. Rev. Lett. 103, 646804 (2009).

Electronic, magnetic and transport properties of Cr(001) surfaces.

P Habibi, C B and A Smogunov

CEA - Saclay, France

Spintronics is a rapidly growing field which aim is to use the spin of electrons in electronic devices. The spin-polarized scanning tunneling microscope (SP-STM) is a perfect example of application of this physics. It involves tunneling transport between a surface and a magnetic tip and is an essential tool for the local analysis of electronic and magnetic properties of surfaces and (adsorbed) nano-objects.

The aim of our study is to understand and simulate spin-polarized scanning tunneling microscopy (and spectroscopy) images of a Cr(001) surface by ab initio methods using Quantum-Espresso package as well as a tight-binding approach (TB). First, we have performed a detailed study of electronic and magnetic properties of Cr(001) surface, specifically the surface states and their symmetry. By analyzing the partial density of states and its decay in vacuum above the Cr(001) surface we were able to identify the origin of the narrow peak observed near the Fermi level by STS experiments.

Then, we have calculated, using ab initio and TB methods, ballistic spin-polarized electronic transport on “ideal” systems made of two Fe(001)-Cr(001) surfaces separated by vacuum. In order to be more realistic, we have replaced the Fe(001) surface by a small pyramid to model the iron STM tip. Finally the case of C60 on Cr(001) has been investigated.

Contrasting acenes and phenyls on Cu(110) and Ag(110): interactions revealed by valence band tomography

T Ules[1], E Reinisch[1], M Ostler[2], G Koller[1], D Lüftner[1], P Puschnig[1] and M Ramsey[1]

[1]Karl-Franzens Universität Graz, Austria, [2]Universität Erlangen-Nürnberg, Germany

The electronic and geometric structure of Pentacene (5A) and Sexiphenyl (6P) monolayers on Cu(110) and Ag(110) are contrasted in this Angle Resolved UPS study. On these substrates the organic rod like molecules form well ordered monolayers which allow the measurement of the 2 dimensional momentum maps of the π emissions. These yield the geometry of the adsorbate orientation (azimuth and tilt) and the electronic effects of hybridisation on the orbital structure in both real and momentum space.

Although the substrate surfaces are quite similar the molecular interactions are very different. On Cu(110) both molecules align along the atomic rows of the crystal, [1-10] azimuth, while on Ag(110) they align across to them. This different alignment is reflected in differences in bonding interaction, which affects the electronic structure of the molecules. On Cu(110) the LUMOs of both molecules are filled via backdonation of electrons from the substrate to the molecules. When comparing the measured momentum map of the LUMO to DFT calculations for the isolated molecules a modification for both molecules is visible which originates from hybridization effects with the substrate s,p band and the surface state. This contrasts to the weaker interacting Ag(110) substrate. Here 6P shows no evidence of backdonation and the aromatic π system is tilted from the surface. While for 5A the LUMO is also filled its structure is essentially unaltered from the isolated molecule.

X ray circular dichroism in adsorbed chiral molecules

J J de Miguel[1], F J Luque[1], I A Kowalik[2], M Á Niño[1], J Ferrer[3], D Arvanitis[4] and R Miranda[1]

[1]Universidad Autónoma de Madrid, Spain, [2]Polish Academy of Sciences, Poland, [4]Universidad de Oviedo, Spain, [4]Uppsala University, Sweden

The relationship between chirality and magnetism has long puzzled researchers. Recently, layers of chiral molecules have been shown to scatter electrons differently depending on their spin [1,2], opening up the possibility to use these materials as spin filters or to control enantio-selective reactions by means of spin polarization.

Enantiomerically pure ultrathin films of chiral 1,2-diphenyl-1,2-ethanediol deposited on Cu(100) at 100 K have been studied using circularly polarized x rays absorption (XAS) at the carbon K edge. This molecule has two chiral centres located at the two carbon atoms of the ethane chain. The measurements were performed at the I1011 beamline of synchrotron MAXlab (Lund, Sweden). XAS excites element-specific core electrons to empty levels in the ground state thus probing the molecule's electronic configuration.

The different features present in the absorption spectra have been identified and assigned to specific electronic transitions [3]. Pairs of spectra with circularly polarized radiation of opposite helicity were acquired and compared by taking their intensity ratio. Several clearly dichroic features have been observed and assigned to C–C and C–H π orbitals; as expected, these dichroic ratios show opposite signs for the two enantiomers studied. These experiments demonstrate that XAS with circular polarization is an efficient probe of molecular chirality, also allowing us to identify specific electronic states associated to the chiral centres.

[1] K. Ray et al., Science 283, 814 (1999).
[2] B. Göhler et al., Science 331, 894 (2011).
[3] J. Stöhr, *NEXAFS Spectroscopy*, Springer Series in Surface Sciences No. 25 (Springer, Berlin, 1996).

UV induced Auger features in catechol adsorbed on single crystal anatase TiO_2(101)

A G Thomas[1], K Syres[2] and P Deák[3]

[1]University of Manchester, UK, [2]The University of Nottingham, UK, [3]Universität Bremen, Germany

The adsorption of catechols on TiO_2 is of interest in the fields of photovoltaics and functionalisation of TiO_2 for phototherapeutic and diagnostic purposes in biomedical applications. In this work we have studied the effect of UV illumination of a monolayer of catechol on the anatase TiO_2(101) surface using resonant photoemission spectroscopy at the Ti 3p - 3d edge.

Illumination of the sample with UV radiation (4.75 eV) results in the appearance of a Ti MVV Auger feature in valence band spectra. This is accompanied by changes in the resonant photoemission spectra, with the Ti3p Ti 3d resonance moving up in energy from 47 to 50 eV. Constant final state spectra recorded over the Ti 3p level under illumination show a strong narrow peak at an energy of 40.4 eV, consistent with excitation to a highly localised state. We attribute these changes to a catechol to Ti 3d ligand to metal charge transfer. We believe the electron to be strongly localised on the Ti 3d states. In addition to the interesting electronic properties of this system, the UV-induced Auger features allow a clear signature for future time-resolved pump-probe studies of the catechol-TiO_2 charge transfer system.

Organic single crystal band structure investigation using the novel multidimensional electron spectrometer ARTOF 10k: a milestone in molecular electronics research

A Vollmer[1], R Ovsyannikov[1], M Gorgoi[1], S Krause[1], M Oehzelt[1], N Martensson[2], S Svensson[2], A Lindblad[2], T Schmeiler[3], J Pflaum[3], A Foehlisch[1], P Karlsson[4], M Lundqvist[4] and N Koch[1]

[1]Helmholtz Zentrum Berlin, Germany, [2]Uppsala University, Sweden, [3]Universität Würzburg, Germany, [4]VG Scienta AB, Sweden

The Angle Resolved Time Of Flight (Scienta ARTOF 10k) electron energy analyzer instrument facilitates the simultaneous recording of kinetic energy and angular pattern of photoelectrons within an angular aperture of 30° with very high energy resolution (100µeV)[1]. Its transmission (250 times higher than in hemispherical analyzers) allows for very mild conditions during the experiment turning the ARTOF into the predestined instrument to investigate sensitive specimens such as organic single crystals, as extremely low photon fluxes can be used. Even though organic single crystals are of increasing fundamental and applied scientific interest, and crystalline organic semiconductors such as rubrene (5,6,11,12-tetraphenyltetracene) [2] have surpassed amorphous silicon in terms of field-effect transistor mobility, the knowledge of their electronic properties is still rudimentary and mainly based on theoretical calculations due to experimental challenges in photoemission studies [3]. Investigating the electronic band structure under gentle conditions is a necessary prerequisite to unravel the electronic structure in organic semiconductors while studying single crystals allows focusing on the intrinsic properties of organic materials, since extrinsic factors like impurities, defects or grain boundaries, which influence the electrical properties, can be minimized. Here we present the full energy dispersion of rubrene and tetracene single crystals obtained with unprecedented quality within only a few hours of measurement time using the ARTOF instrument [4].

[1] G. Öhrwall, et al., J. Electron Spectrosc. 183 (2011) 125.
[2] Sundar, V.C., et al., Science, 2004. 303(5664): p. 1644-1646.
[3] E.-E. Koch Phys. Scripta T 17 (1987), p. 120.
[4] A. Vollmer et al., J. Electron Spectrosc. 185 (2012) 55.

Orbital tomography: deconvoluting photoemission spectra of organic molecules

S Subach[1], P Puschnig[2], E Reinisch[2], T Ules[2], M Wilenbockel[1], B Stadtmüller[1], M Ostler[3], G Koller[2], C Kumpf[1], L Romaner[4], C Ambrosch-Draxl[4], M Ramsey[2] and S Tautz[1]

[1]Forschungszentrum Jülich, Germany, [2]Karl-Franzens Universität Graz, Austria, [3]Universität Erlangen-Nürnberg, Germany, [4]Montanuniversität Leoben, Austria

We present a tomographic method of photoemission data evaluation [1, 2] which uses the energy and momentum dependence of photoemission from adsorbed molecules to deconvolute valence band spectra into individual orbitals beyond the limits of energy resolution. The method allows the purely experimental determination of molecule-projected densities of state (PDOS), to be compared to theoretically calculated PDOS. The method further allows the direct observation of the effects of bonding on individual orbitals, and in so doing, provides stringent tests for the development of ab-initio electronic structure theory.

In the photoemission experiments on different phases of PTCDA molecule on Ag(110) performed at BESSYII storage ring using a toroidal electron energy analyzer, we demonstrate that tomographic deconvolution delivers a precise and model-free energy level alignment even for cases of several molecular orbitals overlapping in very narrow energy range [2] and is capable of disentangling the site-specific electronic properties caused by local differences in molecule-metal interactions.

[1] P. Puschnig et al., Science 326 (2009) 702.
[2] P. Puschnig et al., PRB 84 (2011) 235427.

Semiconductors and their surfaces 4

Magnetic properties of silicon/silicondioxide interface states

M Rohrmüller, W G Schmidt and U Gerstmann

Universität Paderborn, Germany

The interface between silicon and SiO_2 and its defects such as the P_b centers at (111) and (100) surfaces are technologically highly relevant and intensively investigated by experiment [1] and theory [2, 3]. Electron paramagnetic resonance (EPR) gives a magnetic fingerprint of the centers including the electronic g-tensor and the hyperfine splittings. In the past only hf splittings have been calculated theoretically. As a result, the models for the P_b centers are still under discussion.

In this work, we calculate also the elements of the electronic g-tensor for surface states and several oxidation stages from first principles, using the gauge-including projector augmented plane wave (GI-PAW) approach in the framework of density functional perturbation theory [4]. These results are verified using the orbital magnetization, a computational more demanding Berry-phase approach [5].

By investigating various model systems, we find (1) that hydrogen adsorption at the *Si* surface influences the magnetic signature of the material dramatically, whereby a large variety of g-tensors is obtained. (2) After oxidation, however, the g-tensors do not change considerably. They resemble those of hydrogenated surfaces if the surface atoms are coordinated in the same way and are independent of the symmetry of the oxide. This holds for all investigated surface states and the complete EPR fingerprint suggesting this technique to probe sensitively the crystalline part of the interface structures. (3) This holds in principle also for other investigated systems like the interface between crystalline and amorphous *Si*, e.g. technological relevant for low cost solar cells.

[1] A. Stesmans, et al., Phys. Ref. Lett. 58, 15801 (1998).
[2] A. Sterling, et al., Phys. Rev. Lett. 85, 2773, (2000).
[3] U. Gerstmann, et al., C 7, 157 (2010).
[4] Ch. J. Pickard, F. Mauri, Phys. Rev. Lett. 88, 086403 (2002).
[5] R. Resta, J. Phys Condens. Matter 22, 123201 (2010).

Soft X-ray Synchrotron-radiation photoemission study of Au thin films on Si(100) during annealing

G Grenet[1], J Pénuelas[1], D Ferrah[1], B Gobaut[1], C Botella[1], M Silly[2] and F Sirotti[2]

[1]Institut des Nanotechnologies de Lyon, France, [2]Synchrotron SOLEIL, France

During the growth of silicon nanowires by Vapor-liquid-solid (VSL), gold is the most commonly used catalyst since it forms a low-temperature eutectic with silicon. We carried out investigation on the temperature-induced dewetting of Au thin films evaporated on HF-treated Si(100) substrate. The photoemission measurement was carried out using the soft X-ray synchrotron-radiation provided by Soleil facility (beamline Tempo). Special attention was paid to the interfacial reactions between gold, silicon and silicon oxide. As suggested by Hiraki et al [1] and others [2] we obtained clear evidence that Si atoms can migrate at low temperature through Au films to the surface and form a silicon oxide overlayer. Between 200°C and 600°C, a Au silicide is formed on Si(100). When the temperature of ~600°C is reached, a Au-assisted chemical etching process [3] leads to a complete desorption of the SiO_2 overlayer. Even when the Au desorption is viewed as virtually complete on the base of XPS results, it seems that Au clusters remain but trapped in bulk Si as could be attested by X-ray diffraction measurements.

[1] A. Hiraki, M.-A. Nicolet, J. W. Mayer, Appl. Phys. Lett.18, 178, 1971.

[2] Z. Huang , N. Geyer , P Werner , J de Boor , and U. Gösele, Advanced Materials, 23, Issue 2, 285–308, 2011.

[3] Z. Huang, X. Zhang, M. Reiche, L. Liu, W. Lee, T. Shimizu, S. Senzand U. Gösele, Nano Lett., 8 (9), 3046, 2008.

Surface phonons of germanium (001)

N Esser[1], J Räthel[1], E Speiser[1], U Bass[2] and J Geurts[2]

[1]Leibniz-Institut für Analytische Wissenschaften - ISAS, Germany, [2]Universität Würzburg, Germany

The Ge(001) and Si(001) surfaces with their surface dimers are among of the most intensely studied semiconductor surfaces in the last decades. The widespread interest for these surfaces is motivated by the complex structure due to the dimer buckling and temperature dependent flipping, induced by short-range and long-range interactions. For the clean Ge(001) surface three possible surface reconstructions have been suggested: p(2x1), p(2x2), and c(4x2). At room temperature the p(2x1) reconstruction is preferred and at low temperatures the c(4x2) reconstruction is dominant.

Here the p(2x1)/c(4x2) superstructure and the c(4x2) reconstruction of the Ge(001) surface have been studied by polarized Raman spectroscopy at 300K and 40K, respectively. Raman spectroscopy is able to detect surface phonon modes in a broad spectral range and with high spectral resolution, yielding eigenfrequencies and symmetry selection rules. Raman spectra give evidence for the temperature dependent surface structure and ordering due to the well-known flipping of the buckled dimers. The clean Ge(001) shows surface vibration modes, whose energy values agree well with calculated mode patterns found in literature. For the room temperature p(2x1)/c(4x2) phase the Raman spectra reflect the density of surface phonon modes rather than single phonon states due to dimer flipping induced relaxation of the k-conservation rule. The spectra of the low temperature phase with its stable c(4x2) reconstruction show cone-center surface modes which are closely related to backfolded p(2x1) modes.

Directing arsenic dimers on vicinal Ge(100)

O Supplie[1], S Brückner[2], E Barrigón[3], J Luczak[1], P Kleinschmidt[4], I Rey-Stolle[3], H Döscher[2] and T Hannappel[2]

[1]Helmholtz-Zentrum Berlin, Germany, [2]Technische Universität Ilmenau, Germany, [3]Universidad Politécnica de Madrid, Spain, [4]CiS Forschungsinstitut Erfurt, Germany

Vicinal Ge(100) is the common substrate for state of the art multijunction solar cells grown by metalorganic vapor phase epitaxy (MOVPE). One crucial step regarding high performance devices is the surface preparation of the substrate prior to III-V heteroepitaxy. Single domain surfaces with double layer steps are desired to avoid anti-phase disorder, but there is a lack in understanding the surface preparation of vicinal Ge(100) in VPE ambient. Predominantly D_B stepped Ge(100) surfaces terminated by monohydrides have been prepared under clean MOVPE reactor conditions [1]. Exposure to arsenic either from the precursor (TBAs) or from reactor residuals modifies the surface reconstruction differently regarding dimer configuration, step and domain structure [2]. A contamination-free MOVPE to UHV transfer system enabled us to correlate in situ reflection anisotropy spectroscopy (RAS) with surface science tools.

We observed characteristic features in the RA spectra of arsenic terminated vicinal Ge(100) surfaces prepared under TBAs and background arsenic, respectively. The associated LEED patterns showed almost single domain (2x1) and (1x2) reconstructions, respectively. The dominant orientation of the As dimers corresponds to the sign of the most prominent RAS peak. Accordingly, we observed transitions between preferential (1x2) and (2x1) surface reconstructions depending on temperature, supply and source of arsenic in situ with RAS. X-ray photoelectron spectra indicate slight differences in the arsenic coverage and STM images show differences in the step structure, possibly being reflected in the RA spectra at higher photon energies.

[1] S. Brückner et al., *pss-RRL* 6(2012)178.
[2] WE McMahon and JM Olson, *PRB* 60(1999)15999.

Si(100) in hydrogen ambient - new physics of an old suspect

H Döscher[1], P Kleinschmidt[2], S Brückner[1], O Supplie[3], A Dobrich[3] and T Hannappel[1]

[1]Technische Universität Ilmenau, Germany, [2]CiS Forschungsinstitut für Mikrosensorik und Photovoltaik GmbH, Germany, [3]Helmholtz-Zentrum Berlin, Germany

III-V heteroepitaxy on Si(100) substrates is strongly desired for micro- and optoelectronics. One major challenge is preparing single-domain Si(100) surfaces to prevent the formation of anti-phase disorder during III-V nucleation. Numerous theoretical and experimental studies explore the generation of energetically favorable B-type double-layer steps in ultrahigh vacuum (UHV). Atomic hydrogen exposure suppresses their formation, while optoelectronics are usually manufactured by (metalorganic) vapor phase epitaxy (VPE) hydrogen ambient at nearly atmospheric pressure.

We investigate VPE processing of Si(100) by optical in situ spectroscopy and surface science techniques accessible by contamination-free sample transfer to UHV. Cooling under hydrogen flow went along with strong interaction between process gas and Si(100) surface, formation of a monohydride termination, and a rate-dependent imbalance of the (2x1)/(1x2) reconstruction domains. High pressure and slow cooling promotes dimer rows parallel to the step edges equivalent to a preference for A-type double layer steps thought to be energetically unfavorable. We explain the anomalous Si(100) step structure by a kinetic model based on vacancy generation, diffusion, and annihilation as evidenced by vacancy island nucleation and monolayer oscillations in our in situ signals. Anti-phase disorder-free GaP films grown on single-domain Si(100) serve as template for further integration of III-V-based devices.

Analogy between photoemission matrix elements and LEED in superperiodic semiconducting surfaces

A Tejeda[1], W Srour[1], A Nicolaou[2], P Le Fèvre[2], F Bertran[2], A Taleb-Ibrahimi[2] and D Malterre[3]

[1]CNRS/Institut Jean Lamour, France, [2]Synchrotron SOLEIL, France, [3]Université de Lorraine, France

Angle resolved photoemission is a powerful technique to determine the momentum resolved occupied electronic structure of materials. In this technique based on the photoelectric effect, photons induce an electronic transition from an occupied band towards a state out of the solid. However, the determination of the initial state is sometimes not straightforward because the transition probability between the initial and the final state can vary either as a function of the experimental geometry or the light polarisation, which select the allowed transitions due to symmetry [1-4]. Moreover, the probability transition and thus the photoelectron intensity depends also on photon energy or on wave vector, i.e. as a function of the explored region in reciprocal space. Different intensities arise even when probing the same initial and final states |i>, |f> because the matrix elements <f|A.p|i> governing the transition vary. Matrix element effects can be sometimes so strong that ARPES features are misinterpreted.

We present here a procedure for describing matrix element effects in superperiodic surface systems beyond qualitative considerations. It is based on considering the diffraction of photoelectrons when they escape out of the crystal, in a direct analogy with low energy electron diffraction (LEED). We have applied the procedure for explaining matrix element effects in two systems with a superperiodicity. We describe the wavevector dependence for a surface state and we analyse the photon energy dependence of a bulk band replica. We have chosen as model systems the

S1 surface state of the Si(111)-(7x7) reconstruction and Umklapps of bulk bands in Si(557). Both systems can be understood within an analogy with low energy electron diffraction.

[1] H. Fretwell, A. Kaminski, J. Mesot, J. Campuzano, M. Norman, M. Randeria, T. Sato, R. Gatt, T. Takahashi, and K. Kadowaki, Phys. Rev. Lett. 84, 4449 (2000).
[2] M. Asensio, J. Avila, L. Roca, A. Tejeda, G. Gu, M. Lin- droos, R. Markiewicz, and A. Bansil, Phys. Rev. B 67, 014519 (2003).
[3] A. Bansil and M. Lindroos, Phys. Rev. Lett. 83, 5154 (1999).
[4] J. Gadzuk, Phys. Rev. B 12, 5608 (1975).

Temperature dependence of the dielectric function of Si(110) using Reflection Anisotropy Spectroscopy.

E Barritt, T Farrell and P Weightman

University of Liverpool, UK

The temperature dependence of silicon has been measured using ellipsometry techniques in an ultra high vacuum environment over a temperature range of 80 to 320 K [1] which shows a temperature dependence of observed structures based on the electron-phonon interaction. In this work we show the temperature dependence of silicon using reflection anisotropy spectroscopy. We observe two features corresponding to critical points E_1 and E_2 which decrease in intensity and energy with increasing temperature. Using a least squares determination of the temperature coefficient, our values are comparable with those shown by Lautenschlager et al [1]. The reduced intensity of the RA spectra with increasing temperature could be due to a change in anisotropy at the surface as a result of a strain in the surface Brillouin zone or surface reconstructions.

[1] Lautenschlager et al Phys. Rev. B 36 (1986) 4821.

Nanostructures 4

(invited) Revealing magnetic ordering in nitride systems using spin-polarized scanning tunneling microscopy

A R Smith

Ohio University Nanoscale & Quantum Phenomena Institute, USA

Spin-polarized scanning tunneling microscopy (SP-STM) has proven to be a powerful tool for investigation of spin structure at surfaces. Now, this technique is beginning to be utilized to investigate a wider scope of potential technological materials, an excellent example being the nitrides. Nitrides encompass a wide variety of magnetic properties. And from a technological point of view, it is essential to understand how broken symmetries at surfaces along with reduced size and dimensionality affect the magnetic properties of diverse materials. We therefore have applied SP-STM at room temperature to study the local magnetization of manganese nitride nanostructures. Mn_3N_2(001) thin films have been grown on MgO(001) substrates using molecular beam epitaxy and transferred in-situ to a home-built SP-STM system for magnetic imaging. Results show that the surface consists of an array of antiferromagnetic nanopyramids. Using SP-STM with dI/dV mapping, different layers can be clearly discriminated due to their different conductances. These differences in conductance are a result of not only different chemical environments, but also the spin ordering and broken symmetry at the surface. Contrary to expectations, a layer-wise alternating surface anisotropy in these nanopyramids is observed.[1] Out-of-plane anisotropy on every third terrace appears to be linked to the formation of a Mn tetramer reconstruction. The presented study enables further investigations of the interplay between growth defects and the formation of antiferromagnetic domains. We gratefully acknowledge support from the U.S. Department of Energy and the National Science Foundation.

[1] Kangkang Wang and Arthur R. Smith, Nano Letters (http://dx.doi.org/10.1021/nl204192n), (2012).

InAs/InAsSb nanowires: A route towards Sb-based heterostructures

L Sorba[1], D Ercolani[2], M Pea[3], A Li[2], M Gemmi[4] and F Beltram[2]

[1]Istituto Nanoscienze-CNR, Italy, [2]Nest, Scuola Normale Superiore and Istituto Nanoscienze-CNR, Italy, [3]Nest Istituto Nanoscienze-CNR and Scuola Normale Superiore, Italy, [4]Istituto Italiano di Tecnologia, Italy

InAs/$InAs_{1-x}Sb_x$ heterostructured nanowires (NWs) might find applications both as mid-infrared detectors and as building blocks of electronic devices taking advantage of the outstanding electronic and thermal properties of antimonide-based compound semiconductors. InAs/$InAs_{1-x}Sb_x$ single and double heterostructured NWs have been grown by Au-assisted Chemical Beam Epitaxy. The NWs have been investigated by SEM and High Resolution TEM. The $InAs_{1-x}Sb_x$InAs NW segments have been characterized in a wide range of Sb composition. The InAs stem has a wurzite structure with few stacking faults, as typically found in InAs NWs grown in these conditions, while the InAsSb part has a zincblende structure with a regular growth, without twinning or stacking faults. The InAsSb diameter is larger than InAs stem diameter due to the presence of Sb but is smaller than the catalyst particle diameter. This allows to identify and study the presence of a lateral growth in these NWs. The InAsSb width increases linearly with time and the lateral growth rate depends on the As:Sb ratio. It has a maximum at intermediate compositions ($x \approx 0.5$). The dependence of lateral growth on the growth parameters has been studied in this intermediate composition. The lateral growth is independent of the NW diameter, while varies with growth temperature and length of InAs stem. By increasing the InAsSb growth temperature and reducing the length of the InAs stem it has been possible to completely eliminate the lateral overgrowth.

Even if models that explain lateral growth mechanism are present only for homogeneous NWs, we propose a nucleation and step-flow mechanism leading to the lateral growth in these NWs. The reduction of the lateral growth with temperature could be due to an increase of the material re-evaporation from the sidewall of InAsSb, typical in high temperature growth condition, and it could be also due to an increase of the diffusion length with temperature. Also the reduction of the lateral growth with InAs stem length could be due to the material diffusion on the sidewalls of the InAs stem.

Growth of ZnO and ZnMgO nanowires by Au-catalysed molecular-beam epitaxy

I Isakov, M Panfilova, M Sourribes and P Warburton

University College London, UK

ZnO nanostructures have attracted much attention recently because of the wide range of their possible electronical, optical, sensing and spintronic applications [1–3]. Recent progress on the p-type ZnO doping and combination of ZnO with materials such as Mg or Mn and, furthermore, production of ZnO heterostructures are opening new horizons for novel types of semiconductor devices.

The growth of ZnO nanostructures can be accomplished by a wide variety of methods. However molecular beam epitaxy remains the most pure and controlled way to create these structures [4], especially for heterostructure growth which requires atomically abrupt interfaces.

Here we present the study of oxygen-plasma assisted molecular-beam epitaxy growth of ZnO nanostructures catalysed by gold. The growth was carried out at temperatures ranging from 350 to 900 °C. Au-droplets were prepared by annealing a thermally evaporated Au thin film, or by deposition of Au colloidal particles, or by electron-beam lithography with subsequent Au lift-off process. The resulting nanowires grow at temperatures 700 – 800 °C with diameter 40 – 100 nm and with length up to 2 mm. After establishing optimal conditions for ZnO nanowire growth, ZnMgO nanowires were grown with Mg content up to 20 %. We have characterised the nanowires by high-resolution transmission-electron microscopy, showing that the ZnO nanowires are perfect single-crystals in the wurtzite phase. We will also present the results of our energy-dispersive x-ray spectroscopy, x-ray diffraction, photo-luminescence and electrical transport measurements.

[1] Ü. Özgür et al. “A comprehensive review of ZnO materials and devices”, Journal of Applied Physics 98, 041301, 2005
[2] T. Fukumura et al. “Mn-doped ZnO”, Applied Physics Letters, 75, 21, 1999
[3] M. C. Newton and P. A. Warburton, “ZnO tetrapod nanocrystals”, Materials Today, 10, 5, 2007
[4] Y. W. Heo et al. “Site-specific growth of ZnO nanorods using catalysis-driven molecular-beam epitaxy”, Applied Physics Letters, 81, 16, 2002

Morphology and composition of Au catalysts on Ge(111)

S Hajjar[1], A Spiesser[2], L Josien[1], C Renard[3], G Garreau[1], J L Bubendorff[1], T Maroutian[3], A Mehdaoui[1], D Bouchier[3], M.Petit[2], V Le Thanh[2], D Berlig[1], T O Mentes[4], M A Nino[4], A Locatelli[4] and C Pirri[1]

[1]University of Mulhouse, France, [2]CINaM-CNRS, France, [3]Université Paris-Sud, France, [4]Sincrotrone Trieste, Italy

The chemical and morphological structure of the Au nanodots on Ge(111), which serve as catalysts for the formation of epitaxial Ge nanowires, is investigated. These nanodots are formed by thermal dewetting of an Au thin film (1.2 nm) on a clean Ge(111) surface. The spatial localization of Au is investigated by X-ray spectromicroscopy and transmission electron microscopy. These two techniques are used in both image and spectroscopy modes. The dewetting of an Au film on Ge(111) gives rise to a thin Au-Ge wetting layer and Au-Ge islands. For an annealing temperature below the eutectic temperature T_E, only flat platelets are observed. These platelets are in epitaxy with Ge(111) and their composition is analyzed. For an annealing temperature higher than T_E, 3D dots are formed. These dots are crystallized but not with a single crystallographic orientation. Thanks to the spatially resolved X-ray and transmission electron microscopy measurements, a chemical characterization of both binary Au-Ge catalysts and wetting layer is obtained at the nanoscale. It is shown that for both Au-Ge islands type, Ge segregation occurs. As expected from bulk phase diagram, Au seeds incorporate Ge which precipitates to form a pedestal upon cooling down the sample at room temperature. The interesting feature here is that the Ge precipitated amount is larger (at least twice) than that expected from bulk phase diagram. Most surprisingly, we observe that Ge grows vertically for some dots, forming a Ge nanowire precursor even without external Ge supply.

[1] S. Hajjar et al., Phys. Rev. B 84, 125325 (2011).
[2] C. Pirri et al., Unpublished.

A multitechnique study of the interfacial reaction between TiO_2 surfaces and Molybdenum

X Noirfalise[1], D Cossement[2], N Nuns[3], F Renaux[2] and R Snyders[1]

[1]University of Mons, Belgium, [2]Materia Nova, Belgium, [3]Université Lille, France

Since a few years, molybdenum oxides have attracted a lot of interest due to their numerous applications such as catalytic materials, lubricants, memory devices, gas sensors and solid state microbatteries. On the other hand, TiO_2 surfaces supporting metals have generated a lot of works due to the strong relation between the morphology of the deposit and the electronic interactions between TiO_2 and the deposited metal.

In this work, we aim to grow, by non-reactive DC sputtering of a metallic Mo target, MoO_x films on TiO_2 supports differing by their crystallographic constitution (amorphous, anatase and rutile). A particular attention is made on the diffusion mechanism and oxidation process at the interface TiO_2/MoO_x using XPS and Tof-SIMS measurement. Differences were found in this electronic exchange and, as a consequence, in the growth mode for the two TiO_2 substrates. The emphasis is made with the Cabrera-Mott theory, i.e. the dependence of the interface reaction on the bulk electronic structure of the two phases.Growth mechanisms were estimated using analysis of the peak and background shapes of the XPS signal using the “QUASES” software. For example, a layer by layer growth mode is observed for Mo deposited on the (110)-rutile TiO_2 substrate and a Stranki-Krastanov growth on the amorphous one. Tof-SIMS depth profile measurements reveal the diffusion of oxygen at the TiO_2/Mo interface with appearance of an oxygen depleted zone at the surface of the TiO_2 support.

Nanoparticles on metal surfaces: low-energy impact

M Getzlaff, T Veltum and W Rosellen

University of Düsseldorf, Germany

Deposited mass-filtered FeCo nanoparticles were investigated in-situ by means of scanning tunneling microscopy (STM). The particles are generated in the gas-phase by a continuously working, UHV compatible Arc Cluster Ion Source (ACIS) and subsequently mass-, i.e. size-selected by an electrostatic quadrupole. After size-selection these particles were deposited on a clean W(110)-crystal surface. The size of the deposited FeCo particles is tuned between 5 to 15 nm. Because the preparation, deposition and characterization is carried out under UHV conditions nor oxidation neither contamination takes place.

We focus on the landing behavior of these nanoparticles and their possible structural change after the collision with the target surface. The kinetic energy of the nanoparticles can be varied by applying an external field at the substrate because they are charged thus allowing an acceleration or deceleration. It is shown that for different deposition energies slightly above and below the one for softlanding condition a significantly change of the crystallographic structure occurs. We found an unexpected thermal induced phase transition of the nanoparticles after the impact on the surface at kinetic energies being about 0.2 eV/atom.

Self-organization of Ag nano-structures on vicinal metallic surfaces studied by grazing incidence X-ray diffraction

A Coati, A Bellec, A Vlad, M Sauvage-Simkin and Y Garreau

Synchrotron SOLEIL, France

The deposition of small amounts of atoms on surfaces may induce the formation of well-organized nanostructures, which can present a long-range order. These nano-organized surfaces represent a promising way for the realisation of templates with potential applications for the fabrication of magnetic or catalytic nano-objects.

The adsorption of Ag atoms on Cu or Ni surfaces vicinal to (111) planes induces a periodic faceting with well-defined facets for sub-monolayer deposition. The two systems, Ag/Cu and Ag/Ni, present very similar behaviors: Ag is neither miscible in Cu nor in Ni bulk, the Ag cohesive energy and atomic size are very different from the Cu and Ni ones. Consequently, in both cases, this leads to Ag segregation at the bulk surface, and to the formation of an abrupt chemical interface between the adsorbed atoms and the substrate. Despite their resemblances, strong differences between both systems have been demonstrated thanks to the combination of Grazing Incidence X-ray Diffraction (GIXD), Scanning Tunneling Microscopy (STM) measurements and Quenched Molecular Dynamics (QMD) simulations. For sub-monolayer deposition of Ag, periodic faceted surfaces are formed on vicinal Cu surfaces and the Ag coverage enables the tuning of the surface periodicity. In the case of Ag/Ni, only a narrow range of Ag coverage (around 0.6 monolayers - ML) leads to the formation of a faceted surface. For other coverages, a phase separation is observed at the surface between faceted regions and bare vicinal Ni regions.

For depositions superior to 1ML, Ag completely covers the substrate creating a new homogenous surface. We performed GIXD and STM measurements on thin Ag films (4 ML) deposited on Ni(11 9 9) and Cu(2 1 1) surfaces. The Ag film surface results vicinal to Ag (111) planes and presents a step periodicity very close to that of the vicinal substrate surface. Moreover, the Ag films grown are homogenous without any twins or stacking faults. The Ag film stacking is reversed compared to the bulk stacking. These results are found on both Cu and Ni substrates, showing that the substrate step periodicity can be used, in the case of metallic growth, as a key parameter to obtain well-organized heteroepitaxial growth.

The effects of nanostructuring on lattice thermal conductivity

I O Thomas and G P Srivastava

University of Exeter, UK

The thermoelectric efficiency *(ZT)* of nanostructured semi-conductor compounds has attracted much attention in recent years, with increases in *ZT* relative to unstructured compounds being reported in both theoretical and experimental studies as a result of both interface and low-dimensionality effects. However, much remains undone with regard to the characterisation of these effects. Focusing on SiGe superlattices, we discuss some effects of nanostructuring on the phonon contribution (i.e. the lattice thermal conductivity) to *ZT* from a theoretical standpoint, and attempt to quantify these through the use of a semi-empirical approach to anharmonic phonon interactions which builds on Density Functional Theory calculations for phonon eigensolutions.

Surface characterization of diamond-like carbon coated polyethylene

M Rohrbeck[1], C B Fischer[1], S Wehner[1], M Richter[2] and D Schmeißer[2]

[1]University Koblenz-Landau, Germany, [2]Brandenburg University of Technology Cottbus, Germany

Plastic materials are used in a wide variety of fields, e.g. as packaging materials, constructive parts and tubes for diverse utilizations in industry or medicine. Depending on the intended application the material must meet specific well-defined requirements such as flexibility, fracture strength and durability. In many cases it is desirable to combine advantageous properties of different materials, e.g. elasticity on the one hand and abrasion strength on the other hand. In this study the combination of bulk polyethylene (PE) and plasma-deposited diamond-like carbon (DLC) coating is investigated. PE is chosen as the simplest model for a relevant plastic material. DLC with its chemical constitution of C and H is selected since it offers the unique possibility of arranging a great diversity of coatings. In respect of hardness a range from more flexible to more robust is technically feasible. Investigation of two different types of nanometer-scaled DLC films is presented. Surface characterization of PE samples with different DLC layer thicknesses is performed by multiscale microscopic analysis including scanning electron microscopy (SEM) and atomic force microscopy (AFM). Further near edge X-ray fine structure (NEXAFS) spectroscopic measurements are performed. These results will provide an enhanced understanding of layer formation at the interface between the basic plastic material and the DLC coating and will help to find optimal parameters for the coating process to achieve improved product characteristics.

Surface dynamics 2

(invited) Ultrafast magnetization dynamics of gadolinium and terbium studied by XUV photoelectron spectroscopy

R Carley

Free University of Berlin, Germany

I will present recent results from IR-pump-XUV-probe angle-resolved photoelectron spectroscopy (ARPES) experiments on the ultrafast laser-driven demagnetization of thin films of Gd(0001) and Tb(0001) on W (110). The experiments are the first to be done using a newly developed high-order harmonics XUV source and monochromator beamline. Following excitation by an intense IR pulse, ARPES with 35 eV photons allows us to directly probe the response of the exchange-split valance band. As a signature of ultrafast demagnetization by the IR pulse, we see a rapid reduction of the exchange-splitting in the valence band of both metals. However, due to its larger spin-lattice coupling, the response of terbium to laser excitation is much stronger than gadolinium. In gadolinium, we also observe significant differences between the responses of the minority and majority bands in the first picosecond. This ultrafast response is in contrast to quasi-equilibrium thermal demagnetization, and reveals a spin dependence to the exchange coupling between the valence and 4f states responsible for magnetic ordering. This suggests that laser excitation drives the system out of magnetic equilibrium on the picosecond timescale.

Time-resolved optical pump-probe spectroscopy of undoped and Dy-doped $BiFeO_3$ multiferroic thin films

K Doig[1], A-K Axelsson[2], N Alford[2] and J Lloyd-Hughes[1]

[1]University of Oxford, UK, [2]Imperial College London, UK

Magnetoelectric multiferroics, with coupled electric and magnetic order parameters, have been of fundamental interest in recent years, with potential applications in information storage, spintronics and photovoltaics. $BiFeO_3$ is widely studied as a room temperature multiferroic, in particular in thin film form, where compressive strain stabilises a tetragonal phase with higher saturation polarisation and magnetisation than in the bulk rhombohedral phase. Further improvement to the magnetisation has been achieved by substituting bismuth for lanthanides, modifying the incommensurate spiral spin structure; Dy doping has been particularly successful because of its relatively high magnetic moment.

We investigated the static and ultrafast optical properties of $BiFeO_3$ thin films, which were grown by pulsed laser deposition on $LaAlO_3$ (001) substrates. Pump-probe reflectivity spectroscopy (400nm pump, 800nm probe) monitored the ultrafast transfer of electrons from oxygen 2p to iron 3d states. The time-resolved reflectivity exhibited a fast (1ps) and a slow (>10ps) component, indicating the electronic relaxation time. Oscillations in the reflectivity were attributed to the propagation of a strain pulse through the film, created by electron-phonon coupling. The speed of sound in the doped and undoped samples was extracted from the oscillation frequency. Optical ellipsometry provided the refractive index and absorption coefficient, and gave insight into the electric-dipole active charge transfer transitions, which Dy-doping alters. In conjunction these techniques can be used to gain a better understanding of both the electronic properties and strain in multiferroic thin films, thereby enhancing their potential for applications.

Ultrafast dynamics in photoexcited Bismuth surface and bulk states

E Papalazarou[1], J Faure[2], J Mauchain[1], M Marsi[1], I Timrov[2], N Vast[2], B Arnaud[3] and L Perfetti[2]

[1]Université Paris Sud, France, [2]Ecole Polytechnique, France, [3]Institut de Physique de Rennes, France

Nowadays, although the atomic motion in bismuth following the photoexcitation by femtosecond laser pulses is well understood [1,2], the temporal evolution of its electronic states has never been directly measured. To this end, we have performed time-resolved and angle-resolved photoemission experiments in bismuth (111) that allowed us to directly observe electron-phonon coupling with individual Bloch state wavevectors. Our measurements confirmed that the electronic structure of bismuth displays a rich combination of bulk-like bands, surface states and surface state resonances [3,4]. We found that the binding energy of bulk-like bands oscillates with the frequency of the A_{1g} phonon mode whereas surface states are rather insensitive to the coherent motion of the lattice [5]. A strong dependence of the oscillation amplitude on the electronic wavevector is correctly reproduced by ab initio calculations of electron-phonon coupling. Besides these oscillations, all the electronic states display a photoinduced shift towards higher binding energies whose dynamics follows the evolution of the electronic temperature.

[1] D. M. Fritz et al., Science 315, 633 (2007).
[2] Y. Giret et al., Phys. Rev. Lett. 106, 155503 (2011).
[3] A. Kimura et al., Phys. Rev. Lett. 105, 076804 (2010).
[4] Yu. M. Koroteev et al., Phys. Rev. Lett. 93, 046403 (2004).
[5] E. Papalazarou et al., arXiv:1112.3949v1.

Time-resolved spectroscopy of unoccupied NiO(001) thin film states

W Widdra, M Kiel and S Großer

University Halle-Wittenberg, Germany

The structure and the electron dynamics within ultra-thin films of the charge-transfer insulator NiO has been investigated by two-photon photoemission (2PPE), scanning tunneling microscopy (STM) and spectroscopy (STS). Well-ordered epitaxial NiO(100) films have been grown by molecular beam epitaxy on a Ag(001) substrate. By the combination of 2PPE and STS the unoccupied Ni 3d states and the image-potential states are identified for the mono- and bilayer NiO film. The bilayer exhibits a series of three image-potential states with binding energies which are modified by the dielectric thin film properties and which indicate hybridization with Ni states. Their lifetimes have been determined to 30, 50, and 120 fs for the n=1–3 image state, respectively, significantly shortened as compared to the bare substrate. For the unoccupied Ni 3d states which also contribute to the NiO conduction band layer-dependent energy shifts are observed in the range from 2-8 monolayers. Here a detailed spectroscopic comparison between STS and 2PPE exhibits excellent agreement of the observed features with small but distinct shifts in the 100-200 meV range.

(invited) Spectroscopy and dynamics of unoccupied electronic states of periodically rippled graphene

J Guedde, N Armbrust, P Jakob and U Höfer

Philipps-Universitat Marburg, Germany

We present a study of the energies, dispersion and lifetimes of initially unoccupied electronic states between the Fermi and the vacuum level of single graphene layers on Ru(0001) by means of time- and angle-resolved two-photon photoelectron spectroscopy (2PPE). Graphene/Ru(0001) is a particular interesting system because of a relative strong geometrical corrugation of the graphene layer in the form of a periodically rippled moiré superstructure caused by the interaction with the Ru surface. The dissimilar graphene-Ru distances in the hill and valley areas of the moiré superstructure lead to a number of novelties referring to image-potential and interface states. We identify three image-potential states close to the vaccum level and two interface states at energies of 0.91 and 2.58 eV above the Fermi level. The most strongly bound, short lived and least dispersing image-potential state is suggested to have some quantum-well character with a large amplitude below the graphene hills. The two other image-potential states are attributed to a series of slightly decoupled states. Their lifetimes and dispersions are indicative of electrons moving almost freely above the valley areas. The two interface states most likely originate both from the well-kown surface resonance of Ru(0001) and exhibit different confinement and energy shifts in the valley and hill areas. These results will be compared with the energy shift observed for the Shockley surface state of the (111) noble metal surfaces upon adsorption of organic semiconductor layers and the decoupling of image-potential states by dielectric adlayers.

Watching it freeze: a microscopic picture of charge density wave formation at surfaces

S Wall[1], B Krenzer[1], S Wippermann[2], S Sanna[2], F Klasing[1], A Hanisch-Blicharski[1], M Kammler[1], W G Schmidt[2] and M Horn-von Hoegen[1]

[1]University of Duisburg-Essen, Germany, [2]Paderborn University, Germany

Ultra-fast electron diffraction in a reflection geometry was employed to investigate the dynamics of the Peierls-instability-driven phase transition on an Indium-induced (8x2) reconstruction on a Si(111) surface. Far below the critical temperature of 90 K, the (8x2)↔(4x1) phase transition is electronically driven through a weak excitation with a fs-laser pulse and results in a long-lasting super-cooled excited (4x1) phase. This metastable situation – far away from equilibrium – is only accessible through the ultrashort excitation by the fs-laser pulse. A thermal excitation of the phase transition due to laser induced heating was experimentally excluded.

The recovery of the (8x2) ground state on a timescale of 500 picoseconds is triggered by adsorbates that act as nucleation seeds – the same way that super-cooled water in a bottle freezes upon the insertion of seeds. With increasing density q_{ad} of adsorbates the recovery to the groundstate proceeds much faster following a $t \sim 1/q_{ad}$ law. Density functional theory calculations reveal the microscopic scenario of the (4x1)↔(8x2) phase transition, which occurs one-dimensionally along the Indium chains. The metastable (4x1) surface unit cells fall back into their (8x2) ground state one at a time, like a row of falling dominoes. The phase front propagates at about 800 m/s, comparable to the speed of sound.

Dynamics of vibrational modes of Pb adsorbate layers on Si(111): mode conversion and de-excitation

A Kalus, S Wall, S Sakong, T Frigge, A Hanisch-Blicharski, P Kratzer, M Kammler and M Horn-von Hoegen

University of Duisburg-Essen, Germany

Ultrafast time resolved reflection high energy electron diffraction was used to study the vibrational dynamics of adsorbate layers upon excitation with a fs laser pulse in a pump probe setup. We employed the Debye-Waller effect $I = I_0 \exp -\langle (uk)^2 \rangle$ to follow the temporal evolution of the vibrational amplitude u of the adsorbate atoms. The SIC($\sqrt{3}\times\sqrt{3}$) reconstruction of Pb on Si(111) was used as model system and excited by 50 fs, 800 nm laserpulses at a fluence of 4 mJ/cm^2. We observe two time constants of 100 ps and 3 ns for the vibrational de-excitation. With the k dependence of the Debye-Waller effect we identified the fast decay as a mode with dominant parallel amplitude while the slow mode exhibits a dominant vertical amplitude. Both time constants can be explained with classical molecular dynamics simulations. The electronic and phononic band structures of the substrate plus adsorbate layer were calculated using density functional theory. The hot electrons generated by the laser pulse initially excite solely optical phonons. These parallel modes convert on a 100 ps time scale to modes perpendicular to the surface that dissipate their energy into the Si substrate on a ns time scale. This surprisingly long lifetime is explained by the small overlap between the low-energy vertical Pb modes with an energy of 2 – 4 meV and the Si acoustic phonons.

Time resolved, ultrafast surface photovoltage measurements of n-type photovoltaics

B Spencer[1], M Cliffe[1], D Graham[1], S Hardman[1], E Seddon[1], K Syres[1], A Thomas[1], F Sirotti[2], M Silly[2], J Akhtar[1], R Page[1], S Fairclough[3], S Chattopadhyay[4], D Binks[1] and W Flavell[1]

[1]University of Manchester, UK, [2]Synchrotron SOLEIL, France, [3]University of Oxford, UK, [4]Cockcroft Institute, UK

The change in the surface potential upon photoexcitation has been measured in n-type photovoltaics, particularly ZnO, using laser-pump X-ray-probe experiments. Chalcogenide colloidal quantum dot (QD) samples have been chemically linked to the surface, and the change in the surface potential upon deposition of these QDs has been investigated.

The time-dependent change in the surface photovoltage (SPV) upon photoexcitation in ZnO is itself of interest because the photoconductivity and charge carrier dynamics are highly dependent on oxygen vacancies at the surface. This is due to the changes in the surface potential occurring through oxygen chemisorption and desorption mechanisms [1]. As such, the timescales of the photoinduced change upon laser excitation in ZnO have been observed to vary from 134 to 680 μs upon subsequent preparations of the ZnO surface.

The SPV in ZnO upon deposition of colloidal QD samples illustrates direct injection of charge carriers into the ZnO conduction band. This is proven by the use of two different photoexcitation wavelengths: one of the order of the ZnO band gap energy, and one much less than this, but with energy greater than the effective band gap of the QD samples. The QD samples are designed so that the LUMO lies within the ZnO conduction band [2]. Photoexcitation of the QDs leads to carriers being injected into the QD LUMO which subsequently migrate to the ZnO surface, and thus an SPV change is measured in the ZnO.

The experiments involved both continuous wave and femtosecond lasers that were modulated and synchronized to a fast (150 ns time resolution) XPS measurement technique at the TEMPO beamline at Synchrotron SOLEIL.

[1] M. Liu and H. K. Kim, Appl. Phys. Lett. 84, 173 (2004).

[2] S. J. O. Hardman, D. M. Graham, S. K. Stubbs, B. F. Spencer, E. A. Seddon, H.-T. Fung, S. Gardonio, F.Sirotti, M. G. Silly, J. Akhtar, P. O'Brien, D. J. Binks and W. R. Flavell, Phys. Chem. Chem. Phys. 13, 20275 (2011).

Wednesday 5 September

Organic layers and polymers 8

(invited) Understanding nucleation of polypeptide self-assembly

C MacPhee[1], R Morris[1], K Eden-Jones[1], H Cole[1,2], P E Barran[2] and R J. Allen[1]

[1]The University of Edinburgh, UK, [2]School of Chemistry, The University of Edinburgh, UK

Amyloid fibrils are ordered aggregates of misfolded protein. These fibrils are of great interest because of their role in degenerative diseases including Alzheimer's and Type-2 diabetes. Their physical properties also make them potentially useful in the development of novel materials. It is well known that fibril formation occurs with "nucleation-like" kinetics in which a long lag phase is followed the rapid appearance of fibrils. However, despite much work, the molecular mechanisms responsible for fibril formation and growth remain unclear. This is particularly important because it is believed that pre-fibril oligomeric species present during the lag time may be the cytotoxic agents responsible for amyloid associated pathologies. Much recent research has focussed on whether fibril formation is a stochastic nucleation process and the possible role of secondary processes such as fibril fragmentation. We have used a combination of mass spectrometry, high throughput fluorescence spectroscopy experiments and computer simulations to investigate in detail the kinetics of fibril formation in bovine insulin.

Study of plasma– surface interactions during the synthesis of isopropanol plasma polymers by NO chemical derivatization of surface radicals and plasma phase IR spectroscopy

S Ershov[1], F Khelifa[2], P Dubois[2] and R Snyders[1]

[1]University of Mons/Chimie des Interactions Plasma Surface, Belgium, [2]University of Mons/Service des Matériaux Polymères et Composites, Belgium

Relative amounts of surface free radicals were derived from quantitative comparison of N1s spectra for a series of depositions of i-ppf varying the RF discharge power (50-400 W), the derivatization duration (5-30 min), the NO pressure (10-500 mbar), the radical life time under vacuum (up to 1h) and in the air (up to 7 days). Our data reveals that the optimum conditions for NO derivatization are 100 mbar for 15 minutes and that the amount of N on the surface stabilizes at 0.9 ± 0.1 at.% from 100 W to higher power. The radicals seems to be quite stable under vacuum (~0.8 at.%) after 1 hour and relatively stable in the air (~0.4.%) after 1 week. By fitting the N1s peak, it was also possible to identify primary, secondary and tertiary radicals and to study their respective evolutions as a function of the already mentioned experimental parameters.

These XPS findings are supported by in-situ gas phase Fourier-transform infrared spectroscopy data. The latter was used to correlate the degree of precursor’s fragmentation with the results of derivatization experiments and served as an extra tool in understanding of plasma-surface interactions.

Polymer nanodroplets on surfaces

V Koutsos[1], A Evangelopoulos[2], F Madani-Grasset[2] and E Glynos[3]

[1]The University of Edinburgh, UK, [2]Nanolane, France, [3]University of Michigan, USA

The wetting and adsorption behaviour of polymers on solid substrates has raised great interest due to the wealth of practical applications such as adhesion, surface lubrication and friction modification, colloidal stabilization, surface nanopatterning and biocompatibility of artificial organs, stimulating in turn fundamental research. The present work concerns the spreading behaviour of a nanoscopic polymer droplet on a flat, rigid substrate and addresses the following fundamental research topics: the importance of the elastic nature of the material on spreading; a method of theoretically predicting an elastic modulus for the droplet from experimental measurements of its state of adsorption; the effect of droplet size on the elastic modulus. We use a theoretical model that, in conjunction with atomic force microscopy (AFM), can be used as a non-invasive method for the determination of the elastic modulus of a polymer nanodroplet residing on a flat, rigid substrate. The model is a continuum theory which combines surface and elasticity theories for the prediction of the droplet's elastic modulus, given experimental measurement of its adsorbed height. Utilization of AFM-measured heights for relevant droplets reported in the literature and from our own experiments illustrated the following: the significance of both surface and elasticity effects in determining a polymer droplet's spreading behaviour; the extent of a continuum theory's validity as one approaches the nanoscale; a droplet size effect on the elastic modulus.

(invited) The physics of confined DNA: bacteriophage knots and chromosome organisation

D Marenduzzo

The University of Edinburgh, UK

In physiological conditions, ranging from bacteriophages, the viruses of bacteria, to man, DNA is strongly confined. For instance, the human nucleus, which is 10 micron or so in size, contains about 2 meter of DNA in length. In bacteriophages the DNA is instead packed to almost crystalline density, and the subsequent pressure is exploited by them when ejecting their DNA to infect the host.

I will discuss two topics in which confinement has important effects on the behaviour of DNA. First, I will consider the problem of DNA knots inside phages, which recent experiments showed to be sharply different from those formed by DNA in solution. This difference was at first sight surprising, and I will discuss here some evidence from computer simulations that suggest the a key element to lead to these trends is the tendency of contacting DNA to approximately align with each other.

Second, I will show Brownian dynamics simulations of eukaryotic chromosomes interacting with DNA-binding proteins. We show that the interactions can lead to organisation of the chromosome in 3D, and we compare our results with 3C experiments in human nuclei.

Dynamic porosity as a key-feature of soft self-assembeld microporous organic materials

J Jordanovic, M A Lewis, T Mitra, A Trewin and A I Cooper

University of Liverpool, UK

Microporous materials, like MOFs and porous polymer networks, have become popular for energy applications such as H_2 storage or CO_2 sequestration. Therefore it is a challenging aim to design materials with high sorption capacity, and to be able to predict the correct porosity, i.e. by calculating the solvent accessible surface area inside the pores.

Porous molecular crystals are a class of soluble, self-assembled, soft porous organic materials synthesized in our group [1]. Although measured isotherms demonstrate a considerable gas uptake, however, single crystal XRD-data based structure models exhibit disconnected voids pointing out a non-porous structure.

It is the flexibility of the structure that enables hopping of gas molecules, a cooperative diffusion effect as demonstrated earlier [2]. We investigate the dynamics of the structure and key features of “dynamic porosity”, i.e. closing and opening of voids resulting in fluctuations of the solvent accessible surface area over time.

In particular, we are interested in the porous crystal cage4 [3] that is showing a complex stepwise isotherm and a guest-responsive behaviour. Moreover, the simulations hint at a "void-unlocking" mechanism that is depending on the amount of loaded gas molecules. We seek to understanding the impact of the loading on the dynamic of the structure. This may help to develop reliable tools to predict the porosity of structures that are displaying "porosity without pores", and future design strategies for soft porous materials.

[1] *Nature Comm.* 2011, *Nature Mat.* 2009
[2] *Angew. Chem., Int. Ed.*, 2011
[3] *Chem. Eur. J* 2011

Chiral adsorption of free-base corroles studied at the single-molecule level

M Rashidi, S Müllegger and R Koch

Johannes Kepler University, Austria

Corroles are versatile chemically active agents in solution. Acquiring fundamental knowledge of corrole−surface interactions expands their applications toward surface-supported systems. We have investigated the electronic and geometric properties of surface-supported free-base corrole molecules at the single-molecule level by employing low-temperature scanning tunneling microscopy and spectroscopy. To provide a suitable reference for other corrole-based systems on surfaces, we have studied the archetypal 5,10,15-tris(pentafluorophenyl)- corrole [H_3(TpFPC)] as model system, weakly adsorbed on two surfaces with different interaction strengths. We have demonstrated the nondissociative adsorption of H_3(TpFPC) on pristine Au(111) and on an intermediate organic layer that provides sufficient electronic decoupling to investigate geometric and frontier orbital electronic properties of almost undisturbed H_3(TpFPC) molecules at the submolecular level. We have identified a deviating adsorption behavior of H_3(TpFPC) compared to structurally similar porphyrins, characterized by a chiral pair of molecule−substrate configurations.

Theory and modelling 1

(invited) Generalised Langevin equation for treating open classical and quantum systems

L Kantorovich[1] and L Stella[2]

[1]King's College London, UK, [2]Universidad del País Vasco, Spain

Treatment of open systems using the Generalised Langevin Equation method in which the ability of the system to interact and exchange energy with a thermal bath during its evolution is built in explicitly into the model, will be discussed. Initially, I'll describe the classical case, after which a fully quantum consideration will follow. The latter approach allows for ac-number GLE for the fully quantum case to be rigorously formulated based on two main ideas: (i) a harmonisation approximation whereby at each instant the Hamiltonian is harmonic (but time-dependent) and (ii) going beyond the Born approximation for the density operator of the whole system whereby the bath is at equilibrium only on average. It is shown that the stochastic field entering the GLE is Gaussian even in the quantum case and is due to phonon excitations of the bath. Simple examples illustrate the general concepts.

Density-functional theory with screened van der Waals interactions for the modeling of hybrid inorganic/organic systems

V G Ruiz[1], W Liu[1], E Zojer[2], M Scheffler[1] and A Tkatchenko[1]

[1]Fritz-Haber-Institut der MPG, Germany, [2]Graz University of Technology, Austria

The electronic properties and the function of hybrid inorganic/organic systems (HIOS) are intimately linked to their interface geometry. In particular, van der Waals (vdW) interactions are fundamental in determining the structure of the interface and its stability. We propose a method (DFT+vdW^{surf}) that extends pairwise vdW corrections to the modeling of adsorbates on surfaces. Specifically, dispersion-corrected density-functional theory (the DFT+vdW method) [*PRL* 102, 073005 (2009)], is combined with the Lifshitz-Zaremba-Kohn theory [*PRB* 13, 2270 (1976)] in order to include the non–local Coulomb screening inside the inorganic bulk in the determination of the C_6 coefficients and vdW radii. We show that the inclusion of the many–body collective response of the substrate electrons enables us to reliably predict the HIOS geometries and energies. Our method includes both image-plane and interface polarization effects via the inclusion of semi–local hybridization due to the dependence of the C_6^{ab} interatomic parameters on the electron density. We show that DFT+vdW^{surf} yields geometries in remarkable agreement (≈ 0.1 Å) with normal incidence x–ray standing wave measurements for the 3,4,9,10–perylene–tetracarboxylic acid dianhydride ($C_{24}H_8O_6$, PTCDA) molecule on Cu(111), Ag(111), and Au(111). Similarly, accurate results are obtained for xenon and benzene adsorbed on metal surfaces as well as additional inorganic/organic interfaces.

Density functional theory study of the interaction of molecular hydrogen and soft layered materials

G Graziano[1], J Klimeš[1], F Fernandes-Alonso[2] and A Michaelides[1]

[1]London Centre for Nanotechnology, UK and University College London, UK, [2]ISIS Facility, Rutherford Appleton Laboratory, UK

Hydrogen is recognised as one of the most promising clean energy vectors, potentially able to replace fossil fuels. However, due to its low volumetric energy density, technological applications of hydrogen are difficult. Thus research into materials that can easily store large quantities of hydrogen has been a hot topic for the last twenty years or so. Among the many proposed materials, layered materials, like graphite and *hexagonal*-boron nitride, have been shown to offer promising solutions [1,2]. Here, we report results of computational studies, based on density functional theory, for the molecular hydrogen adsorption on and absorption in graphite and *h*-BN. PBE and a van der Waals density functional, namely the optimized Becke88 van der Waals (optB88-vdW) [3] have been used. The comparison of the two functionals highlights that the inclusion of the van der Waals forces is crucial for the description of the physical interaction of hydrogen and layered materials. We find that the hydrogen adsorbed on both graphene and a single layer of *h*-BN is free to diffuse and rotate. By studying the absorption of hydrogen in graphite and *h*-BN, we can infer the optimal interlayer spacing for both materials in order to host the gas molecule. These results can drive the research of the suitable intercalant able to tune the interlayer distance in these materials to the optimal one, in order to reduce the energetic costs for the absorption of hydrogen.

[1] W. I. David, Faraday Discuss. 151, 339 (2011).
[2] S.-H. Jhi and Y.-K. Kwo, Phys. Rev. B 69, 24540 (2004).
[3] J. Klimeš, D. R. Bowler, and A. Michaelides, J. Phys.: Condens. Matter 22, 022201 (2010).

(invited) Van der Waals Interactions in Solids, Surfaces, and Interfaces

A Tkatchenko

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Van der Waals (vdW) interactions are essential for determining the structure, stability, and function for a wide variety of molecules and materials. However, in condensed matter, cohesion is thought to arise mainly from covalent bonding and/or electrostatic interactions, hence it is typically assumed that vdW forces play a minor role. We have recently developed a set of efficient methods for an accurate description of (screened) vdW interactions in molecules, solids, and interfaces [1-4]. We present the challenges for an accurate theoretical modeling of vdW interactions in condensed matter systems and demonstrate that vdW interactions play a significant role for their cohesive properties. Applications will be presented for a few fundamental systems: phase diagram of ice [5], cohesion in ionic and semiconducting solids [2], and stability of hybrid inorganic/organic interfaces [4,6]. For all these cases it is found that vdW interactions play a noticeable if not crucial role, not just for quantitative energies but also for the qualitative behavior. Ongoing work and the remaining challenges in the modeling of vdW interactions will be discussed.

[1] A. Tkatchenko and M. Scheffler, PRL 102, 073005 (2009).
[2] G.-X. Zhang, A. Tkatchenko, H. Appel, J. Paier, and M. Scheffler, PRL 107, 245501 (2011).
[3] A. Tkatchenko, R. A. DiStasio Jr., R. Car, and M. Scheffler, PRL (2012).
[4] V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, PRL (2012).
[5] B. Santra et al., PRL 107, 185701 (2011).
[6] W. Liu et al., JPCL 3, 582 (2012).

Spontaneous polarisation in thin films of molecular solids

A Cassidy, O Plekan, R Balog, N Jones and D Field

Aarhus University, Denmark

Recent experiments have shown that films of molecules; nitrous oxide, methyl formate and others, spontaneously harbour electric fields exceeding 10^8 V/m[1,2,3]. Polarisation within films generates the electric fields and leads to surface potentials at the film-vacuum interface. These potentials are observed using the high-resolution, low-energy electron beam at the SGM2 beamline on the ASTRID synchrotron source (Aarhus University). Films are grown by vapour deposition on a polycrystalline Au substrate cooled to cryogenic temperatures under ultrahigh vacuum conditions. Surface potentials up to 38 V have been recorded on 1200 ML thick films of N_2O deposited at 40K. A simple theory based on a mean field model, which assumes that polarisation results from dipole alignment within the films, has been constructed and can be shown to fit the experimental results.

This report will introduce this new phase of material, describing in detail the experimental observations and put these observations in context with theory. In particular, the counter-intuitive temperature dependence of films of methyl formate, where the electric field increases six-fold between 80 K and 89 K, in sharp contrast to the pronounced fall with deposition temperature seen between 50 K and 75 K both here and in numerous other species, will be described. These experiments provide new insight into the structure of disordered molecular solids and provide a novel route to producing electronic structures in thin films.

[1] R. Balog et al., Phys. Rev. Lett. (2009), 102, 073003.
[2] O. Plekan, A. Cassidy, R. Balog, N. C. Jones and D. Field, PCCP (2011), 13(47), 21035.
[3] D. Field, O. Plekan, A. Cassidy, R. Balog and N. Jones, Euro. Phys. News, (2011), 42(6), 32.

Role of chain-chain interactions in the structure of monolayers of alkanethiolates on Au(111) and Ag(111): do they really matter?

H Fabio Busnengo[1], J G Solano Canchaya[1], P N Abufager[1], Y Wang[2], M Alcamí[2], F Martín[2], M Luz Martiarena[3] and K Reuter[4]

[1]Instituto de Física Rosario - Universidad Nacional de Rosario, Argentina, [2]Universidad Autónoma de Madrid, Spain, [3]Centro Atómico Bariloche and Instituto Balseiro, Argentina, [4]Technische Universität München, Germany

Though Au(111) and Ag(111) are very popular substrates for the grow of self-assembled monolayers (SAM) of alkylthiolates (SC_n), and many theoretical investigations do exist, various fundamental issues remain unclear. For instance, the full coverage SAMs on Au(111) and Ag(111) differ in coverage (1/3 vs. 3/7) and tilt angle (~30° vs. ~0-10°), due to reasons that are not fully understood. It is very often claimed that these differences (between SAMs grown on a priori similar substrates) reflect that the structures of SAMs are dictated by a very subtle competition between the S-surface and the chain-chain interactions.

In this work we compare the stability of many possible structures of SAMs of SC_n on Au(111) and Ag(111) characterized by coverages 1/3 and 3/7 (for chains with n=1 to n=18 C atoms) through DFT-D calculations. As expected, for long enough alkyl chains, the chain-chain contribution to the cohesive energy of the SAMs is larger than the one of the S-surface bond. However, in such cases chain-chain interactions also stabilize other higher coverage competing structures involving multilayers. Therefore, the different structural properties of the up-right monolayers of SCn on Au(111) and Ag(111) are largely determined by the different (coverage dependent) S-surface binding energies, which in turn, are due to the dissimilar reconstructions induced by the SAMs on both substrates. Thus, our results surprisingly show that the structures of the saturation coverage monolayers of SC_n on Au(111) and Ag(111) are barely dictated by the chain-chain interactions in contrast with the usual belief.

Dewetting-assisted formation of novel fluorescent aggregates of rhodamine dyes: contribution of surface SiO_2 layer and underlying Si layer

A Tomioka and K Takada

Osaka Electro-Communication University, Japan

π-conjugated organic dyes have great prospect for photonic applications as well as electronic devices. However in aggregated states, some dye species, including rhodamines (Rh), get quenched and few species, e.g., those providing J-aggregates, remain to be fluorescent. To demonstrate an in situ fluorescence switching, quasi-stable Rh aggregates were formed utilizing dewetting process on a hydrophilic surface and their fluorescence intensity was traced during annealing.

Every as-grown aggregate of Rh 6G, Rh B, and Rh 101 showed fluorescence, when prepared by the dewetting process of an ethanol dye solution: dye molecules were accumulated in droplets by a solution flow during a rapid evaporation of solvent ethanol, which was much faster than the conventional diffusion process. This rapid process implies that the dyes in as-grown aggregates have quasi-stable molecular ordering. Upon annealing to 200°C, every particle showed the identical fluorescence decrease down to 5 % irreversibly, altering its mode of ordering from the quasi-stable dequenched state to the stable quenched state.

To elucidate the driving force toward the dequenched ordering, silicon wafers with surface SiO_2 layer of varying thickness were used as a substrate for dewetting. Dewetted aggregates grown on 30 nm SiO_2 layer showed consistently high fluorescence with the same fluorescence spectrum of those on glass substrates: aggregates grown on 2 nm SiO_2 were in quenched states. When the aggregates on 30 nm SiO_2 were annealed at 200°C, they became quenched and showed the identical fluorescence spectrum as those on 2 nm SiO_2.

Several groups reported that the quenching of Rh adsorbed on SiO_2 patterns on Si formed by local anodic oxidization with AFM tip did not obey the Foerster energy transfer model. This observation is consistent with our results, if the additional quenching was due to an alteration of molecular ordering in case of thin underlying surface SiO_2 layer.

Reactions on surfaces 5

(invited) Atomic structure of graphene supported metal nanoparticles

A Stierle

DESY and University of Hamburg, Germany

Small metallic nanoparticles exhibit altered structural, chemical and magnetic properties as compared to their bulk counterparts, making them attractive for highly active heterogeneous catalysts or high storage density magnetic media. To pinpoint structure - functionality relationships for such systems an atomic scale understanding of their structure is mandatory. This is frequently hampered for real catalyst materials by the intrinsic complexity given by random nanoparticle orientation, large size and shape variations as well as low particle concentration. Recently it was discovered that Ir or Ru supported graphene acts as a template for the tailored growth of 3d and 4d transition metal nanoparticles with diameters < 2 nm in the form of highly ordered, hexagonal arrays adopting the graphene moiré unit cell of 2.5 nm x 2.5 nm [1].

In my presentation I will demonstrate that Ir nanoparticles on graphene / Ir(111) form a crystalline superlattice with high crystallographic perfection and long range order, which opens the door for an atomic scale characterization using surface x-ray diffraction (SXRD) with high crystallographic precision. The atomic structure of nanoparticles with 1-2 nm in diameter can be resolved including internal strain and gas adsorption induced structural changes.

[1] A. T. N'Diaye, T. Gerber, C. Busse, J. Myslivecek, J. Coraux, T. Michely, New J. Phys. 11, 103045 (2009).

First-principles investigation of NO_x and SO_x adsorption on anatase-supported BaO and Pt overlayers

D Toffoli[1], R Hummatov[1], O Gulseren[2], E Ozensoy[2] and H Toffoli[1]

[1]Middle East Technical University, Turkey, [2]Bilkent University, Turkey

We present a density functional theory investigation of the adsorption properties of NO and NO_2 as well as SO_2 and SO_3 on BaO and Pt overlayers on anatase $TiO_2(001)$ surface. Mono-layers, bilayers and trilayers of BaO grow without strain-induced large scale reconstructions.

While the bilayer and trilayer preserve, to a large extent, the NO_2 adsorption characteristics of the clean BaO(100) surface, the effect of the support is evident in SO_2 and SO_3 adsorption energies, which are significantly reduced with respect to the clean BaO(100) surface. When a Pt(100) layer is added on the TiO_2 surface, four stable adsorption geometries are identified in the case of NO while NO_2 is found to adsorb in only two configurations.

Surface and interface studies of metal nanoparticles grown on TiO_2 and its oxidation behavior under oxygen exposure

J Pan[1], C S Lau[2] and E S Tok[2]

[1]Institute of Materials Research & Engineering, Singapore, [2]National University of Singapore, Singapore

TiO_2 has attracted remarkable interest as photocatalyst since initial work by Fujishima and Honda on the photolysis of water on TiO_2 electrodes without an external bias. Although TiO_2 itself can be used for the photocatalytic reduction of carbon dioxide, most of time a suitable co-catalyst is needed to obtain a high photocatalytic activity and reasonable reaction rates. In this study, surface science approach was employed to study the growth of Pt and Co nanoparticles as co-catalysts on rutile TiO_2 (110) single crystal surfaces. Two types of surfaces were used, a sputtered surface and an annealed surface. The co-catalysts were grown through e-beam evaporator in UHV. Only metallic Pt was observed on TiO_2 surface. Pt was found to grow in 3D Volmer-Weber growth mode. Interfacial charge transfer on sputtered surface was detected, with electrons transferring from TiO_2 to Pt. Binding energy shift due to cluster effect was observed. Both metallic Co and Co oxides were observed on TiO_2 surface, with more oxide species on sputtered surface as compared to annealed surface. Co was found to grow with higher wetting compared to Pt, with a growth mode that is similar to layer by layer growth. Co-Ti interactions were found, with electrons transferring from TiO_2 to Co. Oxygen exposure on sputtered TiO_2 surface was found to result in dissociative adsorption that filled oxygen vacancies. The presence of Pt and Co did not impede this adsorption. Pt was observed to not be oxidized after exposure to oxygen, while Co was oxidized. The growth of Pt and Co on the same TiO_2 surface was investigated. The initial deposition of Pt followed by the deposition of Co did not alter the growth mode of Co. The presence of Pt did not affect the oxidation of Co when exposed to oxygen. A shift to higher binding energy of Pt was discovered and a possible explanation was put forth involving an induced work function change of Pt due to the oxidation of Co that resulted in the electron transfer of Pt to TiO_2.

Heats of adsorption and surface reaction for carbon monoxide and oxygen on Pd nanoparticles as determined by UHV single crystal adsorption microcalorimetry

M Peter, S Adamovsky, J M Flores-Camacho, J H Fischer-Wolfarth, S Schauermann and H-J Freund

Fritz-Haber-Institute, Germany

Understanding the energetics of surface processes and establishing the correlation with the structural properties is an essential issue in heterogeneous catalysis. To achieve this, one can obtain the heat release during chemisorption or reaction. This can be realized by a method of single crystal adsorption calorimetry (SCAC) that relies on measuring the temperature rise on ultrathin (1-10 µm) single crystals during these processes with a pyroelectric detector [1, 2].

We apply a newly developed SCAC set up to determine the adsorption heats of CO and oxygen on Pd nanoparticles in the range of approximately 2 nm – 6.4 nm, supported on a well-defined Fe_3O_4/Pt(111) film [3]. Interesting insights into the change of the adsorption properties of O_2 with changing particle size and surprising results compared to earlier TPD studies [4, 5] are obtained. To get insight into the influence of preadsorbed oxygen on the CO adsorption energy right before CO_2 evolution, the adsorption heat of CO on pristine Pd and on O-covered Pd are compared on Pd(111) and Pd nanoparticles at low temperatures. In adsorbing CO on O covered Pd at room temperature, the CO oxidation heats are obtained.

By this means, the energetics of the full reaction path for the CO oxidation reaction on Pd(111) and Pd particles of different sizes is probed.

[1] Ajo, H., et al., Rev. Sci. Instrum., 2004. 75: p. 4471-4480.
[2] Wolfarth, H.F., et al., Rev. Sci. Instrum., 2011. 82(2).
[3] Fischer-Wolfarth, J., et al., Physical Review B, 2010. 81(24).
[4] Penner, S., et al., J. Phys. Chem. B, 2006. 110: p. 24577-24584.
[5] Putna, E.S., J.M. Vohs, and R.J. Gorte, Surf. Sci., 1997. 391: p. L1178-L1182.

Characterization of catalytically-active Pt-alloy surfaces and core-shell nanoparticles using atom probe tomography

P Bagot[1], T Li[1], E Marquis[2], E Tsang[1] and G Smith[1]

[1]University of Oxford, UK, [2]University of Michigan, USA

Bimetallic heterogeneous catalysts have proven remarkably successful in catalysing a wide range of important processes, in fuel-cells, exhaust emission control and in hydrocarbon processing. However, the effects of the operating environment on the surface composition, structure and stability of the noble metal catalysts are poorly understood at the atomic-scale. This knowledge will be required to produce the improved catalysts needed for future energy- and materials-efficient technologies.

Atom probe tomography offers a unique method for studying these materials, offering atomic-scale chemical identities of the catalyst surfaces and chemisorbed species. We have used APT to show a rich variety of behaviour in Pt-based alloys, investigating the effects of high temperature/pressure oxidation. These reveal pronounced surface segregation behaviour, strongly dependent on the treatment conditions, crystallographic plane and alloy composition. Furthermore, while subsequent reduction treatments remove oxides, the marked changes to the metallic surface compositions remain. Such results suggest using sequential oxidation and reduction treatments as an alternative synthesis method for designing and preparing nano catalysts with controlled surface compositions. Finally, an exciting development in heterogeneous catalysis has been the ability of chemists to produce core-shell nanoparticles, where a shell of one (typically expensive, catalytically active) metal surrounds the core of a second, more inert metal. Core-shell nanoparticles offer the possibility of finely-tuning a catalyst to meet exacting reaction requirements.

We have recently started using APT to characterize core-shell nanoparticles and can now deposit catalyst nanoparticles for fuel cell applications directly onto atom probe specimen substrates for successful analysis. Alongside a description of the sample preparation methods, we will present a range of results from these materials, highlighting the correlation between catalytic efficiency and the atomic-scale chemical/structural information uniquely provided by APT.

Adsorbates on metal-oxide supported Pd nanoparticles

C Yim[1], C Muryn[2], C L Pang[1] and G Thornton[1]

[1]University College London, UK, [2]The University of Manchester, UK

We have prepared a model catalytic system by depositing Pd onto a $TiO_2(110)$ surface held at ~720 K. Scanning tunneling microscopy (STM) reveals well-defined Pd nanocrystals consisting of (111) top facets with (111) and (100) side-facets. The Pd nanocrystals go down to about 10 nm in width and 1.3 nm in height. The top facets can be imaged with atomic resolution, indicating no TiO_x encapsulation. This is in line with our XPEEM data that found such nanoparticles to be metallic [1]. We have exposed these nanocrystals to CO and O_2. By varying the CO exposure, different CO domains were formed, namely $(\sqrt{3} \times \sqrt{3})$-R30° at 1/3 ML, top-bridge and bridge-bridge c(4 × 2)-2CO at 0.5 ML, as well as (2 × 2)-3CO at 0.75 ML. Complex structures formed at intermediate coverages were also observed. These structures are reminiscent of those observed for Pd(111) single crystals [2].

Island edges and island/oxide interface regions have been posited as active sites for catalysis and our model system offers the opportunity to study any such effect directly with STM. To this end, we have focused on imaging the island edges after exposure to O_2, finding that the structures which form at island edges are different to those formed on the top facet.

[1] D. S. Humphrey *et al*, Nano Lett. 9, 155 (2009).
[2] M. Rose *et al*, Surface Science 512, 48 (2002).

Designing storage and reduction catalysts with improved sulfur tolerance: an ab-initio study on γ-Al_2O_3 supported bimetallic systems

H Toffoli, Z Artuc and D Toffoli

MIddle East Technical University, Turkey

γ-Al_2O_3 is the most commonly used support material in NO_x storage and reduction catalysts (NSRs) due to its open structure, thermal and mechanical integrity, and surface acidity. The adsorption properties of NO_x and SO_x (x=2,3) on atomic and dimeric Pt and Rh dispersed on the (001) surface of γ-Al_2O_3 has been investigated through large scale first-principle density functional theory (DFT) calculations. Possible adsorption sites for a single metallic atom have been sistematically examined for both Pt and Rh. Our results indicate a strong sinergetic effect involving both the adsorbed metallic atom and the support toward NO_2 adsorption. Although the interaction of NO_2 with a second metallic center in various configurations (O-O' bridge, O-N bridge and N-down) generally stabilizes the adsorbate, independently of the nature of the second metallic center, greater adsorption energies are observed for the bimetallic Pt-Rh system. Furthermore, the interaction of SO_x with the redox-component is strongly destabilized on the supported Pt-Rh dimer. The potential use of bimetallics as a more efficient and sulphur tolerant redox component for NSRs catalysts is accordingly highlighted.

Magnetism 5

(invited) Imaging and manipulating single and interacting spins on surfaces: towards atomic-scale spintronic devices

R Wiesendanger

University of Hamburg, Germany

The developments of novel magnetic materials as well as spin-based electronics are hot topics of current research in nanoscale science. Both research fields could profit tremendously from atomic-scale insight into magnetic properties and spin-dependent interactions at the atomic level. Based on the development of spin-polarized scanning tunneling microscopy (SP-STM) [1] we have recently established the novel method of single-atom magnetometry [2,3] which allows the measurement of magnetization curves and the determination of magnetic moments on an atom-by-atom basis. While the sensitivity level of single-atom magnetometry is below one Bohr magneton, it can easily be combined with the atomic-resolution imaging and manipulation capabilities of conventional STM, thereby offering a novel approach towards a rational material design based on the knowledge of the atomic-level properties and interactions within the solid state. Moreover, an atom-by-atom design and realization of all-spin logic devices [4] has recently been demonstrated by our group based on the combined knowledge derived from surface physics, nanoscience, and magnetism. Alternatively, self-assembly of atomic magnetic chains on nanostructured substrates has been employed in order to create model-type systems for atomic-scale information transfer based on the concept of vector-spin chirality.

[1] R. Wiesendanger, Rev. Mod. Phys. 81, 1495 (2009).
[2] F. Meier et al., Science 320, 82 (2008).
[3] L. Zhou et al., Nature Physics 6, 187 (2010).
[4] A. A. Khajetoorians et al., Science 332, 1062 (2011).

Magnetism of single Co atoms on graphene/Pt(111)

Q Dubout, F Donati, F Calleja, F Patthey and H Brune

Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

We present low-temperature Scanning Tunneling Microscopy results on the magnetic properties of single Co atoms adsorbed on graphene on Pt(111). A giant magnetic anisotropy was predicted for a Co dimer adsorbed on a C_6 ring [1], and could also exist on graphene. The choice of Pt(111) as a substrate is motivated by the fact that graphene is particularly weakly bound to this surface compared with other close-packed metal surfaces [2], and therefore expected to behave like free-standing graphene.

Scanning Tunneling Spectroscopy measurements performed at 400 mK reveal a single spin-excitation feature. Using an effective spin Hamiltonian [3], these measurements yield an effective spin $S = 1$, a magnetic ground state $m_Z = 0$, two excited states $m_Z = \pm 1$, a giant magnetic out-of-plane anisotropy $D = 8.2 \pm 0.4$ meV, and a Landé g factor $g = 2.2 \pm 0.4$.

H adsorption on the Co atoms can drastically modify their magnetic properties. Exposing Co atoms to H_2 gas, we found three different types of complexes, clearly distinguished by their apparent height and spectroscopic features. Two of these complexes, interpreted as CoH and CoH_2, show very prominent non-magnetic inelastic features attributed to vibrational modes. The third one, probably CoH_3, displays spin-excitations in a similar fashion as clean Co, but a considerably reduced magnetic anisotropy of $D = 1.7 \pm 0.2$ meV.

[1] R. J. Xiao, D. Fritsh, M. D. Kuz'min, K. Koepernik, M. Richter, K. Vietze and G. Seifert, Phys. Rev. B 82, 205125 (2010).
[2] J. Wintterlin and M. L. Bocquet, Surf. Sci. 603, 1841 (2009).
[3] C. F. Hirjibehedin, C. Y. Lin, A. F. Otte, M. Ternes, C. P. Lutz, B. A. Jones and A. J. Heinrich, Science 317, 1199 (2007).

Three-dimensional spin texture of the Fermi surface of a strongly spin-orbit coupled interface

J Schäfer[1], P Hoepfner[1], A Fleszar[1], J Hugo Dil[2], B Slomski[2], W Hanke[1] and R Claessen[1]

[1]University of Würzburg, Germany, [2]Paul-Scherrer Institute, Switzerland

Semiconductor surfaces with metal adatom reconstructions of the (root3 x root3)-type are attracting increasing scientific interest in the last years. This is owed to the rich body of lowdimensional physics encountered therein, which comprises, e.g., highly correlated Mott-Hubbard insulating phases which may give rise to magnetic ordering, as well as twodimensional superconductivity. Moreover, this metal-semiconductor interface is of high technological interest. Since the space inversion symmetry is broken, a Rashba-type spinorbit coupling must be expected to lift the spin degeneracy of the metal-induced surface states. A significant spin-splitting in a conducting, two-dimensional electron system at a semiconductor surface would be highly desirable, since it offers the perspective to manipulate spins electronically.

We report on a fully three-dimensional analysis of the spin properties in the metallic surface system Au/Ge(111) based on spin-resolved photoelectron spectroscopy as well as advanced density functional modeling [1]. Surprisingly, and contrary to a conventional Rashba picture, we find that the spin texture exhibits strong out-of-plane spin components, which follow the threefold symmetry of the substrate lattice. Moreover, additional radial spin components are observed in experiment for the first time. Notably, these findings bear close resemblance to theoretical predictions for topological insulators. As we will illustrate in conjunction with model Hamiltonians, these findings reveal an interplay with Dresselhaus-like spin-orbit effects as a result of the crystalline anisotropies. This points at the complexity of the spinorbit interaction in such real-world systems.

[1] P. Hoepfner, J. Schaefer, et al., Phys. Rev. Lett. 108, 186801 (2012), Editors' Suggestion.

Functional single molecule magnets on Au(111) and TiO_2(110) deposited by in-situ electrospray deposition

K Handrup, M Weston, J O'Shea, V Richards and N Champness

University of Nottingham, UK

Single molecule magnets built from a $Mn_{12}O_{12}$ core encapsulated by 16 organic ligands [1] are amongst the most fascinating nanoscale magnets to date. A little over a decade ago, single crystals of Mn_{12}(acetate)$_{16}$ were shown to demonstrate macroscopic quantum tunnelling of magnetization [2] and are currently amongst the most promising candidates data storage at the molecular level. Technological applications require monolayers of these molecules on suitable substrates. Unfortunately, previous studies of Mn_{12}(acetate)$_{16}$ and the Mn_{12}(benzoate)$_{16}$ have shown that their magnetic properties are destroyed when the core of the molecule is not isolated from the substrate. To protect the magnetic core we have introduced the much larger ligand of para-terphenyl. Due to the non-volatile and fragile nature of these molecules, we have deposited the Mn_{12}(terphenyl)$_{16}$ molecule on Au(111) and TiO_2(110) surfaces with ultra-high vacuum electrospray deposition at surface coverages from a fraction of a monolayer to multilayer films. X-ray absorption spectroscopy at the Mn L-edge combined with high resolution synchrotron-based photoemission show that the magnets are intact on the surface even at sub-monolayer coverage. These results are significant because they show that UHV electrospray deposition can indeed be used to deposit intact single molecule magnets without contamination and most importantly without destroying the crucial Mn(III) and Mn(IV) oxidation states in the core [3], offering a valuable strategy for using single molecule magnets building blocks for functional nanostructures on surfaces.

[1] A. Saywell et al, Nanotechnology (2011).
[2] L. Thomas et al, Nature, 383, 145 (1996).
[3] A. Saywell et al, Nature Communications 1, 75 (2010).

Multiscale study of thermodynamical properties of fcc-(Fe,Co)/Cu(001) overlayers

M Kotrla[1], M Masin[1], L Bergqvist[2], J Kudrnovsky[1] and V Drchal[1]

[1]Institute of Physics ASCR, Czech Republic, [2]KTH Royal Institute of Technology, Sweden

The Curie temperature is one of the most important characteristics of the magnetic state. Its evaluation in the framework of the parameter-free approach is now well-stablished for both elemental transition metals [1] and their alloys [2]. Very little is known, however, for two-dimensional systems [3], in particular for random surfaces.
We develop the theory suitable for an estimate of critical temperatures of random magnetic overlayers on non-magnetic surfaces utilizing multiscale approach. As a case study, we consider fcc-(Fe,Co)/Cu(001) overlayer. We construct the effective two-dimensonal alloy Heisenberg Hamiltonian whose parameters, the exchange interactions among Fe- and Co-atoms in the overlayer are concentration dependent and determined from first principles. We introduce the magnetic anisotropy term (Mermin-Wagner theorem) [3]. The Monte-Carlo simulations are used to estimate critical temperatures as a function of the overlayer composition. Results of simulations will be compared with a simplified treatment using the random-phase approximation for an effective model with concentration-weighted exchange interactions [2]. We also calculate magnon spectra using spin dynamics for both ordered and disordered overlayers.

[1] M. Pajda, J. Kudrnovsky, I. Turek, V. Drchal, and P. Bruno, Phys. Rev. B 64 (2001) 174402.
[2] J.Kudrnovsky, V. Drchal, and P. Bruno, Phys. Rev. B 77 (2008) 224422.
[3] M. Pajda, J. Kudrnovsky, I. Turek, V. Drchal and P. Bruno, Phys. Rev. Lett. 85 (2000) 5424.

Joule heating and spin-transfer torque investigated on the atomic scale

S Krause, G Herzog, A Schlenhoff, A Sonntag and R Wiesendanger

University of Hamburg, Germany

Reorienting the magnetization of a nanostructure by injecting a spin-polarized current is in the focus of ongoing research because of its relevance for future spintronic and magnetic memory devices. Recent experiments using spin-polarized scanning tunneling microscopy (SP-STM) [1] demonstrated current-induced magnetization switching (CIMS) across a vacuum barrier, driven by Joule heating, spin-transfer torque and Oersted field [2,3].

In our study, we specially utilize a superparamagnetic Fe/W(110) nanoisland to explore CIMS with SP-STM. By simultaneously observing and manipulating its switching behavior with a spin-polarized tunnel current, we separate and quantitatively determine the individual contributions of Joule heating and spin-transfer torque, with the nanoisland serving as a combined local thermometer and spin-transfer torque analyzer. Comparing our results to experiments performed on magnetic nanopillar tunnel junctions reveals a very high spin-transfer torque switching efficiency for SP-STM [4].

Our studies allow for a detailed investigation of Joule heat generation and spin-transfer torque switching on the atomic scale, thereby providing new insight into the details of CIMS.

[1] R. Wiesendanger, Rev. Mod. Phys. 81, 1495 (2009).

[2] S. Krause, L. Berbil-Bautista, G. Herzog, M. Bode, and R. Wiesendanger, Science 317, 1537 (2007).
[3] G. Herzog, S. Krause, and R. Wiesendanger, Appl. Phys. Lett. 96, 102505 (2010).
[4] S. Krause, G. Herzog, A. Schlenhoff, A. Sonntag, and R. Wiesendanger, Phys. Rev. Lett. 107, 186601 (2011).

Tuning the reactivity and spin state of iron phthalocyanine on Cu(111) by oxygenation, nitrogenation, and temperature treatment

O Snezhkova, J Knudsen, K Schulte and J Schnadt

Lund University, Sweden

Surface-adsorbed metal-organic compounds such as metal porphyrins and phthalocyanines have highly interesting chemical and magnetic properties for areas such as catalysis, molecular sensing, solar cells, fuel cells, etc. Of particular interest is that the properties can be tuned quite easily and deliberately by modification of the chemical environment. For example, it is possible to tune the spin state of the central metal atom of metal phthalocyanines (MPc) to different values by adsorption of different ligands [1,2] or by design of the molecule-support interface [3]. Here we investigate how one can influence both the magnetic and chemical properties of iron phthaloycanine (FePc) adsorbed on a Cu(111) surface by different preparation and modification protocols and compare it to the case of FePc on Au(111). The experimental tools of study are x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and ambient pressure x-ray photoelectron spectroscopy (APXPS).

FePc is able to couple to the metallic support through both its metallic centre and the surrounding macrocycle. We find that the coupling can be influenced strongly by the FePc layer preparation protocol: annealing to moderate temperatures increases the macrocycle/support coupling and renders the molecule unreactive towards atomic oxygen attack, while the benzene rings of room temperature-deposited FePc molecules are chemically modified by subsequent atomic oxygen dosing. Oxidation or nitrogenation of the Cu(111) surface prior to FePc deposition, on the contrary, efficiently decouples both the metal centre and macrocycle of the FePc molecules from the surface. Also the spin state of the central metal atom is affected by the different preparation and modification methods; while the spin is similar to that of the free molecules when FePc is deposited on a oxygenated or nitrogenated surface it is quenched for deposition on bare Cu(111).

Metal-supported FePc is unreactive towards molecular oxygen and carbon monoxide adsorption at room temperature. Using APXPS we find that oxygen and carbon monoxide uptake is enabled at higher pressures up to 1 mbar. This finding opens up for study of how the catalytic properties of phthalocyanines can be tuned by modification of the state of support and metal ion and by changes in the preparation protocol.

[1] C. Isvoranu et al. J. Phys.: Condens. Matter 22 (2010) 472002.
[2] C. Wäckerlin et al. Nature Commun. 1 (2010) 61.
[3] N. Tsukahara et al. Phys. Rev. Lett. 102 (2009) 167203.

Neutron diffraction 1

(invited) In-situ investigation of functional materials by synchrotron and neutron scattering

H Fuess

Technische Universität Darmstadt, Germany

Detailed knowledge of the crystal structure is a prerequisite for the understanding and optimization of functional materials. Furthermore any modification under external parameters especially those related to the specific function are of considerable importance for succesful applications. Synchrotron x-ray and neutron radiation are the methods of choice for in-situ or in-operando investigations. The materials investigated and presented are piezoceramics (lead-titanium-oxide, PZT), Li-batteries and fuel-cells (PEMFC).Whereas synchrotron radiation allows for data acquisition in the range of milliseconds, neutron diffraction will provide the position of light elements like lithium and oxygen. PZT-ceramics and lead free piezoceramics were studied in form or pellets under an electric field up to 7 KeV at the Swiss Light Source (SLS) [1] and at neutron research reactors [2]. In the BNT-BT (Bi-Na-Ti-oxide and Bi-Ti-oxide) system neutrons evidenced the presence of trigonal and tetragonal phases and the combination of both radiations elucidated the phase diagram. The results were supported by transmission electron microscopy (TEM) work under electric fields [3]. Charge and discharge in the battery material $LiCoO_2$ and in commercial batteries is under study by neutron diffraction and neutron tomography. Thus the formation of phases as a function of external voltage is observed in parallel to the distribution of lithium. The variation of valence in PEMFC is followed by x-ray absorption methods. The importance of a combination of methods for in-situ and in-operando studies will be emphasized.

[1] M. Hinterstein, M. Knapp, M. Hölzel, W. Jo, A. Cervellino, H. Ehrenberg, H. Fuess Field-induced phase transition in $Bi_{1/2}Na_{1/2}TiO_3$-based lead-free piezoelectric ceramics J. Appl. Cryst. 43, 1314 – 1321 (2010).

[2] M. Hinterstein, J. Rouquette, H. Haines, Ph. Paquet, M. Knapp, J. Glaum, H. Fuess Structural description of the macroscopic piezo-ferroelectric properties of high performance lead zirconate-titanate (PZT) Phys. Rev. Lett. 17, 077602 (2011).

[3] J. Kling, W. Tan, X., Jo, H.-J. Kleebe, H. Fuess, J. Rödel In situ transition electron microscopy of electric field triggered reversible domain formation in Bi-based lead-free piezoceramics J.Am. Ceram. Soc. 93, (9) 2452-2455 (2010).

(invited) Polarised neutrons as a tool to study smart materials

J Brown

Loughborough University, UK

Many so-called smart materials owe their useful properties to the interaction between their nuclear and magnetic structures. Both structures are usually temperature dependent and whilst the former is sensitive to exterior constraints such as stress or electric fields the latter may be modified by application of magnetic fields. Polarised neutron diffraction provides a powerful tool to study the way in which the magnetic and nuclear structures interact since it gives access to the phase relationship between the nuclear and magnetic structure factors. This phase relationship is a much more direct indication of the interaction between the magnetic and structural degrees of freedom than the moduli of the two structure factors measured separately. The multiferroic rare-earth manganates show a complex interdependence of magnetic and electrical properties. Neutron polarimetry on several materials has demonstrated that the ferroelectric polarisation depends on the population of magnetic chiral domains but such experiments must be made in zero magnetic field. To study the effects of magnetic fields information can be obtained from the polarisation dependence of the intensity of purely magnetic reflections for which the diffraction geometry permits measurements in which the scattering vector is not perpendicular to the polarisation direction. The symmetry relationships between the intensity asymmetries of symmetrically equivalent reflections give vital data about the phase differences between different components of the magnetic interaction vectors. The experiments on YMn2O5 reveal inconsistencies with magnetic structure models and give evidence for a small nuclear component in the magnetic reflections.

(invited) Local susceptibility of frustrated pyrochlores. A tool to assess the anisotropic exchange interaction

A Gukasov

LLB CEA-CNRS, France

Rare earth frustrated pyrochlore magnets are among the materials that exhibit no long range order down to the lowest explored temperatures. To better understand the many complex phenomena observed in the pyrochlores, knowledge of the local interactions present in these materials is necessary. In the pyrochlore lattice, selection between Ising, Heisenberg, or XY types of the anisotropy cannot be based on the analysis of the macroscopic properties because of the presence of four equivalent local anisotropy (<111> -type) axes. Then only an average over the four axes can be measured by classical methods. Polarized neutron diffraction based on the ‘site susceptibility approach’ (A Gukasov and P. J. Brown, J. Phys.: Cond. Matt., 14, 8831, 2002) allows to determine the local susceptibility tensor on the magnetic site. Its temperature dependence in the paramagnetic phase can be accounted for by the crystal field anisotropy and a molecular field tensor that encompasses exchange and dipolar interactions. It was found that for rare earth pyrochlores an isotropic exchange model is not suitable to explain their magnetic behavior and that, instead, the exchange interaction appear anisotropic to large extent (H. Cao et al., PRL 103, 056402, 2009). The experimental evaluation of the anisotropic exchange in pyrochlores can provide a clue to the richness of the phase diagram observed in rare earth frustrated magnets.

Stripe order and the "Hour-Glass" dispersion of $(La,Sr)_2CoO_4$ measured using Inelastic Neutron Scattering

S M Gaw[1], A Boothroyd[1], C Frost[2] and P Dharmalingam[1]

[1]University of Oxford, UK, [2]Rutherford Appleton Laboratory, UK

The insulating, hole-doped antiferromagnet, $La_{2-x}Sr_xCoO_4$ exhibits the same “hour-glass” dispersion as many of the high-temperature superconducting cuprates. While there are several interpretations as to the origin of this excitation spectra in the cuprates, it has previously been shown by Boothroyd, et al, [1] that in the case of the x=1/3 doped cobaltates this is due to charge and magnetically ordered stripes in the two-dimensional Co-O planes of the perovskite structure. In this study, we have looked at the x=1/4 and 0.3 doped samples, measuring a qualitatively similar “hour-glass” dispersion to that of the x=1/3 doped material, using inelastic neutron scattering. We present a spinwave model that goes toward explaining the transition from the stable stripe order of the rational fraction, x=1/3 doping to the x=1/4 doping via phase mixing of the two stripe ordered states. We also look at the origin of the different dispersive features that come together to make the distinctive “hour-glass” spectra in the cobaltates.

[1] A.T. Boothroyd,et al, Nature, 471, 341 (2011).

Liquids and liquid interfaces 1

Interaction model between a liquid surface and an AFM probe

R Ledesma-Alonso, D Legendre and P Tordjeman

Institut de Mécanique des Fluides de Toulouse (IMFT), France

Nowadays, the analysis of solid surfaces at the nanoscale is commonly performed using Atomic Force Microscopy (AFM). On the other hand, the study of liquid interfaces is a challenging issue due to the undoubted wetting process. Indeed, in AFM experiments, a "bump-like'' deformation of the air/liquid interface is observed, which systematically conceals the reference position. The aim of this presentation is to show how we can forecast the tip wetting phenomenon by modeling the tip/liquid surface interaction, and determine the experimental conditions for the AFM analysis. Employing an augmented Young-Laplace equation, which includes an exact expression of the London-van der Waals volume attractive potential, the interface deformation due to a quasi-static approach of a nanoscopic probe is studied. The resulting non-linear equation is solved with a numerical method, and an equilibrium interface shape is obtained for a given dimensionless separation distance D/R, a modified Hamaker number $A=4H/(3\pi\gamma R^2)$ and a Bond number $B=(\Delta\rho g R^2)/\gamma$, where R is the sphere radius, g the acceleration of gravity, H the Hamaker constant of the tip/liquid system, and $\Delta\rho$ and γ the density difference and the surface tension of the air/liquid interface, respectively. Examples of the equilibrium profiles will be shown. Despite the complexity of the attractive potential, the apex curvature obeys a simple power-law dependency on the corresponding deformation. A semi-analytical solution points out the existence of a bifurcation behavior of the apex deformation as a function of the tip distance. The bifurcation diagrams are characterized by a critical separation distance D_{min} below which no static deformation profiles are found. Thus, simple relationships between physical parameters allow the determination of D_{min}/R at which the probe can approach the liquid before capillarity provokes a "jump-to-contact''.

Our model allows the determination of the attractive force created by an approaching tip. The results of our analysis are in good agreement with the force curves obtained from standard AFM measurements over a liquid puddle. Furthermore, a good estimate of the probe/liquid system Hamaker constant is obtained, as well as the identification of the interface original position before deformation. In practice, this work allows to establish the optimal experimental conditions to contrive quantitative AFM measurements over liquid surfaces.

Underlayer absorption at ionic liquid surfaces

R Jones and S Hessey

University of Nottingham, UK

In this study we describe firstly the bonding of 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide, $[C_2C_1Im][Tf_2N]$ to Au(111) and secondly the adsorption and absorption of acetone at the surface, and just below the surface of this thin film of ionic liquid glass. Molecular simulations and experimental studies indicate that ionic liquid surfaces are structured, in the case of $[C_2C_1Im][Tf_2N]$ with an outmost layer of alkyl and CF_3 groups surmounting an ionic layer of the charged anionic and cationic parts of the IL.

Multilayers of $[C_2C_1Im][Tf_2N]$ deposited on Au(111) at 100 K desorbed with zero order kinetics, leaving a well-defined chemisorbed layer that desorbed across a wide temperature range, corresponding to activation energies from 111 to 130 kJ mol^{-1}. This is consistent with the sequential collapse of a structured chemisorbed layer during desorption. The adsorbate, acetone, was found to adsorb molecularly on multilayers of IL glass on gold, forming a physisorbed monolayer with a desorption activation energy of 32 kJ mol^{-1}. However, on depositing multilayers of IL glass on top of physisorbed acetone on gold, temperature programmed desorption showed “volcano” desorption of the multilayers, followed by a new high temperature state with a desorption activation energy spanning 38 to 46 kJ mol^{-1}. This high temperature state exhibited a fixed sub-monolayer coverage irrespective of the quantity of physisorbed acetone used, or the thickness of IL deposited. We interpret this state as being due to acetone that is trapped within the surface layer of the IL glass, most probably within the ionic layer.

Adsorption of $[C_8C_1Im][BF_4]$ ionic liquid multilayers on Cu(111) and subsequent absorption of H_2O and SO_2

K Syres and R Jones

University of Nottingham, UK

Ionic liquids are composed of ions which are held together by a strong Coulomb potential. They have ultra-low vapour pressures at room temperature allowing them to be studied using ultra-high vacuum surface science techniques. In addition, it is possible to tune ILs to selectively absorb gases such as H_2O, SO_2 and CO_2. Bulk 1-octyl-3-methylimidazolium tetrafluoroborate, $[C_8C_1Im][BF_4]$, has been shown to adsorb a monolayer of H_2O, probably within an ionic layer which lies below the octyl chain surface[1].

In the present study, a multilayer of $[C_8C_1Im][BF_4]$ was deposited on a Cu(111) surface by evaporation in UHV. XPS spectra show that the IL multilayer adsorbs without decomposition, and desorbs at ~413 K, leaving a monolayer adsorbed on the surface. The monolayer was found to desorb at ~463 K, suggesting it is significantly more strongly adsorbed than the multilayers. In addition, H_2O was co-adsorbed with the IL at 123 K. Multilayers of H_2O were easily removed by heating but monolayer quantities were found to be strongly absorbed within the IL. A further XPS study has shown it is also possible to absorb SO_2 within the IL multilayers.

[1] J. Lovelock, E. F. Smith, A. Deyko, I. J. Villar-Garcia, P. Licence and R. G. Jones, Chem. Commun., 2007, 4866-4868.

Dynamics of an Ionic Liquid surface on a pico-second timescale

E McIntosh[1], D Ward[1], P Licence[2], J Ellis[1], W Allison[1] and R Jones[2]

[1]University of Cambridge UK, [2]University of Nottingham, UK

Ionic liquids (ILs) are an emerging class of materials, which with simple and systematic chemical modifications have a wide variety of uses, including in electrolytes for energy applications, and in drug delivery, due to their ability to host both polar and non-polar solvents [1]. The intrinsic low vapour pressure of room temperature ILs makes them suitable for UHV scattering experiments [2].

We present the first measurements of liquid surface dynamics using the helium Spin-Echo technique [3], which allows resolution of atomic scale motion on pico- to nano-second timescales. We consider the Ionic Liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, known as $[C_2C_1Im][Tf_2N]$, on an Au(111) substrate.
We examine the changes in structure and dynamics of the surface with temperature, both for a self-assembled monolayer, and multilayers of the IL. Rapid dephasing of the polarisation is seen on sub-picosecond timescales, supporting the picture that has emerged in recent years of the polar headgroups adsorbing at the solid interface, forming an underlayer beneath the alkyl chains [4].

[1] E. W. Castner and J. F. Wishart, J. Chem. Phys. 132 (2010).
[2] K. R. Lovelock et al., Phys. Chem. Chem. Phys. 12 (2010) 8893.
[3] A. P. Jardine et al., Prog. Surf. Sci. 84 (2009) 323.
[4] T. Cremer et al., Langmuir 27 (2011) 3662.

(invited) Time-resolved study of phase transition in the nanoscopic water bridge: formation and rupture processes

W Jhe

Seoul National University, South Korea

The formation and rupture processes of nanoscale water bridges are studied by time-resolved dynamic force microscopy. With this technique, it allows one to study time-dependent behaviour of interfacial forces due to the water bridges.

Stability and dynamics of Pickering droplets in a gravitational field

P Clegg[1], J Tavacoli[2], G Kim[3], J Thijssen[1] and M Cates[1]

[1]University of Edinburgh, UK, [2]ESPCI, France, [3]Changwon National University, South Korea

We demonstrate, using conventional colloidal particles, that Pickering emulsion droplets become unstable beyond a threshold droplet size in a gravitational field. Our subsequent experiments, using droplets stabilized by supra-colloidal glass beads, reveal the mechanism: the gravitational forces acting on the beads can accumulate to promote ejection of beads towards the droplet base [1]. The number of beads that act together in these ejection events reduces with time (if droplet coalescence is avoided) until eventually a stable configuration is reached. We observe that the smallest number of beads in an unstable region is equal to the ratio of the interfacial trapping force and the buoyancy force acting on an individual bead. A permanently stable droplet is one that is too small to ever accommodate such an unstable region. We include simulation results which suggest that the three phase contact angle at the particle surface may have an important influence over the failure mode of the droplet [2].
During this project we serendipitously observed the formation of a composite capsule that sinks and rises in response to a temperature gradient [3]. This diving capsule self assembles when particles are poured into a vial containing two immiscible liquids. A thin shell of particles is essential to tuning the average density of the capsule while the volatile solvent, trapped bubble and temperature gradient create height dependent buoyancy.

[1] J. W. Tavacoli, G. Katgert, E. G. Kim, M. E. Cates, and P. S. Clegg,submitted.
[2] E. G. Kim, K. Stratford, P. S. Clegg, and M. E. Cates, Phys. Rev. E 85, 020403 (2012).
[3] J. W. Tavacoli, J. H. J. Thijssen, and P. S. Clegg, Soft Matter, 7, 7969 (2011).

Speed of solidification fronts in supercooled liquids: why rapid fronts lead to disordered glassy systems

A Archer[1], M Robbins[1], U Thiele[1] and E Knobloch[2]

[1]Loughborough University, UK, [2]University of California at Berkeley, USA

We determine the speed of a crystallisation (or more generally, a solidification) front as it advances into the uniform liquid phase after the system has been quenched into the crystalline region of the phase diagram. We calculate the front speed by assuming a dynamical density functional theory model for the system and applying a marginal stability criterion. Our results also apply to phase field crystal (PFC) models of solidification. As the solidification front advances into the unstable liquid phase, the density profile behind the advancing front develops density modulations and the wavelength of these modulations is a dynamically chosen quantity. For shallow quenches, the selected wavelength is precisely that of the crystalline phase and so well-ordered crystalline states are formed. However, when the system is deeply quenched, we find that this wavelength can be quite different from that of the crystal, so that the solidification front naturally generates disorder in the system. Significant rearrangement and ageing must subsequently occur, for the system to form the regular well-ordered crystal that corresponds to the free energy minimum. We also find that the advancing solidification front undergoes a transverse instability leading to transverse density modulations that grow as the front advances. The wavelength of the density modulations selected by this instability also differs from that of the desired final crystal and so provides an additional mechanism for generating disorder in the system. We illustrate these findings with results obtained from the PFC.

Osmosis in a minimal model system: a molecular dynamics simulation study

T Lion and R Allen

University of Edinburgh, UK

We present a minimal model system which allows the microscopic dynamical processes underlying osmotic pressure and concentration gradients to be investigated. In our model, solute and solvent are represented by repulsive particles with identical interactions; the solute particles are confined to the solution by an external potential. Using molecular dynamics simulations, we show that the osmotic pressure difference can be predicted using a simple virial-like relation, and that the solute interactions with the solvent play a key role. We present a simple and intuitive picture to explain the underlying basis of osmosis in this system.

Semiconductors and their surfaces 5

Interaction of potassium and water with InN surfaces

S Reiß, A Eisenhardt, S Krischok and M Himmerlich

TU Ilmenau, Germany

The properties of group III-nitrides have been intensively studied in the last years. This has been partially motivated by the high potential for applications e.g. in high speed electronic devices, solar cells, optical applications, and biosensors. In this context the interaction of the nitride surfaces with its environment is critical for the device degradation or even the working principle (sensors). In this study we investigate the interaction of water and potassium with in situ grown InN surfaces. Whereas water is present in typical environments for all devices, the investigation of the potassium-nitride interaction is motivated by the importance of potassium in biological processes. In this contribution we will discuss the interaction processes of each of the chosen atoms/molecules (K and H_2O) separately as well as the coadsorption of both based on photoelectron spectroscopy (XPS and UPS) spectroscopy. Particular attention will be paid to the exposure dependence of the coverage, the formed adsorbate species and its impact on workfunction and surface band bending, which are expected to have strong impact on the device performance. For the investigated InN surfaces water and potassium adsorption leads to changes in workfunction and surface band bending depending on the surface orientation. For the water adsorption two new valence band states occur, most likely related to O-adsorbates, whereas the coadsorption of K and H_2O leads to a different workfunction change and hydroxide formation.

Sulfur passivation of InN and InAlN surfaces

E Davis[1], J Mudd[1], M Walker[1], C Burrows[1], C McConville[1], T Brazzini[2], F Calle[2] and M A Sánchez Garcia[2]

[1]University of Warwick, UK, [2]Universidad Politécnica de Madrid, Spain

The fundamental properties of InN and its alloys make it a promising material for use in opto-electronic and electronic devices that operate in the THz frequency band. However, the intrinsic electron accumulation observed at the surfaces and interfaces of InN presents significant difficulties when trying to incorporate this material into devices [1]. Sulfur passivation, commonly used for several other III-V compounds, has been found to reduce the downward band bending of undoped InN by 0.15 eV and decrease the surface sheet charge density by 30 % [2,3]. In this work, different sulfur-based solutions of varying concentrations have been used to treat InN and InAlN surfaces. High resolution x-ray photoemission spectroscopy (XPS) has been used to determine the effect on band bending at the surface and the associated surface electron accumulation. The stability of the surface treatments and electronic properties was also studied following exposure to air. The one-electron potential, carrier concentration profile, quantized subband state energies, and parallel dispersion relations have all been calculated for an accumulation layer at the surface of these semiconductors. This is achieved by solving Poisson's equation within a modified Thomas-Fermi approximation and numerically solving the Schrödinger equation for the resulting potential well. Kane's k·p approximation for a non-parabolic conduction band is also incorporated in the model to compare the experimental data. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were also used to examine the topological effects of the sulfur passivation process on the InN and InAlN surfaces.

[1] T.D. Veal, P.D.C. King and C. F. McConville, in Indium Nitride and Related Alloys, (eds) T.D. Veal, C. F. McConville and W. J. Schaff (CRC Press, New York, 2009).

[2] L.R. Bailey, T.D. Veal, C. E. Kendrick, S. M. Durbin and C. F. McConville, Appl. Phys. Lett. 95, 192111 (2009).

[3] Y.H. Chang, Y. S. Lu, Y. L. Hong, C. T. Kuo, S. Gwo and J.A. Yeh, J. Appl. Phys. 107, 043710 (2010).

Investigation of the electronic structure of dislocations in GaN/Si(111) by using scanning tunneling microscopy

F-M Hsiao[1], M-C Shih[1], Y-C Huang[2], Y-C Chen[2], L-W Tu[1] and Y-P Chiu[1]

[1]National Sun Yat-Sen University, Taiwan, [2]National Cheng Kung University, Taiwan

By using scanning tunneling microscopy, this study demonstrates a correlation between the surface morphology and the corresponding electronic states of the dislocations terminated at the GaN(1-100) surfaces grown by molecular-beam expitaxy (MBE). Both scanning tunneling spectroscopy and analysis of the dislocations on electronic structures suggest that local regions surrounding the surface termination of dislocations register prominent gap states in the fundamental band gap of GaN, even in the absence of impurities in n-GaN/Si(111) grown by MBE.Additionally, spectra measurements support that the electronic levels in the gap may act as electronic traps thus becoming negatively charged. Meanwhile, closely examining the recognition of the band edges revealed that the defect levels could also provide the possibility of the yellow luminescence, involving a transition from the conduction-band edge to the level at 1.2 eV above the valence band edge.

Angle Resolved Photoemission of CdO Quantized Subbands

J Mudd[1], T Veal[2], C McConville[1], J Zúñiga-Pérez[3], V Muñoz-Sanjosé[4], P King[5], M Bianchi[6] and P Hofmann[6]

[1]University of Warwick, UK, [2]University of Liverpool, UK, [3]CNRS Valbonne, France, [4]Universitat de Valéncia, Spain, [5]University of St Andrews, UK, [6]University of Aarhus, Denmark

Surface electron accumulation has now been observed on a range of materials including InN, CdO, InAs and In_2O_3 [1-3]. This electron accumulation layer results in a quantised 2D electron gas (Q2DEG) being formed at the material surface. This Q2DEG provides an interesting opportunity to study many body interactions due to its reduced dimensionality and high electron density. Many body effects are thought to play a significant role in this Q2DEG by renormalizing the band structure near the surface as the conventional one electron model does not describe the ARPES data sufficiently [2]. In this work, the quantised subbands on the CdO (100) surface have been studied by angle resolved photoemission spectroscopy (ARPES), an ideal technique for studying 2D electronic surface phenomena. By modifying the surface electron accumulation via Rubidium deposition, the surface state density can be modified and the effects of this on the subband renormalisation are investigated.

[1] T.D. Veal, C. F. McConville, and W. J. Schaff (eds.), Indium Nitride and Related Alloys (CRC Press, Boca Raton, London, New York, 2010).

[2] L.R. Bailey, T.D. Veal, C. E. Kendrick, S. M. Durbin, and C. F. McConville, Appl. Phys. Lett. 95(19), 192111:1–3 (2009).

[3] Y.H. Chang, Y. S. Lu, Y. L. Hong, C. T. Kuo, S. Gwo, and J.A. Yeh, J. Appl. Phys. 107(4), 043710:1–5 (2010).

Sol-gel ZnO: microstructural and electrical properties

J Nel and R Steyn

University of Pretoria, South Africa

ZnO thin films have been deposited by spin-coating sol-gel solutions. The resulting thin films have been studied using various techniques, including atomic force microscopy, Raman spectroscopy and the electrical properties of the films have also been studied using current-voltage and capacitance voltage measurements. This paper will present comparisons of these properties for thin films of varying thicknesses which have been annealed at different temperatures.

Smoothing of the ZnO(0001) surface via thermal annealing of thin Co films

L Deacon[1], R Bennett[1] and S Cavill[2]

[1]University of Reading, UK, [2]Diamond Light Source Ltd., UK

Zinc Oxide, a wide band-gap semiconductor (~3.2eV) with many industrial applications, has great potential in the next generation of opto-electronic and spintronic devices. The {0001} surfaces are polar and are theoretically unstable due to diverging dipole moment[1,2]. We find that the clean Zn-terminated surface is stabilized by reconstruction to form many triangular pits and islands of various sizes, in agreement with the work of others[3–5]. Thin films of Co on ZnO(0001) have been investigated using a combination of surface science techniques and show Co metal particulates on top of the underlying ZnO structure after deposition at room temperature. Thermal annealing of thin Co films forms smooth, flat surfaces in contrast to the reconstructed clean surface. The as-deposited Co films are metallic, but oxidize upon thermal annealing, as determined by changes to the Co 2p states by XPS. This indicates either the formation of a cobalt oxide overlayer, or a substitution of Co into Zn sites in the ZnO wurtzite matrix[6]. We discuss the implications for the creation of a ZnO based dilute magnetic semiconductor (DMS) and the removal of the electrostatic dipole moment.

[1] P. W. Tasker, Journal of Physics C: Solid State Physics 12, 4977–4984 (1979).
[2] Claudine Noguera, Journal of Physics: Condensed Matter 12, R367–R410 (2000).
[3] Georg Kresse, Olga Dulub, and Ulrike Diebold, Phys. Rev. B 68, 245409 (2003).
[4] Frank Ostendorf, Stefan Torbrügge, and Michael Reichling, Phys. Rev. B 77, (2008).
[5] H. Meskine and P. A. Mulheran, Phys. Rev. B 84, 165430 (2011).
[6] J. A. Dumont, M. C. Mugumaoderha, J. Ghijsen, S. Thiess, W. Drube, B. Walz, M. Tolkiehn, D. Novikov, F. M. F. de Groot, and R. Sporken, Journal of Physical Chemistry C 115, 7411–7418 (2011).

Isotope enrichment and substitution in the study of impurities and defects in ZnO semiconductors

C Gray, D Byrne, M Henry and E McGlynn

Dublin City University, Ireland

This work presents the initial results of a study of Cu-related defects in ZnO nanorods using low temperature photoluminescence. Defects in semiconductors offer possibilities for the study of electronic and vibrational properties of materials and the interaction of these properties. Extrinsic defects such as Cu impurities in ZnO have been studied extensively in the past. Our study is concerned with the effect of both extrinsic impurities/defects such as Cu impurities and intrinsic, native defects such as Zn vacancies/interstitials, and how the effects of these defects are manifested in ZnO semiconductor material grown with isotopically enriched Zn. The samples are in the form of nanorods grown by Vapour Phase Transport on silicon substrates with ZnO buffer layers. Our earliest measurements are on non-isotopically enriched ZnO nanorods grown using one sixth of the ZnO source powder quantity previously used, which is an important first step to enable further studies due to the relative small quantities of isotopically enriched material available. SEM images show dense, vertically aligned nanorods whose optical properties (as determined from photoluminescence measurements by spectral feature intensity and linewidths at low temperatures) are excellent. We will study the introduction of isotopically pure Zn in the crystal lattice and associated shifts of the Cu-related Zero Phonon Line emission at 2.86eV and we will compare this to any shift in the bound exciton positions. This will enable us to determine the involvement of Zn vacancies and interstitials in the 2.86eV emission from this Cu-related defect in ZnO.

Impact of atom electromigration on morphology of vicinal surfaces

V Usov[1], S Stoyanov[2], C O Coileain[1], O Toktarbaiuly[1], T Lyons[1], S I Bozhko[3], S A Krasnikov[1] and I V Shvets[1]

[1]Trinity College Dublin, Ireland, [2]Bulgarian Academy of Sciences, Bulgaria, [3]Russian Academy of Sciences, Russian Federation

The biased drift of atoms on crystalline surfaces induced by applied electric field and electric current has been intensively studied due to its complex temperature and electric field orientation dependences. Under certain conditions adatom electromigration on vicinal surfacescauses atomic steps to gather together and creates step bunches whose height grows with time and reaches tens to hundreds of nm. This phenomenon has always been associated with Si low index surfaces, which was the only material where the phenomenon of electromigration induced step bunching had been observed to date. For the first time we demonstrate that the coarsening step bunching can be induced by electric fields at high temperatures of 1500 °C on a variety of crystallographic surfaces including insulating oxides such as Al_2O_3(0001) and metals such as W(110).

Prolonged annealing of Si(111) with dc current further develops the surface morphology, giving rise to new patterns, namely the antibands, *i.e.* step bunches with the opposite slope to the primary bunches. We give theoretical description of the atomic step's shape evolution towards development of antibands and illustrate it with our experimental data. We also theoretically derived conditions required for the onset of the antiband instability resulting from sublimation controlled by slow adatom surface diffusion. The validity of this theoretical criterion was examined experimentally by analysing initial stages of antiband formation on Si(111) under conditions of constant temperature (1270 °C), whilst systematically varying the applied electromigration field. The experiment strongly supports the validly of the derived theoretical criterion and provides strong evidence that adatom transport on Si(111) at high temperatures is diffusion limited and characterized by relatively slow surface adatom diffusion and fast kinetics at the atomic steps. These results are of broad interest as they are applicable to a range of materials and can be used to develop new bottom-up self-assembly strategies.

Probing strain in In_2O_3 thin films

D Wermeille[1], H Zhang[2], A Regoutz[2], R Egdell[2] and R Cowley[2]

[1]XMaS - ESRF, France, [2]University of Oxford, UK

Transparent conducting oxides (TCOs) combine the properties of optical transparency in the visible region with a high electrical conductivity, and have widespread application as window electrodes in photovoltaic devices, liquid crystal displays and organic light emitting diodes. In_2O_3 is a prototypical TCO, which is amenable to degenerate n-type doping with Sn to give so-called indium tin oxide (ITO). In spite of the undoubted technological importance of ITO, many of the basic physical properties of In_2O_3 have proved to be controversial, including the nature and magnitude of the band gap. Recently it has been shown that the band gap can be modified by epitaxial strain when In_2O_3 is grown on cubic Y-stabilised ZrO_2. This opens the possibility of using strain to tune the band gap for device applications. First principles density functional theory calculations reveal that the magnitude of the reduction of the band gap depends critically on the exact numerical value of the Poisson ratio, the parameter that links longitudinal compression with transverse expansion. The missing piece in this jigsaw is provided by X-ray diffraction experiments conducted on the XMaS beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France in which in-plane expansion and out-of-plane contraction were measured by reciprocal space mapping of non-specular reflections from high quality single crystal films grown by plasma assisted molecular beam epitaxy (MBE). Typical results will be presented, allowingus to derive a value of 0.31 for the Poisson ratio. This work provides a sound basis for using strain to engineer the band gap in ITO thin films and heterostructures.

ECOSS student prize

Ene-like reaction of cyclopentene on Si(001)–2x1: an XPS and NEXAFS study

A Khaliq, D Pierruci, H Tissot, J-J Gallet, F Bournel and F Rochet

UPMC Paris VI, France

The control and the understanding of single-molecule covalent coatings on silicon surfaces are increasingly important in designing nano scale electrical elements, such as organic/inorganic semiconductor hybrid structures. In this respect ordered arrays of cyclopentene deposited on Si (001)–2x1 appear as promising buffer layers for further molecular crystal growth on the substrate. In this work, we examine the adsorption of cyclopentene on Si(001)–2x1 in the temperature window 130 °C-280 °C, by means of C 1s XPS and NEXAFS. Until now cryogenic and room temperature adsorption studies tended to prove that cyclopentene adsorption results from a formal cycloaddition ([2+2]-like) reaction of the C=C double bond with a silicondimer. Our XPS/NEXAFS study reveals that an ene-like reaction competes with the [2+2]-like reaction channel, leading to the formation of products bearing a C=C bond, already at deposition temperature as low as ~130 °C. This work helps to determine the optimum conditions leading to optimal chemical order in view of applications of cyclopentene as a buffer layer.

TEOS adsorption on Si(001)-2x1: an XPS and STM study combined with electronic structure calculation

H Tissot[1], J-J Gallet[2], F Bournel[2], A Khaliq[2], D Pierucci[2], A Naitabdi[2], F Rochet[2], F Finocchi[2] and A Pietzsch[3]

[1]synchrotron SOLEIL, France, [2]Université Pierre et Marie Curie (UPMC), France, [3]Lund University, Sweden

Organosilanes as tetraethoxysilane (TEOS, ($Si[OCH_2CH_3]_4$)) are used as precursors for chemical vapor deposition of silicon dioxide (SiO_2) on clean silicon surfaces. In presence of an adsorbed water layer, they form self-assembled monolayers (SAMs) on hydroxylated silica surfaces. Other applications include the adhesion of polymers or the fixation of biological molecules on surfaces.

The adsorption of TEOS on Si(001)-2×1 surface in ultra high vacuum is studied in the low coverage regime, through a joint experimental and theoretical approach. The experimental study consists in scanning tunneling microscopy (STM) and synchrotron radiation X-ray photoelectron spectroscopy (XPS) while DFT calculation will provide adsorption energies.

XPS shows that TEOS dissociatively adsorbs on the surface via the scission of all Si-O bonds despite of the high Si-O bond energy of 430 kJ mol^{-1} compared to 270-280 kJ mol^{-1} for C-O.

The STM images of filled states reveal a main adsorption configuration corresponding to the adsorption of the four etoxy groups on two silicon dimers and to the formation of a silicon monomer on the neighboring silicon dimer row. On the basis of Density Functional Theory (DFT) calculations, TEOS adsorption energy for different configurations was calculated and the corresponding STM images were simulated and compared with the experiments.

The understanding of TEOS reactivity on clean silicon and the presence of a silicon monomer paves the way to its possible use as an anchoring unit enabling the grafting of complex multifunctional molecules.

Nanostructuration of O/Cu(110) and its role on the surface reactivity toward H_2S

C Poulain, F Wiame, V Maurice and P Marcus

Laboratoire de Physico-Chimie des Surfaces (ENSCP-CNRS), France

Due to the need to find alternative ways to create smaller systems in the microelectronics industry, self-organized growth of nanostructures on metallic surfaces attracts much interest [1]. Among such surfaces, the O/Cu(110) nanostructure consists of O-induced (2x1) reconstructed stripes periodically aligned in the [001] direction and alternating with bare Cu stripes [2]. It is an ideal playground to study the relationship between structure and reactivity at the nanometer scale since periodicity and stripes width are easily tunable.

We will present a process to elaborate nanostructured surfaces exhibiting periodicities significantly diverging from the generally admitted Marchenko-Vanderbilt model [3, 4] and a systematic study of the interaction with H_2S as a function of structure. Auger electron spectroscopy data will be presented to show the critical dependence of the reaction kinetics on the structure and scanning tunnelling microscopy data will be presented to discuss the reaction mechanisms involved.

The results show that the reaction leads to the formation of sulpur c-(2x2) islands preferentially on oxidized stripes and that this is favoured on nanostructures with larger oxidized stripes. The reaction mechanism involves the formation of Cu-S complexes at the edges of the oxidized stripes, and the detachment of Cu-O row segments from these edges. The segmented Cu-O rows diffuse on the oxygen-free areas due to short-range repulsion with the oxidized stripes.

[1] J. V. Barth, G. Costantini, K. Kern, Nature 437 (2005) 671.
[2] K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. Goerge, G. Comsa, Phys. Rev. Lett. 67 (1991) 855.
[3] V. Marchenko, JETP Lett. 55 (1992) 73.
[4] D. Vanderbilt, Surface Science 268 (1992) L300.

Two steps synthesis of 2D covalent networks on metal substrates

T Faury [1,2], S Clair [1], M Abel [1], M Koudia [1], F Dumur [2], D Gigmes [2] and L Porte [1]

[1]IM2NP, France, [2]ICR, Aix-Marseille Univ, France

The chemistry of boronic acids is currently one of the ways used for the formation of covalent organic 3D frameworks (COF), which are novel porous extended crystalline structures made entirely from light elements. Our goal is to apply this concept to the formation of two-dimensional organic nanostructures on metal surfaces to prepare organic nanoporous masks of various sizes and functionalities.

Previous work carried out in our laboratory with the molecule 1,4-Benzene DiBoronic Acid molecule (BDBA) led to the formation of 2D covalent honeycomb-like nanoporous networks with 15 Å pores, as observed by STM.[1] However due to the irreversibility of the covalent bond formation, numerous defects were present in the polymer film.

To improve the quality of the 2D network, a promising approach consists in controlling the kinetics of formation by the use of two successive reactions. Each reaction is activated in a specific range of temperature. Herein, we present our results obtained during the sequential polymerization of 1-Bromo Benzene 4-Boronic Acid (BBBA) on a Au(111) surface.[2]The formation of the boroxine rings was obtained by dehydration of the boronic acid moieties at room temperature and was followed by C-C bond formation via an Ullmann coupling at temperature higher than 200°C. Using this particular stepwise approach, a polymer network of high quality with 23 Å hexagonal pores was obtained.

[1] Zwaneveld N. A. A.; Pawlak R.; Abel M.; Catalin D.; Gigmes D.; Bertin D.; Porte L. Journal of the American Chemical Society 2008, 130, (21), 6678-6679.
[2] Faury, T. ; Clair, S. ; Abel, M. ; Dumur, F. ; Gigmes, D. ; Porte, L. ; J. Phy. Chem. C 2012.

Spin-transfer torque and Joule heating generated by spin-polarized field-emitted electrons

A Schlenhoff, S Krause, A Sonntag and R Wiesendanger

University of Hamburg, Germany

High electric fields can discharge electrons from a solid, thereby generating an emission current, which becomes spin-polarized when using a magnetic emitter [1]. Although field emission is used for microscopy purposes since the 1930's [2], a detailed understanding of the interaction of spin-polarized field-emitted electrons with magnets was missing up to now.

In our studies, we utilize spin-polarized scanning tunneling microscopy (SP-STM) in the field emission mode [3] for the direct observation and manipulation of atomic-scale superparamagnets. A high spin-polarized emission current injected into the first field emission resonance (FER) of individual nanomagnets is found to strongly affect the switching behavior. A combined current-dependent lifetime analysis performed in the tunneling and in the field emission mode reveals that for field-emitted electrons Joule heating is less effective due to a lower phonon excitation probability, and the spin-transfer torque is increased due to additional Stoner excitations. On a quasistable nanomagnet, a spin-polarized emission current of only a few nA already triggers magnetization reversal, thereby demonstrating the robust manipulation capability of spin-polarized field-emitted electrons. Our studies provide deep insight into the microscopic processes involved in field-emitted electrons interacting with magnets on the atomic scale, thereby opening the pathway to a new type of spin-emission based read-write technique for future high-density magnetic data storage applications.

[1] M. Hofmann *et al.*, Phys. Lett. 25A, 270 (1967).
[2] E. W. Müller, Z. Physik 108, 668 (1938).
[3] A. Kubetzka *et al.*, Appl. Phys. Lett. 91, 012508 (2007).

Substrate-induced doping domains in graphene: DFT and STS studies

J Slawinska, I Wlasny, P Dabrowski, Z Klusek and I Zasada

University of Lodz, Poland

Weak interaction between graphene and the metallic substrate preserves the Dirac cones in the band-structure, but they are shifted with respect to the Fermi level, which results in effective doping of graphene. We have studied graphene/metal interfaces by first-principles including van der Waals corrections. In particular, it is revealed that graphene could be nearly free-standing on a perfect Au(111) surface. The interface has been found to be extremely sensitive to the adsorption distance and to the structure of surface, for example imperfections of the substrate induces non-zero doping [1].

Scanning tunneling spectroscopy has shown the presence of energetic heterogeneity in terms of the changes in the local density of states (LDOS) measured at different places on the sample. They have been identified to be domains of doping by comparing measured and simulated LDOS with specific features reflecting the Dirac cones defined in the band-structure [2]. Domains of zero-doping and p-type (0.25-0.55 eV) doping have been then associated with polycrystalline character of the gold surface [3]. The results demonstrate the possibility of tuning the doping across one flake which can be useful for applications of graphene in electronic devices.

[1] J. Slawinska, et al., PRB 83, 245429 (2011).

[2] J. Slawinska, I. Zasada, PRB 84, 235445 (2011).
[3] J. Slawinska, et al., arxiv:1201.5243, submitted to PRB.

The bonding mechanism for PTCDA on Ag surfaces – a correlation between the formation of O–Ag bonds and the adsorption geometry

O Bauer[1], G Mercurio[2], M Willenbockel[2], W Reckien[1], C H Schmitz[1], B Fiedler[1], S Soubatch[2], T Bredow[1], F S Tautz[2] and M Sokolowski[1]

[1]Bonn University, Germany, [2]Jülich Research Centre, Germany

The surface bonding mechanism of large π-conjugated molecules is of immense interest for understanding the structural and electronic properties of organic thin films [1]. Insight into relevant interaction channels and their relative contribution to the bonding can be obtained from a detailed determination of the bonding configuration of the same molecule on different crystal faces of one substrate, including the positions of all relevant atoms.
We have investigated the adsorption geometry of 3,4,9,10-perylenetetracarboxylic acid dianhydride (PTCDA) on the Ag(111), Ag(100), and Ag(110) surfaces with the normal incidence x-ray standing waves (NIXSW) technique. The adsorption height decreases and the distortion of the molecular C backbone increases with decreasing surface atom coordination number. Of importance are the attractive local O–Ag bonds on the anhydride groups. They are the shorter the more open the surface is, and lead even to partly repulsive interactions between the perylene core and the surface. In parallel, there is an increasing charge donation from the Ag surface into the π-system of the PTCDA, as dispersion-corrected density functional theory (DFT) calculations show. This result is in good agreement with the increasing shift of the molecular (F)LUMO state towards higher binding energies observed in ultraviolet photoemission spectroscopy (UPS) experiments. Furthermore, DFT reveals a significant buckling of the Ag surfaces upon PTCDA adsorption. We present a conclusive picture of the complex, synergistic bonding mechanism that explains the out-of-plane distortion of the adsorbed PTCDA and the surface buckling in detail.

[1] A. Hauschild et al., Phys. Rev. B 81, 125432 (2010).

Oxygen adsorption on ferromagnetic platinum

M Escano, Q T Nguyen, H Nakanishi and H Kasai

Osaka University, Japan

As an oxidation catalyst, platinum (Pt) is one of the best studied systems in surface science. Thus far, the dissociative adsorption of oxygen on paramagnetic Pt surfaces is activated. Reduced activation barrier implies strongly bound dissociated oxygen atom on surface, which is often undesirable. Our work employs manipulation of the magnetic state of Pt surface (paramagnetic to ferromagnetic) to change the reaction energy profile of oxygen. The ferromagnetic Pt is modeled by a spin-polarized Pt layer on a magnetic substrate, M (where M:Fe,Co). Using constrained local moment (CLM) approach and Heisenberg model to get the Pt-M exchange interaction and the Monte Carlo (MC) simulation to get magnetization curves, the obtained Pt layer transition temperature is above the room temperature (322 K,394 K). The potential energy surface (PES) for dissociative adsorption from density functional theory (DFT) calculations shows that on ferromagnetic Pt, the activation barrier for dissociation is reduced and the binding energy of the separated oxygen atoms is also reduced. An emergence of a non-activated dissociative adsorption is noted on Pt/Fe. The same trend is found in the case of molecular adsorption (Pt/Co). The Fermi-level density of states was found to be an appropriate basis for the O-O bond elongation mechanism. The study is going further into investigations on magnetic phases of oxides and molecular assemblies on ferromagnetic metal surfaces.

[1] M.C. Escaño, T.Q. Nguyen, H. Nakanishi and H.Kasai, Surf. Sci. 602, 3415 (2008).

[2] M.C. Escano, TQ Nguyen, H. Nakanishi, H. Kasai. J. Phys.: Condens. Matt. 21, 49221 (2009).
[3] M.C. Escaño, H. Nakanishi and H. Kasai, J. Phys. Chem. A 113, 14302 (2009).
[4] Y. Kunisada, M.C. Escano, H. Kasai. J. Phys.: Condens. Matt. 23, 394207 (2011)

Layer-by-layer assembly of organic molecular donor-acceptor heterojunctions on vicinal gold surfaces

J Wang, J-M Tang, G Miller and K Pohl

University of New Hampshire, USA

Molecular co-self-assembly of organic electron-donor and electron-acceptor molecules into ordered heterostructures on surfaces provides a fundamental molecular-level insight into how these two kinds of molecules would interact in a model organic photovoltaic cell. We will present a study of the self-assembly of functionalized pentacenes (electron donors) and fullerenes (electron acceptors) into a layer-by-layer heterojunction on stepped gold surfaces by scanning tunneling microscopy (STM) characterization and density functional theory (DFT) calculations. The pentacene derivative -- 6,13-dichloropentacene (DCP) -- forms a striking long-range ordered brick-wall self-assembled monolayer (SAM) on a stepped Au(788) vicinal surface, with the long-axis parallel to the step edges [1]. Subsequently deposited fullerene (C_{60}) molecules form parallel triple, double, and single long molecular chains on-top the intact DCP SAM on Au(788) [2]. The novel organic-metal and organic-organic interfacial interactions, as well as the adsorption geometry, have been explored by DFT. The adsorbed C_{60}'s form parallel commensurable (3:2) molecular chains on-top the DCP lattice -- exactly three fullerenes line up with two DCP molecules along their long axis. The initial C_{60} chains will always grow along the upper step edge of each DCP/gold terrace. DFT suggests the optimized adsorption site for the second C_{60} chain is on-top the trough between two DCP molecular rows, to form a double chain. The calculated C_{60}--C_{60} spacing of 1.1 nm agrees well with experimental results. This subtle nanostructure formation is attributed to the delicate balance of intermolecular bonding interactions, interfacial dipole fields, and stepped-substrate interactions. The DFT-based electronic properties for this model 3-component organic/metallic system, such as charge transfer between donors and accepters, will also be discussed.

[1] J. Wang, I. Kaur, B. Diaconescu, J.-M. Tang, G. P. Miller, and K. Pohl, ACS Nano 5 (2011) 1792.
[2] J. Wang, J.-M. Tang, G. P. Miller, and K. Pohl, in preparation, (2012).

Ordered array of single Au adatoms on Fe_3O_4(001) with remarkable thermal stability

Z Novotny, G Argentero, Z Wang, M Schmid, U Diebold and G S Parkinson

Vienna University of Technology, Austria

We present a scanning tunneling microscopy investigation of gold deposited at the magnetite Fe_3O_4(001) surface at room temperature. This surface forms a reconstruction with ($\sqrt{2}\times\sqrt{2}$)R45° symmetry [1], where pairs of Fe and neighboring O ions are slightly displaced laterally, forming undulating rows with 'narrow' and 'wide' adsorption sites. At fractional monolayer coverages, single Au adatoms adsorb exclusively at the narrow sites, with no significant sintering up to annealing temperatures of 400 °C [2]. The strong preference for 'narrow' site is possibly related to charge and orbital ordering within the first subsurface octahedral layers of the reconstructed Fe_3O_4(001) surface [3]. Because of their high thermal stability, the ordered Au atoms at Fe_3O_4(001)-($\sqrt{2}\times\sqrt{2}$)R45° should provide useful insights into the chemical reactivity of single atomic species.

Tl/Si(111) - Rotation of the Rashba spin perpendicular to the surface: the unoccupied electronic structure

S D Stolwijk[1], K Sakamoto[2], A B Schmidt[1], P Krüger[1] and M Donath[1]

[1]Westfälische Wilhelms-Universität Münster, Germany, [2]Chiba University, Japan

The development of semiconductor spintronic applications depends on the generation of spin-polarized electrons at room temperature. Thin films of heavy metals on semiconductor surfaces promise to be excellent candidates for this purpose. In this context the Tl/Si(111)-(1x1) surface shows outstanding properties. Spin-resolved photoemission experiments reveal an occupied Rashba-split surface state with a peculiar spin structure in reciprocal space [1]. Along the ΓK direction of the hexagonal two-dimensional surface Brillouin zone the spin polarization is rotating from the normal Rashba direction to the direction perpendicular to the surface. This is due to a spin frustration at the K point and can be simply understood as a consequence of the 2D symmetry of the hexagonal system.

With spin-resolved inverse photoemission we observe an unoccupied spin-orbit split surface state along ΓK with the same out-of-plane rotation of the spin polarization. Remarkably, at the K point the two spin components are split in energy by more than 0.6 eV. Here, the lower surface band approaches the Fermi level, which gives rise to a nearly complete spin polarization at E_F. As the out-of-plane spin polarization is always negative for K and positive for K', interesting transport properties can be expected. Our results are supported and discussed on the basis of calculations within the local-density approximation including spin-orbit coupling.

[1] K. Sakamoto *et al.*, Phys. Rev. Lett. 102, 096805 (2009)

Thursday 6 September

Organic layers and polymers 6

(invited) High throughput materials discovery adventures with polymer microarrays

M Alexander

The University of Nottingham, UK

Polymer micro arrays have proven to be useful tools for the discovery of new synthetic materials to support and guide cells [1]. This high throughput (HT) materials discovery approach is attractive because, the paucity of understanding of the cell-material interface hinders the *ab initio* rational design of new materials [2]. The large number of polymer chemistries that can be investigated on a single polymer micro array act as a wide net in the search for materials that can achieve a certain cell response. These micro array *hits* are the starting point from which new materials may be developed.

Combinatorial acrylate libraries formed on standard glass slides were first presented as a HT platform by Anderson and Langer [3]. In collaboration with this group we have gained both a greater understanding of the relationship between material surface chemistry and cellular response, and we have identified materials which show promise as synthetic substrates for pluripotent stem cell culture [4,5]. To complement HT materials screening, we developed the approach of *high throughput surface characterisation* employing a range of analytical techniques [6]. This surface characterisation is necessary to directly relate the effect of the material on attached cells to the actual surface on which they sit, and to enable effective scale up from micro array to culture ware dimensions. Application of chemometrics, to handle the large amounts of complex data, reveals the importance of certain surface moieties, informing the process of materials discovery and increasing our understanding of the cell-material interface [7,8,9]. Most recently, we have expanded this approach to the identification of materials which resist bacterial attachment and biofilm formation with application in the reduction of medical device centred infection, such as for urinary catheters [10].

[1] Hook, A. L. *et al.* High throughput methods applied in biomaterial development and discovery. *Biomaterials* 31, 187-198 (2010).
[2] Kohn, J., Welsh, W. J. & Knight, D. A new approach to the rationale discovery of polymeric biomaterials. *Biomaterials* 28, 4171–4177 (2007).
[3] Anderson, D., Levenberg, S. & Langer, R. Nanoliter-scale synthesis of arrayed biomaterials and application to human embryonic stem cells. *Nature Biotechnology Letters* 22, 863-866 (2004).
[4] Mei, Y. *et al.* Combinatorial Development of Biomaterials for Clonal Growth of Human Pluripotent Stem Cells. *Nature Materials* 9, 768-778 (2010).
[5] Saha, K. *et al.* Surface engineered substrates for improved human pluripotent stem cell culture under fully defined conditions. *Proc. Natl. Acad. Sci. USA* 108, 18714-18719 (2011).
[6] Urquhart, A. *et al.* High through-put surface characterisation of arrayed biomaterials. *Advanced Materials* 19, 2486–2491 (2007).
[7] Urquhart, A. *et al.* TOF-SIMS Analysis Of A 576 Micro-Patterned Co-Polymer Array Reveals Surface Moieties That Control Wettability. *Analytical Chemistry* 80, 135-142 (2008).
[8] Davies, M. C. *et al.* High Throughput Surface Characterisation – a review of a new tool for screening prospective biomedical material arrays *Journal of Drug Targeting* 18, 741-751 (2010).
[9] Yang, J. *et al.* Polymer surface functionalities that control human embryoid body cell adhesion revealed by high throughput surface characterization of combinatorial material microarrays. *Biomaterials* 31, 8827-8838 (2010).

[10] Hook, A. L. *et al.* Combinatorial discovery of novel polymers resistant to bacterial attachment *Nature Biotechnology* (2012, in press).

An XPS and NEXAFS based comparison of biomolecules adsorbed on two substrates: Gold nanoparticles vs. single crystals

R Acres, N Tsud, M Iakhnenko and K Prince

Sincrotrone Trieste, Italy

The biomolecules histidine (His) and tryptophan (Trp) (both aromatic amino acids) have been adsorbed onto the surface of gold nanoparticles (AuNP) from solution and studied using synchrotron radiation x-ray photoelectron spectroscopy (SRXPS) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy at the Materials Science Beamline (MSB) at ELETTRA. The AuNPs have diameters of 6 ± 1 nm. Comparison spectra were collected from monolayers of His and Trp adsorbed onto single crystal gold surfaces by evaporation in UHV.

Nitrogen K edge SRXPS and NEXAFS spectra from His adsorbed onto AuNPs from solution are in good agreement with those obtained from His adsorbed onto Au(111) by evaporation in UHV as well as adsorbed from solution [1]. This similarity leads to the conclusion that the binding mechanism of His on AuNPs is comparable to that on single crystal gold. The spectra collected from Trp on AuNPs, however, show significant variations compared to those of Trp adsorbed on Au(111) in UHV, particularly with respect to N 1s photoemission and NK-edge NEXAFS spectra. Such differences lead to the conclusion that Trp binds to AuNPs differently than to Au(111), with the relative bonding strength of the two nitrogen functional groups changing.

[1] Feyer, V., Plekan, O., Tsud, N., et al., Langmuir 26, 8606 (2010).

Modeling the Mn 1s near edge absorption fine structure X-ray spectra of the oxygen evolving complex in photosystem II by Density Functional Theory

B Brena[1], H Ågren[2] and P Siegbahn[3]

[1]Uppsala University, Sweden, [2]Royal Intitute of Technology (KTH), Sweden, [3]Stockholm University, Sweden

Oxygen molecules in the atmosphere are mostly produced in the photosynthetic water oxidation. The reaction is catalyzed by the oxygen-evolving complex (OEC), a cluster containing four Mn and one Ca atoms. The OEC is part of the photosystem II (PSII), a multiprotein enzyme situated in the thylakoid membrane of plants, algae and cyanobacteria. Water oxidation involves four flash-induced steps with intermediates denoted as S_0 to S_3.

The near edge absorption fine structure X-ray spectra (NEXAFS) is a technique well known to be sensitive to the oxidation states of the excited atomic centers. Here we have computed Mn 1s NEXAFS spectra by means of transition potential gradient corrected Density Functional Theory (DFT) on four Mn_4Ca clusters modeling the successive S_0 to S_3 states [1]. Each of the model clusters are composed of Mn(III) and Mn(IV) atoms, progressing from $Mn(III)_3Mn(IV)$ for S_0, to $Mn(III)_2Mn(IV)_2$ for S_1, to $Mn(III)Mn(IV)_3$ for S_2, and to $Mn(IV)_4$ for S_3: a Mn centered oxidation takes place during each step of the photosynthetic oxygen evolution. Our DFT simulations of the Mn 1s absorption spectra reproduce the known experimental observation of the increase of the energy position of the edge (or inflection point energy, IPE) for complexes containing Mn atoms with higher oxidation states.

Reference calculations were performed on mono-nuclear compounds $Mn(II)(acac)_2(H_2O)_2$, $Mn(III)(acac)_3$ and $Mn(IV)(sal)_2$ (bipy). For these compounds, the up-shift of the computed IPE amounts to about 1 to 3 eV as the oxidation state on Mn is increased by one unit.

The theoretical IPE's of the tetra-nuclear Mn complexes are shifted by about 0.93 eV in the S_0 to S_1 transition, by about 1.43 eV in the S_1 to S_2 transition, and by 0.63 eV in the S_2 to S_3 transition. These results are in agreement with previous experimental studies. The smaller energy shift of the S_2 to S_3 transition is qualitatively explained in terms of the potential model for core electron chemical shift.

(invited) Bio-inspired approaches to crystals with composite structures

F Meldrum

University of Leeds, UK

Advances in technology demand an ever-increasing degree of control over material structure, properties and function. As the properties of monolithic materials are necessary limited, one route to extending them is to create a composite by combining contrasting materials. The potential of this approach is beautifully illustrated by the formation of biominerals where organic macromolecules are combined with brittle minerals such as calcite to create crystals with considerable fracture toughness. This talk will discuss a number of bio-inspired approaches leading to crystals with composite structures. Polymer particles have been entrapped within calcite single crystals by a simple one-pot method, using the particles as soluble additives. Very high levels of entrapment can be achieved, generating crystals occluding over 20 vol% of particles, according to the particle surface chemistry and reaction conditions. A range of techniques including IR spectroscopy, high resolution powder XRD and high resolution TEM were used to compare the structures of these crystals with calcite single crystals of geological and biogenic origin. This strategy has also been extended to the incorporation of inorganic particles such as magnetite and gold within calcite. An alternative method is also being explored in which we profit from the demonstrated ability to entrap gels within calcite single crystals. Prior functionalisation of the gels with inorganic particles then provides an efficient method of introducing these secondary particles within a crystal without the necessity for a specific surface coating. These results therefore demonstrate that the biomimetic strategy of creating composite crystals by occlusion of macromolecules or fibres can be successfully applied to synthetic crystal growth, yielding crystals with selected compositions and properties.

Polymer Pen Lithography (PPL) for bio-applications

F Brinkmann, M Hirtz and H Fuchs

Karlsruhe Institute of Technology, Germany

Patterning of biofunctional materials into microarrays on a chip is a key challenge for many applications related to screening, sensing and observing the response of living cells on presented chemical stimuli. We optimized polymer pen lithography (PPL) to enable the patterning of a variety of so called bioinks on one surface enabling different experimental setups simultaneously.

Microcontact printing (µCP) and dip-pen nanolithography (DPN) are two well-established direct printing methods. µCP produces patterns in the cm^2 range easily and with high throughput, but is limited in pattern flexibility due to the need of a pre-fabricated pattern mask as master. DPN allows a flexible deposition of different inks (multiplexing) in sub-micron registry, but with a smaller throughput compared to µCP.

With PPL, however, we combine the advantages of both µCP and DPN, especially in the micron scale often most relevant to biological applications. Some hundred thousand polymer pyramids are attached to a piezoelectric system via a glass support. Defined lateral movements of the whole tip-array with sub-micrometer sensitivity lead to specific micrometer features on a cm^2 scale area.

We have optimized PPL in the face of bio research in two ways:

One, the use of a specific surface-ink-combination forms an array, which enables the immobilization of all biotinylated molecules on the pattern in a further incubation step.

Two, different inking strategies allow the fabrication of multiplexed patterns. Proof-of-principle experiments underline the diversity of microarrays and flexibility in pattern control fabricated by PPL.

Investigating the enantioselectivity of alanine on chiral copper surfaces

M Gladys[1], L Thomsen[2], A Tadich[2] and B Cowie[2]

[1]University of Newcastle, Australia, [2]Australian Synchrotron, Australia

The chiral surface termination of Cu(421) was found via full hemisphere angle-resolved X-ray Photoelectron Diffraction (XPD) and Fermi Surface (FS) mapping measurements, which were conducted using a novel toroidal-geometry electron spectrometer located at beamline UE56/2 at BESSY II. Saturated chemisorbed layers of D- and L-alanine amino acids were then adsorbed onto the surface. Little enantioselectivity was observed in the HR-XPS thermal desorption, however there was a large difference in the dissociation products left on the surface between the two enantiomers. NEXAFS spectroscopy also exhibited only minor differences in the molecular adsorption of the two enantiomer layers however Low Energy Electron Diffraction (LEED) images revealed significant differences in the structure of the adsorbed layers. D-alanine forms a p(2x3) overlayer while L-alanine forms a combination of p(1x2) overlayer and faceted steps oriented in the [-110] direction. Intermolecular bonding and steric effects play a significant role in these stereo-selective differences by maximizing the hydrogen bonding between the molecules. This study clearly shows that single chiral tests are not adequate to ascertain the true enantioselective properties of the given system. We compare this work to Alanine on Cu(531).

Click-Chemistry Dip-Pen Nanolithography (DPN) for patterning of bio-molecules

M Hirtz[1], H-Y Chen[2], S Oberhansl[3], J Lahann[4] and H Fuchs[1]

[1]KIT/INT, Germany, [2]Nanyang Technological University (NTU), Singapore, [3]Institute for Bioengineering of Catalonia (IBEC), [4]KIT/IFG, Germany

When studying cell responses to bioactive compounds, it is often beneficial to perform these experiments on surfaces patterned with the molecules under investigation instead of relying on delivery in solution. Firstly, it is easier to screen cells already attached to surfaces, but moreover immobilizing and patterning investigated compounds enables more detailed studies that look into the effect of geometry or concentration gradients on cell response. Patterning in sub-cellular dimensions or even the nanoscale enables investigators to look into cell receptor co-localization and interaction with presented small molecules or proteins in a stable and spatially restrained way not accessible by experiments in solution. From the various existing methods to chemically functionalize surfaces (e.g. microcontact printing (µCP), e-beam lithography, optical lithography), dip-pen nanolithography (DPN) offers some great advantages especially while dealing with delicate bioactive molecules like proteins: DPN patterning processes generally take place at mild environment conditions (no excessive temperatures, no toxic chemicals), are quite flexible in the use of materials for substrates and inks, offer the capability for multiplexing (writing different compounds at the same time) and require usually less processing steps than e.g. photolithographic routes.

We present here a click-chemistry approach for the immobilization of bioactive molecules on substrates by DPN. Almost arbitrary substrate materials (e.g. PMMA, PS, PTFE, steel, glass) can be used as basis for this technique by pre-functionalization of the samples with a reactive layer deposited by chemical vapor deposition (CVD) [1]. Additionally, silicon oxide or glass surfaces can readily be functionalized by a self-assembled monolayer providing reactivity for the click-chemistry approach to take place [2]. The so prepared substrates allow for the coupling of azide functionalized inks and the subsequent binding of biotinylated proteins. Taking advantage of the specific strengths of DPN in comparison to techniques like µCP in regard to resolution and multiplexing of inks, click-chemistry DPN offers and interesting and promising route for the generation of bioactive surface patterns.

[1] H.-Y. Chen; M. Hirtz; X. Deng; T. Laue; H. Fuchs; J. Lahann, Journal of the American Chemical Society 2010, 132, 18023-18025.
[2] S. Oberhansl; M. Hirtz; A. Lagunas; R. Eritja; E. Martinez; H. Fuchs; J. Samitier, Small 2012, 8, 541-545.

Carbon, graphene 6

(invited) Title and abstract not available

B I Yakobson

Rice University, USA

Nitrogen-doped graphene on Ni(111)

C Papp, R Koch, J Gebhardt, W Zhao, O Höfert, K Gotterbarm, T Seyller, A Görling and H-P Steinrück

University Erlangen, Germany

We report the production of nitrogen-doped graphene from CVD growth on Ni(111) using a nitrogen containing precursor and from low energy nitrogen implantation. We studied the system with XPS and ARPES. The experimental findings are supported by DFT calculations. The chemical analysis of the layers shows two nitrogen species, whose concentration and relative abundance can be altered by the experimental conditions. The ARPES measurements show a broadening and a shift of the bands. In order to decouple the nitrogen-doped graphene from the nickel surface we used gold intercalation, leading to the electronic structure of quasi free standing graphene, while preserving the nitrogen doping.

B and N stripes in graphene ruled by grain boundary defects

R Miwa, R Kagimura and W Brito

Universidade Federal de Uberlândia, Brazil

The energetics and electronic properties of substitutional B and N doping, and BN codoping in graphene with distinct grain boundary defects were investigated by ab initio simulations. The energetic stability of B and N impurities has been examined as a function of the doping concentration. Our results reveal that B and N atoms and B-N pairs prefer to incorporate into the grain boundary region. In particular, we find that the formation of substitutional N atoms along the grain bounday sites is an exothermic process. It suggests that the formation of carbon nitride (CN) as well as BNC domains may be patterned by these defective regions, giving rise to CN or BCN stripes embedded in graphene sheets. The electronic properties of those doped grain boundary systems have been examined through STM simulations and electronic band structure calculations. We find a quite different STM picture for the B and N doped grain boundaries when compared with the same impurities on the perfect graphene sheet. On the other hand, similar to the perfect graphene sheet, we find that the n-type (p-type) doping behavior has been maintained even for the N (B) impurities occupying the grain boundary sites.

Atomic scale characterization of nitrogen-doped graphite: effects of the dopant nitrogen on the electronic structure at the surrounding carbon atoms

T Kondo[1], S Casolo[2], T Suzuki[1], T Shikano[1], M Sakurai[1], Y Harada[3], M Saito[3], M Oshima[3], M I Trioni[4], G Franco Tantardini[2] and J Nakamura[1]

[1]University of Tsukuba, Japan, [2]University of Milan, Italy, [3]University of Tokyo, Japan, [4]CNR National Research Council of Italy, Italy

Nitrogen doping in graphite-related materials such as graphene and carbon nanotubes has been reported to induce peculiar physical and chemical properties. Various applications of N-doped graphite (NG) materials have also been reported, such as biosensors, fuel cells, capacitors, electronic devices, and spin filter devices. However, a detailed picture of the electronic modifications induced by N atoms is difficult to obtain because a wide variety of defects with different types of C-N bonding configurations can coexist in NG. Here, we report comprehensive atomic-scale characterization of the defects in a nitrogen-doped graphite surface by scanning tunnelling microscopy (STM), scanning tunnelling spectroscopy (STS), photoemission spectroscopy (PES), and first-principles calculations. Nitrogen-doped graphite was produced by nitrogen ion bombardment followed by thermal annealing. Two types of nitrogen species were identified at the atomic level: pyridinic N (N having two C nearest neighbours) and graphitic N (N having three C nearest neighbours). The distinct local electronic states of the non-bonding p_z orbital of carbon are found to appear at occupied and unoccupied region near the Fermi level at the carbon atoms around pyridinic N and graphitic N species, respectively. The origin of these states is discussed based on the experimental results and the calculated results.

Synthesis, structure and properties of high quality boron-doped single layer graphene

S Agnoli, M Cattelan and G Granozzi

University of Padova, Italy

Most of the excitement surrounding graphene stems from the possibility to build a completely new carbon-based nanoelectronics. [1] However, a necessary step in this direction is the development of efficient synthetic routes for the development of materials with tailored properties. In this sense, chemical vapor deposition (CVD) is a powerful method for preparing high quality graphene layers even at industrial scale. [2] Recently, the forefront of research has moved from the study of pure graphene to the investigation of chemically modified systems (i.e. doped systems), because the ability to modify important properties, like the type and the concentration of charge carriers, is crucial for the realization of most basic electronic devices. While the preparation of n-doped graphene layers by introducing nitrogen heteroatoms is already a well establish topic, the synthesis of p-doped films is still at the very beginning. Many theoretical works envisage in boron a suitable dopant for inducing p-doping, [3] however just few boron doped materials have been reported so far. Generally solid states routes, solid-gas reactions, or wet chemistry methods were used, but the quality (in terms of morphology purity and control of dopant chemical state) of the obtained materials was not optimal.[4] Here we report for the first time the synthesis by CVD of boron-doped graphene films. By carefully optimizing the process parameters, we were able to obtain boron doped, single layer graphene on polycrystalline copper foils. The films were characterized by core level photoemission spectroscopy, scanning electron microscopy, Raman spectroscopy, and micro angle resolved photoemission spectroscopy. The body of the experimental data indicate the formation of high quality, few microns wide, single layer flakes with homogeneously distributed substitutional boron impurities. The band structure of these chemically modified layers is still very similar to pure graphene, preserving the formation of Dirac cones at the K point of the Brillouin Zone, but with a Fermi energy shifted of about 0.3 eV.

[1] A. K. Geim, K. S. Novosëlov Nat. Mat. 2007, 6, 183-191.
[2] S. Bae et al. Nat. Nanotech. 2010, 5 574-578.
[3] (a) A. Lherbier et al. Phys. Rev. Lett. 2008, 101, 036808; (b) B. Zheng et al. ACS Nano 2010, 4, 4165-4173.
[4] (a) L. S. Panchakarla et al. Adv. Mat. 2009, 21, 4726-4730, (b) T. Lin et al. Energy Environ. Sci. 2011, 4, 862-865 (c) Z.-H. Sheng et al J. Mat. Chem. 2012, 22 390-395.

Parahexaphenyl thin film growth on graphene invetstigated by AFM

M Kratzer[1], B Vasic[2], R Gajic[2] and C Teichert[1]

[1]Montanuniversitaet Leoben, Austria, [2]University of Belgrade, Serbia

Graphene is the most prominent representative of novel 2D materials and is already used in a number of applications. For further technological development it is necessary to explore the possibilities for tuning the material properties by growth, functionalization, and multistacking [1]. As a model system we investigated the growth morphology of the rodlike para-hexaphenyl (6P) molecule on graphene. As substrate exfoliated graphene flakes on silicon oxide (SiO$_x$) were used. The 6P was deposited by means of hot wall epitaxy at sample temperatures above room temperature. The resulting film morphologies were investigated via atomic force microscopy. While on the SiO$_x$ just 6P islands of upright standing molecules were found, the 6P film on the flake consisted partially from upright standing molecules and from needle like structures which are known to consist of flat lying molecules [2]. This is different from recent findings, where 6P was deposited onto epitaxially grown graphene on Ir(111) [3].

[1] A.H. Castro Neto, K. Novoselov, Mater. Express 1 (2011) 10.
[2] C. Teichert, G. Hlawacek, A. Andreev, H. Sitter, P. Frank, A. Winkler, N.S. Saricifci, Appl. Phys. A 82 (2006) 665.
[3] F.S. Khokhar, G. Hlawacek, R. v. Gastel, H. J. W. Zandvliet, C. Teichert, B. Poelsema, Surf. Sci. 606 (2012) 475.

Giant anisotropy of the orbital and spin moment of FePc molecules assembled on the moiré superlattice of graphene/Ir

C Mariani, S Lisi, M Scardamaglia, P Gargiani and M Grazia Betti

Sapienza Universita' di Roma, Italy

Supramolecular ordered assembly of metalorganic molecules on graphene is a suitable way to obtain regular nano-architectures with the metallic atoms ordered in a spin network . Iron-phthalocyanine (FePc, Fe-C$_{32}$N$_8$H$_{18}$) molecules have been adsorbed on graphene grown on the Ir(111) surface, exploiting its nanostructured long-range ordered moiré structure with ~2.5 nm surface periodicity. This surface offers a suitable template for preparing an ordered array of transition metal (TM) atoms caged into an organic macrocycle [1], thus avoiding the expected clustering of TMs on graphene [2]. The FePc layer presents a flat-lying orientation, as determined by X-ray Linear Dichroism (XLD) at the N K edge [3] and Fe L2,3 edges.

The spin and orbital configuration of the Fe d-orbital of the FePc layer has been measured by X-ray Magnetic Circular Dichroism (XMCD) across the Fe L$_{2,3}$ edges, with 5 T applied magnetic field and at liquid-He temperature, at the European Synchrotron Radiation Facility (ESRF). The FePc single-layer (SL) on graphene/Ir presents a strong dichroism and a giant in-plane/out-of-plane anisotropy, both heavily reduced at lower coverage and for few-layers FePc. The dichroism results lower for the FePc-SL adsorbed on graphite, maintaining the anisotropy, suggesting a magnified in-plane magnetic moment for SL FePc interacting with graphene/Ir.

[1] J. Mao, H. Zhang, Y. Jiang et al., J. Am. Chem. Soc. 131, 14136 (2009).
[2] C. Vo-Van, S. Schumacher, J. Coraux, V. Sessi, O. Fruchart, N.B. Brookes, P. Ohresser, T. Michely, Appl. Phys. Lett. 99, 142504 (2011).
[3] M. Scardamaglia, G. Forte, S. Lizzit, A. Baraldi, P. Lacovig, R. Larciprete, C. Mariani and M.G. Betti, J. Nanop. Res. 13, 6013-6020 (2011).

Polar molecules adsorbed on graphene: influence of the metal substrate

S Böttcher[1], M Weser[1], H Vita[1], F Bisti[2], Y Dedkov[3] and K Horn[1]

[1]Fritz-Haber Institute of the Max-Planck Society, Germany, [2]University of L'Aquila, Italy, [3]Specs Surface Science GmbH, Germany

Graphene adsorbed on transition metals has become a widely studied topic, since it shows promises as a single molecule gas sensor [1], as a possible spin filter [2,3] or as a step in the preparation of graphene on insulators [4]. Here we present adsorption studies of water and ammonia on graphene/Ni(111) and graphene/Ir(111), a strongly and weakly bonded graphene layer, respectively, using near edge x-ray absorption fine structure (NEXAFS) and photoelectron spectroscopy (PES). NEXAFS from graphene is unique since we can study the adsorption-induced changes in the adsorbate *and the substrate* when probing the substrate carbon K absorption edge, because for graphene the substrate information is not masked by bulk contributions. Apart from the adsorbate-related nitrogen K and oxygen K edges, we observe features in the carbon K edge NEXAFS that are specific to the adsorbed species. Moreover, we find that the interaction of water and ammonia with the graphene surface is enhanced by going from weakly bonded graphene on Ir(111) to strongly bonded graphene on Ni(111). This finding clearly reflects the relative bonding strength of graphene to the supporting metal, as suggested in a recent theoretical study which predicts that a strong graphene-metal bond enhances the interaction of graphene with adsorbed water [5].

[1] Schedin *et al., Nat Mater* 6 (2007) 652.
[2] Karpan *et al., Phys. Rev. Lett.* 99 (2007) 176602.
[3] Karpan *et al., Phys. Rev. B* 78 (2008) 195419.
[4] Bae *et al., Nature Nanotechnology* 5 (2010) 574.
[5] Li *et al. Phys. Rev. B* 85 (2012) 085425.

Reactions on surfaces 6

Adsorption of Se, Na, and O on the molybdenum back contact of CIGS solar cells: a density functional study

G Roma

CEA-Saclay, France and Uni-Mainz, Germany

Thin film solar cells based on copper/indium/gallium/selenide chalcopyrite semiconductors as light absorbers (known as CIGS) are rapidly growing in the market. Further optimisation of their efficiency and cost is necessary and should be possible, but experimental approaches based on trial and error are lengthy and expensive. CIGS solar cells are made by stacking several layers of different materials, all of which play an important role.

It is known that the role of sodium impurities, typically provided by the glass substrate, are beneficial for the performance of the device, but the mechanisms by which this happens are not clear. One proposal has been that Na would catalyse the formation of $MoSe_2$ at the interface between the molybdenum back contact and the CIGS absorber[1]. In this respect the effect of sodium on the adsorption of CIGS elements during deposition could be crucial [2]. The presence of oxygen in the process has also to be taken into account.

We used Density Functional Theory to investigate the basic energetics of Se, Na, and O adsorption on the Mo<110> surface. We determined adsorption energies at various adsorption sites at low and high coverage and we discuss, on this basis, the influence of sodium on Se mobility and the possible mechanisms driving the formation of a $MoSe_2$ layer.

[1] R. Caballero et al., Appl. Phys. Lett. 96, 092104 (2010).
[2] D. Braunger, et al. Thin Solid Films 361-362,161 (2000).

Collision dynamics for the interaction of oxygen atoms and molecules on a silica surface

M Rutigliano[1], C Zazza[2], S Orlandini[1], N Sanna[2], V Barone[3] and M Cacciatore[1]

[1]CNR-IMIP, Italy, [2]CASPUR, Italy, [3]Scuola Normale Superiore di Pisa, Italy

Reactive and non-reactive processes due to the interaction of oxygen atoms and molecules with silica and silica-based materials are of great importance both for the chemistry at the gas-surface interlayer or in the bulk of the dissociated gas of various laboratories and natural oxygen plasma systems. Of particular interest is the dynamics and energetics of O atom recombination at surface. This reaction is, in fact, exothermic so that part of the exothermic energy can be shared among the internal degrees of freedom of the formed O_2 molecules while the remaining part is transferred to the silica surface as heat flux. The energy shearing mechanism depends on the catalytic activity of the silica substrate that controls the dynamics of various chemical-physics processes involving O and O_2 at the surface.

In this contribution we focus on the dynamics of: 1) O atoms adsorption; 2) O atoms recombination, via Eley-Rideal mechanism; 3) O_2 molecule dissociation and deactivation. We performed Molecular Dynamics calculations using the accurate Potential Energy Surface for the interaction of O, O_2 with the silica substrate determined by electronic structure calculations in Ref.[1]. The semiclassical collisional method [2] is applied to describe the dynamics of the nuclear motions of the atoms/molecules over the calculated potential energy surface.

[1] Rutigliano M., Zazza C., Sanna N., Pieretti A., Mancini G., Barone V. and Cacciatore M. J. Phys. Chem. A 2009, 113, 15366.
[2] Billing G. D., Dynamics of Molecule Surface Interactions, John Wiley&Sons, NY, 2000; Cacciatore M. and Billing G.D. Surf.Sci. 1990, 232, 35.

Internal detection and enhancement of chemiluminescence during chlorination of potassium films

H Nienhaus, U Hagemann, D Krix and F Becker

University of Duisburg-Essen, Germany

The interaction of halogen gas molecules with alkali metal surfaces results in the emission of photons. This phenomenon reveals the strong non-adiabatic character of the chemical energy dissipation with this type of reactions. It is somehow surprising as at metal surfaces chemiluminescence is typically quenched. We investigate the reaction of chlorine with potassium films applying an internal light detection scheme. Thin potassium layers are deposited on Ag/*p*-Si(111) Schottky photodiodes with silver film thicknesses well below 200nm. The alkali film is exposed to chlorine at 120K inducing an internal photocurrent. The time evolution of the current can be fully described by the reaction kinetics. At low coverages it is governed by second-order adsorption at defect and terrace sites. After forming a top chloride layer, field-assisted diffusion of potassium atoms from the bulk to the surface is dominating and leads to a photocurrent in the diode exhibiting the typical logarithmic growth law. The extent of bulk chlorination is monitored by photoelectron spectroscopy (XPS) as well. By varying the silver film thickness of the Schottky diode between 10 and 200nm the photocurrent yield shows a pronounced maximum at a thickness of around 50nm. We attribute the enhancement of the current signal to a coupling of the near electric field to silver plasmons resulting in a metal-induced enhancement of the chemiluminescence. The coupling strength changes with the roughness of the metal films controlled by the film thickness.

Structure and water dissociation activity of nano-scaled TiO_2/Pt(111) polymorphs

L Gavioli[1], C Emanuele[1], L Artiglia[2], G Andrea Rizzi[2], S Agnoli[2] and G Granozzi[2]

[1]Università Cattolica, Italy, [2]Università degli studi di Padova, Italy

Ultrathin TiO_2 films recently emerged versus their bulk counterparts, as strategic route to systems where morphology could play a role to enhance photocatalytic and water splitting (WS) activity.[1,2]

We comparatively study for the first time the reactivity towards water of various polymorphs surfaces in the form of stoichiometric ultrathin TiO_2/Pt(111) films, by several in-situ surface science tools: STM, LEED and X-ray absorption spectroscopy (XAS) for the film structure, temperature programmed desorption (TPD) on isotopic labelled TiO_2 films grown in $^{18}O_2$ environment to probe WS activity.

Different TiO_2 polymorphs with distinct surface terminations are prepared depending on growth temperature and Ti amount (ML_{eq}). In the 2-10 ML_{eq} range, (001)-TiO_2(B) nanosheets are grown[3] and their activity toward water dissociation is observed herein for the first time.

In the 10 to 20 Ti ML_{eq} range (100)-rutile platelets with a quasi-(1x2) reconstruction are observed. While TPD data reflect a bulk-like (100)-rutile surface behaviour,[4] STM and XAS reveals a more complex situation. Disordered TiO_2 precursor areas coexist with ordered islands, with STM contrast different from the (1x3) microfacet (bond breaking) model of the bulk (100) rutile surface:[5] new (1x3) and (1x6) superlattices are proposed. Moreover, the thick polymorph surface is intrinsically reactive, rather independently from the amount of defects, that depends on post-annealing treatments in O_2 atmosphere.

The possibility to grow rutile-TiO_2 films with (100) termination on substrates with an hexagonal symmetry like Pt(111), opens perspectives in the production of photocatalytic devices on cheaper substrates like sapphire (0001).[6]

[1] W. Li et al. J. Phys. Chem. C 2008, 112, 20539.
[2] X. Chen et al. Chem. Rev. 2007, 107, 2891.
[3] A. Vittadini et al. ChemPhysChem 2010, 11, 1550.

[4] M.A. Henderson Langmuir 1996, 12, 5093.
[5] U. Diebold Surf. Sci. Rep. 2003, 48, 53.
[6] S. Chen J. Vac. Sci. Technol. A 1993, 11, 2419.

(invited) Size dependence of surface, interface, and field state properties on metallic and insulating islands

K Morgenstern

Ruhr-Universität Bochum, Germany

The electrostatic potential of a surface has important consequences for e.g. its reactivity. A sensitive method to determine the surface's electrostatic potential is the measurement of surface derived state, e.g. surface states or image potential states. We investigated size-dependent changes to unoccupied states at surfaces due to the presence of nano-sized islands on noble metal surfaces by low-temperature scanning tunneling spectroscopy (STS) and mapping.

In the first part of this talk, I will discuss the interface state between NaCl bilayer islands and Ag(111) with respect to its onset and intensity for islands of sizes in the range of a few ten nanometers. Apart from size-dependent changes to the onset energy of this state, we discuss size-dependent changes to its effective mass.

In the second part of this talk I will discuss the field states above an alloyed surface created by deposition of Cu onto Ag(100) at room temperature with respect to their energy and life time in the range of a few nanometers. A transition region between 4 nm^2 and 7 nm^2 is identified below which there are remarkable changes in the position and width of the field states. Our results give spatially resolved information about the local variation in electrostatic potential

Lost bistability: how preferential surface stabilization can prevent molecular switching at metal surfaces

R J Maurer and K Reuter

Technical University Munich, Germany

Reversibly switching surface adsorbed functional molecules by external stimuli is a main ingredient for their possible application in future nanotechnological devices. Unfortunately, the presence of the surface introduces changes to the electronic structure of molecular switches that drastically alter or even inhibit isomerization mechanisms. Recent investigations have especially focused on a chemical design of molecular switches where strong coupling of the photochromic moiety to the surface is avoided. In this work we show that a mere focus on decoupling the stable states from the surface is not enough to successfully carry over the gasphase isomerization behaviour to the surface mounted system. We use dispersion-corrected density-functional theory to compute energy profiles of commonly studied isomerization mechanisms for the prototypical switch azobenzene adsorbed on a Ag(111) surface and analyze the electronic structure along the way. We find that surface adsorption strongly reduces the ground state barrier separating the two minima and at the same time destabilizes the metastable state, leading to an effective loss of bistability. Changing the underlying surface to Au(111), a small barrier is reestablished, but not without further relative destabilization of the cis state. These findings suggest that future chemical design of functional molecules must achieve a balanced interaction of all molecular geometries involved in the isomerization process with the surface and especially prevent overly strong stabilization of transition states.

Epitaxial growth of ultra-thin Fe-Si layers on Si(111): determination by STM, STS and XPD of the path between different metastable phases.

G Garreau, I Maafa, S Hajjar and C Pirri

Université de Haute-Alsace, France

Iron silicide growth on silicon has attracted a lot of interest in the last 2 decades due to its potential for technological applications as well as the remarkably rich variety of phases that are exciting to investigate from a fundamental point of view. Indeed, besides the bulk stable semiconducting b-FeSi$_2$, metastable Fe silicides have been epitaxially grown on Si(111). In particular, typical phases grow with cubic CsCl-type FeSi$_x$ structure in which randomly distributed Fe vacancies are progressively formed when the stoichiometry evolves from FeSi to FeSi$_2$ In the ultrathin regime (d_{Fe}< 3 ML), a German team [1] and our group [2] found a new striking phase of c(4x8) periodicity above 500°C. Although a structural model could be proposed in line with STM and STS analysis [1,3], Sugimoto et al [4] suggested, from NC-AFM measurements, that the structure of this phase has to be reinvestigated. The major problem so far was the heterogeneous growth in the ultrathin regime, which prevents the structural investigations with macroscopic analysis tools such as XRD or XPD. Indeed, the surface exhibits several phases (up to 6) that show different atomic contrast signatures on STM images.

STM, STS and XPD studies have been performed by varying the nominal Fe coverage and three kinetic parameters: the annealing temperature (300°C < Ta< 700°C), the annealing time and annealing procedure (either step by step up to Ta or directly to Ta). We will show that it is possible to grow by SPE each of these 6 phases separately on vicinal Si surfaces. By selecting each phase, we will i) show that XPD confirms the model of the c(4x8) proposed in references 1 and 3, ii) show with STM a kinetically limited path between the 6 phases, iii) demonstrate that these distinct phases are derived from the CsCl structure. Another striking result is that the long range ordering of the defects responsible of the p(1x1) → c(4x8) ordering process upon annealing is not limited to only one film thickness (d_{Fe} ~1.5 ML) as previously observed. Nevertheless it is localized right at the Si/silicide interface, which suggests that this interface is the same for all metastable phases.

[1] M. Krause et al, PRB 68, 125306 (2003).
[2] S. Hajjar et al, PRB 68, 033302 (2003).
[3] G. Garreau et al, PRB 71, 193308 (2005)
[4] Y. Sugimoto et al, Nanotechnology 18, 084012 (2007).

Magnetism 6

(invited) Magnetism and structure of single atom adsorption complexes

H Brune

École Polytechnique Fédérale de Lausanne, Switzerland

We show STM spin-excitation spectroscopy (SES) and X-ray magnetic circular dichroism (XMCD) measurements taken out on individual magnetic atoms adsorbed on different substrates, such as graphene, hexagonal boron nitride (h-BN), copper nitride, and close-packed single crystal metal surfaces. On each of the substrates, the magnetic atom creates an adsorption complex with different hybridization, induced moment, crystal field, and structure. We show how these parameters influence the overall magnetic moments and magneto-crystalline anisotropies. Unexpectedly, magnetic impurities on graphene have anisotropies approaching the giant value of Co/Pt(111). For several transition metal atoms on h-BN/Rh(111) we find bi-stable adsorption states implying structural rearrangements over 60 h-BN unit cells and thus highlighting the role of the sp^2-monolayer substrate bond.

Single molecule memory in spin-crossover complexes

T Miyamachi[1], M Gruber[2], V Davesne[2], E Beaurepaire[2] and W Wulfhekel[1]

[1]Karlsruher Institut für Technologie (KIT), Germany, [2]Institute of Physics and Chemistry of Materials of Strasbourg (IPCMS), Germany

A nano-scale molecular switch conventionally is based on a conductance change by external stimuli. A spin-crossover (SCO) molecule is promising candidate to additionally attach spin switching functionality to the molecular switch due to its switchable nature between a high-spin (HS) state and a low-spin (LS) state. Controlling charge and spin of a single molecule is the key concept to realize molecular spintronics devices. We show scanning tunneling microscopy (STM) study of individual SCO molecules, $Fe(phen)_2(NCS)_2$ (phen = 1,10-phenanthroline) directly anchored on surfaces. When the molecules are adsorbed on a metallic Cu(100) surface, two different configurations of the molecule were found. Spectroscopic measurements revealed that one of the configurations shows a Kondo resonance but the other the absence, indicating the coexistence of HS and LS states. However, a strong coupling of the NCS-groups to the surface prohibits the molecule to switch its spin states. Spin state switching of the molecule has been achieved by introducing thin insulating CuN layer, which considerably reduces the interaction with the surface. Injecting tunneling electrons with a tip of STM changes the configuration of the molecules between two states, resulting in on (HS-state) and off (LS-state) of a Kondo resonance accompanied with high and low conductance states. Real time traces of the tunneling current demonstrate reversible and deterministic switching behaviors of the molecules. The observed robust memory effect gives a perspective to future molecular spintronics devices with the smallest unit.

Kondo effect of all-organic radical spin chains

S Mullegger, M Rashidi, M Fattinger and R Koch

Johannes Kepler University, Austria

The competition between screening of local spins and magnetic interactions of neighbouring spins determines many of the electronic and magnetic properties of dilute magnetic systems. We report on low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) experiments performed on linear chains of surface-supported all-organic spin-1/2 radicals. The spin chains are prepared by self-assembly of stable *sp* magnetic radicals on a single-crystal metal surface under ultrahigh vacuum conditions. Below about 50 K the chains exhibit many of the characteristic properties of the Kondo effect observed by STM-based electron transport experiments at the atomic scale. Moreover, we find strong evidence for a parallel alignment of neighbouring spins within the chains mediated by the electron gas of the supporting metal substrate. Our model system helps to understand coupled spin clusters with an impact on the development of molecular-based magnetic logic applications for future spin- and molecular electronics.

Inelastic spin excitations in STM from first principles calculations

M Persson[1], M Paulsson[2], C Canali[2], I Rungger[3] and S Sanvito[3]

[1]University of Liverpool, UK, [2]Linnaeus University, Sweden, [3]Trinity College Dublin, Ireland

A breakthrough in the characterization and manipulation of localized spins on the atomic scale has been the ability to carry out inelastic electron tunneling from spin excitations in a scanning tunneling microscopy (STM) junction [1-4]. Using a non-magnetic tip, they were able to measure the spin excitation energies and IET signals of localized spins in adsorbed magnetic atoms and molecules, whereas using the spin-polarized current from a magnetic tip, they were able to manipulate the adsorbate spins by pumping into a high spin state at higher electron currents. The observed IET spectra were rationalized successfully in terms of a model spin Hamiltonian incorporating Zeemann splitting, magneto crystalline anisotropy and spin-spin interactions, and phenomenological spin-matrix elements. However, such an analysis cannot address any material-specic parameters such as the magnitude of the inelastic signal relative to the elastic signal, the lateral spatial dependence of the inelastic signal, the spin-pumping parameter and spin relaxation times. We have extended a recent theory of IET from localized spin excitations in the impulsive approximation [4] to transport through a molecule with non-magnetic or magnetic leads. Using an implementation of this theory in the TransSIESTA and GPAW code, we are carrying out calculations of the inelastic electron coupling and tunneling from spin-excitations in Mn, Co and Fe adatoms on a c(2x2)N-Cu(100) surface. The results from these calculations should be able to address the adsorption site dependence of the IET signal, the spin-pumping parameter and spin relaxation times.

[1] C. F Hirjibehedin, C. P. Lutz, and A. J. Heinrich, Science 312, 1021 (2006).
[2] C. F. Hirjebehedin et al., Science 317, 1199 (2007).
[3] S. Loth et al., Nature Physics 6, 340 (2010).
[4] M. Persson, Phys. Rev. Lett. 103, 050801 (2009).

Magnetic phase transitions in dipolar gases in optical lattices

Y Sherkunov, V Cheianov and V Falko

Lancaster University, UK

A recent breakthrough in the cooling of dipolar gases in optical lattices, following a decade of intensive research, has opened a door into the earlier inaccessible many-body physics of lattice systems with anisotropic long-range interaction.

In this work we analyze theoretically a series of magnetic phase transitions in a classical dipolar gas in deep (square and triangular) optical lattices obtained from bipartite monolayer lattices by vertical separation, z, of the two sublattices.

We find that, upon the variation of z, each system experiences a sequence of easy-plane magnetically ordered phases separated by incommensurate spin-wave states, which could be detected with the help of Bragg diffraction of light.

Selective control of spins in a supramolecular 2D network by a chemical stimulus

C Wäckerlin[1], J Nowakowski[1], M Jäggi[2], D Siewert[1], J Girovsky[1], T Hählen[1], S-X Liu[2], A Kleibert[1], P M Oppeneer[3], F Nolting[1], S Decurtins[2], T A Jung[2] and N Ballav[4]

[1]Paul Scherrer Institut, Switzerland, [2]Universität Bern, Germany, [3]Uppsala University, Sweden, [4]Indian Institute of Science Education and Research (IISER), India

Spin-bearing transition metal complexes assembled on ferromagnetic substrates [1] offer a unique platform to fabricate metal-organic interfaces with potential applications in organic spintronics. We use a bottom-up approach to fabricate highly ordered bi-molecular 2D layers [2]. The building-blocks are functionalized to direct the self-assembly and to form a supramolecular structure as evidenced by scanning tunneling microscopy (STM).

Furthermore, the electronic and magnetic properties of the supramolecular 2D layer are programmed by the choice of the central transition metal ion, as demonstrated by X-ray absorption (XAS) and X-ray magnetic circular dichroism (XMCD) spectroscopy. An additional chemical stimulus (c.f. [3]) is used to selectively and reversibly control the magnetic properties of this engineered, bi-molecular metal-organic interface.

[1] A. Scheybal, T. Ramsvik, R. Bertschinger, M. Putero, F. Nolting, and T. A. Jung. “Induced Magnetic Ordering in a Molecular Monolayer.” Chemical Physics Letters 411, 214-220 (2005)
[2] S. De Feyter, and F. C. De Schryver. “Two-dimensional Supramolecular Self-assembly Probed by Scanning Tunneling Microscopy.” Chemical Society Reviews 32, 139-150 (2003)
[3] C. Wäckerlin, D. Chylarecka, A. Kleibert, K. Müller, C. Iacovita, F. Nolting, T. A. Jung, and N. Ballav. “Controlling Spins in Adsorbed Molecules by a Chemical Switch.” Nature Communications 1:61 (2010)

Spatially mapping the Kondo resonance across a magnetic molecule by scanning tunneling spectroscopy

R Ohmann, J Meyer, A Nickel, C Toher, F Moresco and G Cuniberti

TU Dresden, Germany

On metal surfaces a magnetic impurity such as a cobalt atom leads to an electronic feature at the Fermi level known as the Kondo resonance. This resonance is caused by the screening of the magnetic spin of the impurity by the conduction band electrons of the supporting metal surface. Measurements with scanning tunneling spectroscopy show a peculiar line shape at the Fermi level. The spectra are reproduced by a Fano line shape, with fitting parameters such as the width and the form factor q. For atomic impurities it has been shown that the form factor q decays with radial symmetry around an impurity. Here, we show by spatially mapping the Kondo resonance of a Co atom embedded in an aza-BODIPY molecule adsorbed on Ag(100), that the form factor q does not decay with radial symmetry, but reveals an asymmetry. We ascribe this spatial asymmetry to the specific coupling of the Co atom with the surrounding asymmetrically located nitrogen atoms of the Co-aza-BODIPY complex. To confirm that the peak observed at the Fermi level on this metal-organic complex is indeed caused by the Kondo effect, we measured the temperature dependence of its width. This shows a characteristic behavior, from which we deduce a Kondo temperature of 90 K for this particular complex.

Thermostats in Atomic Spin Dynamics

P Thibaudeau and D Beaujouan

CEA, France

The use of lower than femtosecond laser sources has pushed limits down to time scale where the physical processes underlying the response of the magnetization on this very short time is complicated and far from being understood. This involves the out of equilibrium interaction of more than spins together including electronic and lattice excitations. Such extreme conditions suggest that the magnetic relaxation processes, occurring on this time, may be remarkably different from those typical for dynamics at longer time scales.

To get insights, when isothermal ensembles with a constant number of spins are considered, two methods are commonly reported to describe finite temperature effects for the coupling between classical particles and spins: the stochastic and the deterministic methods in which their corresponding merits are discussed. One shows that the temperature dependence of magnetic properties of nano materials is demonstrated by a dynamical system composed of interacting vector spins coupled together and additional friction variables. A set of coupled variables is formed according to the conservation of the extended phase space probability. The whole system is integrated simultaneously in time domain following the Baker-Campbell-Hausdorf formula for each evolution operators. A spin temperature expression is found and followed in time. The analysis of the time behavior of the space-average magnetization is performed and compared to conventional stochastic spin dynamics. To make the deterministic spin dynamics more ergodic, an increase of the size of the phase space is formulated by means of a chain of thermostats. Analogies are formulated by comparison with an extended Miyazaki-Seki multi-spins dynamics and are investigated.

Low temperature physics 3

Effect of correlated disorder on thermodynamic properties of a p-wave superfluid

I Fomin and E Surovtsev

P.L. Kapitza Institute for Physical Problems, Russia

Using a high porosity silica aerogel filled with the superfluid 3He as an example we consider effect of structural correlations of pair-breaking impurities on a temperature dependence of the square of the absolute value of the average order parameter ψ^2 of a Fermi superfluid. With respect to the superfluid silica aerogel is a structure intermediate between the system of standard impurities and of a porous media. Diameter of the silica balls, forming aerogel d≈3 nm is much smaller than the correlation length ξ_0 of the superfluid 3He, but the radius of structural correlations in aerogel R≈50 nm is comparable with ξ_0. We assume that structural fluctuations of correlated impurities can be treated as a perturbation. This is justified if the ratio $R^2 / l\xi_0$, where l is the mean free path of quasi-particles, is small. We show that due to the correlations the temperature dependence of ψ^2on $(T_c - T)$ deviates from linear in a vicinity of the transition temperature T_c. In a principal order on $R^2 / l\xi_0$ the deviation is determined by the structure factor of aerogel. Similar deviations in the vicinity of T_c will exhibit directly observable physical quantities, such as the superfluid density and the shift of the NMR frequency. For a realistic correlation function satisfactory agreement of the calculated NMR frequency shift with the experimental data is achieved for both superfluid phases of 3He.

Bose-Einstein condensation of magnons in rotating superfluid ^{3}He-B

P Heikkinen[1], S Autti[1], Y Bunkov[2], V Eltsov[1], J Hosio[1], P Hunger[2], M Krusius[1] and G Volovik[1]

[1]Aalto University, Finland, [2]Institute Neel, CNRS, France

In superfluid ^{3}He-B magnon excitations may spontaneously form a coherent state where the magnetization processes with uniform phase in a large sample volume in an external field. These coherent states are interpreted as Bose-Einstein condensation of magnons.

In our experiments at temperatures below 0.2 T_c a 3-dimensional potential trap for magnons is formed in the axially symmetric order-parameter texture of ^{3}He-B with additional minimum in the polarizing magnetic field. Using continuous-wave NMR techniques we can populate either the ground state or different excited levels of the trap with magnons. Owing to the interaction of magnons with the texture, the profile of the trap can be changed from harmonic to a box with impenetrable walls. This is the first experimental example of BEC in a box.

Long lifetime of the magnon condensates after switching off the pumping proves the formation of BEC also at the excited levels for the first time. At the lowest temperatures, when the density of thermal excitations vanishes exponentially, the lifetime rapidly increases. This makes magnon-BEC a sensitive probe for additional relaxation sources, for example, connected to Majorana fermionic states both on the surfaces of ^{3}He-B and in the cores of the quantized vortices.

Our measurements in equilibrium rotation show the relaxation rate which has two contributions: one with exponential temperature dependence from bulk quasiparticles and another approximately temperature-independent contribution, which is proportional to vortex density. Whether the latter part is associated with the vortex-core-bound fermionic states remains to be established. Measurements with the magnon condensates close to free surface indicate coupling of mechanical oscillations of the surface to magnetic relaxation of the condensates. Simultaneously quantized vortices are found to significantly damp surface oscillations.

NMR Identification of Possible One-Dimensional Behaviour of Helium-3Nanopores

B Yager[1], J Nyeki[1], A Casey[1], B P Cowan[1], C P Lusher[1], J Saunders[1], D Drung[2] and T Schurig[2]

[1]Royal Holloway University of London, UK, [2]Physikalisch-Technische Bundesanstalt Berlin, Germany

^{3}He confined in mesoporous media is a candidate system for the observation of one-dimensional Fermi behaviour at low temperatures. We have made thermodynamic and NMR relaxation time measurements of ^{3}He adsorbed in the one-dimensional 23 Å pores of zeolite MCM-41 down to 1.5 K.

Two systems have been studied, the first a multilayer isotopically pure ^{3}He film and the second where 0.01 monolayer of ^{3}He was added to a preplating monolayer of ^{4}He. The broadband NMR spectrometer with SQUID detection allowed the frequency and temperature dependences of the relaxation times to be measured.

The $T_1 \rightarrow \omega^{1/2}$ behaviour observed in the mixtures film has been attributed to effective 1D motion. For the isotopically pure ^{3}He measurement below monolayer the relaxation times were consistent with two-dimensional film behaviour exhibiting quantum tunnelling and thermally activated motion. At higher coverages the relaxation times could be analysed as the sum of two exponentials which we have attributed to relaxation times in the first and second layers. The behaviour of the second layer is consistent with mixtures film measurement where all of the ^{3}He is expected to be in the second layer.

Macroscopic bundles of vortex rings in superfluid helium

D Wacks and C Barenghi

Newcastle University, UK

It is well known that two co-axial vortex rings can leap-frog about each other. By direct numerical simulation, we show that in superfluid helium the effect can be generalised to a large number of vortex rings, which form a stable bundle. The bundle can be shown to travel a significant distance compared to its diameter. We also discuss the effect of friction at non-zero temperatures, and show how in this case the presence of normal fluid rotation is necessary for the stability of the bundle.

(invited) Dynamics of quantized vortices in rotating superfluid ^{3}He-B in the zero-temperature limit

M Krusius[1], V E Eltsov[1], J J Hosio[1], P J Heikkinen[1], R Hanninen[1], V L'vov[2], J Makinen[1] and G E Volovik[1]

[1]Aalto University, Finland, [2]Weizmann Institute of Science, Israel

It has been believed that vortex motion in superfluids is turbulent, but perhaps non-dissipative, in the limit $T \rightarrow 0$. This question can be studied in ^{3}He-B at microkelvin temperatures in smooth-walled cylindrical containers, where the influence of surface pinning can be neglected. The vortices are monitored with NMR techniques or with vibrating mechanical oscillators, by making use of Andreev reflection of quasiparticle excitations from the flow field of the vortices. The basic measurement is the response to a rapid change in rotation velocity, called spin up or spin down of the superfluid component. Vortices experience two bulk-volume forces, the Magnus force from the flow field of the superfluid component and the mutual-friction force from the interaction with the normal component. Towards low temperatures, the latter vanishes exponentially so that laminar vortex flow is expected to be easily destabilized, leading to reconnections among vortices and to the formation of a turbulent vortex tangle.

It is found that in undisturbed axially symmetric flow, spin down in the bulk volume is laminar at least to below 0.2 T_c, while deviations, such as solid obstacles or the presence of surface friction, cause the response to become turbulent. A steady state of turbulence can be studied by monitoring spin up at constant rotation when a vortex front propagates axially along the long rotating cylinder. Reconnections and turbulence are then concentrated in the front, owing to the different rotation velocities of the front and the trailing vortex bundle behind it. From such studies one can compare dissipation in laminar and turbulent vortex flow. It is found that large temperature-independent dissipation is observed in the limit T → 0, when vortex reconnections are involved.

Quantum Turbulence in Superfluid ^{3}He-B at Ultra Low Temperatures

V Tsepelin[1], D I Bradley[1], S N Fisher[1], A M Guénault[1], R P Haley[1], M Jackson[2], G R Pickett[1] and D Potts[1]

[1]Lancaster University, UK, [2]CNRS, France

We measure the properties of quantum turbulence, a tangle of quantised vortex lines, in superfluid ^{3}He-B in the low temperature limit, where there is negligible normal fluid and no associated viscosity. These are the simplest conditions to study pure quantum turbulence, and such studies might eventually lead to a better understanding of turbulence in general. We use a vibrating grid resonator to produce ballistic vortex rings at low grid velocities, or a vortex tangle at higher velocities. Our measurements show evidence for the development of turbulence via the entanglement of vortex rings. At low temperatures the kinetic energy contained in the turbulent flow greatly exceeds the thermal energy carried by ballistic quasiparticles. This allows us to directly measure the energy released by the decaying turbulence using bolometric techniques. We find that the decay of turbulence is remarkably similar to that expected for the decay of turbulence in a classical fluid. We discuss new developments and recent results.

Rotating quantum turbulence in superfluid ^{4}He in the T = 0 limit

P Walmsley and A Golov

University of Manchester, UK

Observations of quantum turbulence in pure superfluid ^{4}He in a container rotating at angular velocity Ω_0 are reported. New techniques of large-scale forcing (rotational oscillations of the cubic container at frequency ω and amplitude $\Delta\Omega$) and detecting (monitoring ion transport along the axis of rotation) turbulence were implemented. With increasing the amplitude of forcing, three states of vortex lines near the rotational axis were observed. In the first one, from 0 to $\Delta\Omega_{c1}$, the rectilinear vortex lines are perturbed but not reconnecting yet. In the second one, between $\Delta\Omega_{c1}$ and $\Delta\Omega_{c2}$, a boundary layer of vortex tangle near the axial walls coexists with perturbed rectilinear vortex lines. Above $\Delta\Omega_{c2}$ a bulk vortex tangle fills the cell. The critical amplitudes follow the relations $3\Delta\Omega_{c1} \approx \Delta\Omega_{c2}$ proportional to $(\Omega_{0/}\omega)^{1/2}$. Above $\Delta\Omega_{c2}$, the vortex line length increases rapidly. Resonances of inertial waves are observed in both laminar and turbulent states.

Liquids and liquid interfaces 2

(invited) Water on surfaces: structure, binding and reactivity

P Cabrera-Sanfelix

Donostia International Physics Center (DIPC), Spain

Most surfaces are covered by a thin layer of water under ambient conditions. In spite of its importance in biology, material sciences and chemistry, many of the properties and growth of this wetting are not fully understood yet. From the environmental point of view, the molecular level investigation of the water adsorption on ionic and carbonaceous substrates is fundamental to determine the microscopic behaviour of certain aerosols and to estimate their chemical response under different atmospheric gases. Density functional theory (DFT) calculations have been applied to study the most favourable water adsorption geometry at monolayer and at the submonolayer coverage on NaCl(100).[1, 2] The first steps of the deliquescence, occurring at the monolayer regime, are characterized by the spontaneous emergence of chlorine ions on top of the water layer.[3] Graphene represents a good surface science model to reproduce the water structure and interaction with carbonaceous particles. By DFT we show the enhanced water reactivity on defective graphene compared with pristine graphene.[4, 5]

Comprehending water wetting on metal substrates is basic to understand phenomena such as corrosion and surface reactivity. Self-organization of water on metallic surfaces occurs well by molecules clustering in a 3D-phase, by wetting the surface following a well-ordered 2D-adlayer or even, by undergoing partial dissociation within the water layer. A review of water wetting on different substrates such as Cu(110), Ru(0001) and O(2x1)/Ru(0001) will discuss the competition of self-assembled structures of different dimensionality, possible water dissociation, water induced surface reconstructions and substrate induced cooperative effects on water-water interactions.[6-9]

[1] P. Cabrera-Sanfelix, A. Arnau, G. R. Darling, et al., Journal of Physical chemistry B 110, 24559 (2006).
[2] P. Cabrera-Sanfelix, A. Arnau, G. R. Darling, et al., Journal of Chemical Physics 126, 214707 (2007).
[3] P. Cabrera-Sanfelix, D. Sanchez-Portal, A. Verdaguer, et al., Journal of physical Chemistry C 111, 8000 (2007).
[4] P. Cabrera-Sanfelix and G. R. Darling, Journal of Physical Chemistry C 111, 18258 (2007).
[5] P. Cabrera-Sanfelix, Journal of Physical Chemistry A 113, 493 (2009).
[6] Y. Shi, P. Cabrera-Sanfelix, B.-Y. Choi, et al., (2012, To be published).
[7] P. Cabrera-Sanfelix, A. Arnau, A. Mugarza, et al., Physical Review B 78 (2008).
[8] S. Maier, P. Cabrera-Sanfelix, I. Stass, et al., Physical Review B 82, 075421 (2010).
[9] P. Cabrera-Sanfelix, M. V. Fernandez-Serra, A. Arnau, et al., Physical Review B 82, 125432 (2010).

Unusual acidity of water monolayer on Ru(0001)

H Kang, Y Kim, E-S Moon and S Shin

Seoul National University, South Korea

Understanding the acid-base properties of adsorbed water on solid surfaces is fundamentally important to heterogeneous catalysis, corrosion, and electrochemistry. We studied the acid-base properties of adsorbed water on a Ru(0001) surface, a system which has become a case study example for the interaction of water with metal surfaces. The study shows that the water monolayer on a Ru(0001) surface is anomalously acidic compared to bulk water. The observation was made by conducting ammonia adsorption experiments and various surface spectroscopic measurements for adsorbed water on Ru(0001) at temperature of 80-240 K. The water molecules in the first intact H_2O bilayer spontaneously release a proton to ammonia adsorbates to produce ammonium ions.

Such proton transfer, however, does not occur for H_2O in a thick ice film surface or for a mixed adsorption monolayer comprising H_2O, OH, and H.

Substrates influence on CdS thin films grown by Electrochemical Atomic Layer Epitaxy

F Carla[1], M Innocenti[2], M Luisa Foresti[2], J Drnec[1], O Balmes[1] and R Felici[1]

[1]European Synchrotron Radiation Facility, France, [2]Universita' degli studi di Firenze, Italy

The Electrochemical Atomic Layer Epitaxy (ECALE) represent an attractive method for the production of thin films of semiconductor compounds with high grade of crystallinity. Electrodeposition can be very competitive respect to vapor phase deposition or vacuum methods for several reasons: the low cost, the possibility of room-temperature operation and the control of film composition and thickness.

In the ECALE method a semiconductor film can be formed on the electrode surface by an alternate Underpotential Deposition (UPD) of the elements that form the compound. UPD is a surface-limited phenomenon, so the electrodeposition in UPD conditions is generally limited to one atomic layer. UPD processes are "substrate dependent", thus different structures of the deposited layer should be expected on substrates with different orientation. For this reason it's not clear how and if the substrate orientation may affect the structural order of the film during the growth. Results of the structural and electrochemical characterization of CdS thin films deposited by ECALE on Ag(111), Ag(110), Ag(100) will be presented. Electrochemical experiments demonstrate that the CdS deposition mechanism is consistent with a layer-by-layer growth and the stoichiometric composition correspond to a 1:1 ratio between the elements. The structural characterization performed by Surface X-ray Diffraction revealed a strong influence of the substrate orientation on the film structure and order.

An innovative electrochemical setup for in-situ Surface X-ray diffraction experiment developed at ID03 beamline at European Synchrotron Radiation Facility will be also presented.

Tuning surface wetting via surface templating

A Massey[1], F McBride[1], M Nakamura[2] and A Hodgson[1]

[1]University of Liverpool, UK, [2]Chiba University, Japan

In this study we demonstrate that the structure of water at interfaces may be tuned by surface templating, potentially affording the ability to control surface wetting at the nanoscale. Aqueous interfaces are of fundamental importance to many key technological systems with wetting properties governing nucleation, diffusion and friction at the surface, but our knowledge of the interaction between water and metallic surfaces at the molecular level remains partial. The conventional model of wetting assumed that water must form a surface ice ‘bilayer’ structure, similar to bulk ice (Ih(0001)), for wetting to occur, but it is now known that a variety of different water networks will wet metal surfaces [1]. Recent research has shown the formation of an idealised ice bilayer, akin to the structure of an ice layer in Ih(0001), can be promoted by engineering a suitable surface template [2]. The SnPt(111) $(\sqrt{3} \times \sqrt{3})R30°$ surface alloy forms a buckled surface ideal for formation of a water bilayer with water binding to Sn to form an H-down ice bilayer. Sn also forms a $(\sqrt{3} \times \sqrt{3})R30°$ surface alloy on a variety of transition metals substrates, including Ni(111), Cu(111), Pd(111) and Rh(111) as well as Pt(111). The buckling of the tin surface alloy is dependent on the lattice parameter of the underlying surface [3], increasing as the lattice parameter of the substrate is reduced. Here we report how varying the lateral repeat and local electronic environment of the Sn atoms affects the wetting properties of the surface alloy.

[1] Hodgson A and Haq S 2009 Surf. Sci. Rep. 64 381.
[2] McBride F, Darling G R, Pussi K and Hodgson A 2011 Phys. Rev. Lett. 106 226101.

[3] Li Y D, Voss M R, Swami N, Tsai Y L and Koel B E Phys. Rev. B 56 15982.

Graphene: a protective wetting-transparent coating

J Fraxedas, L López, G Sauthier, J José Segura and A Verdaguer

Centre d' Investigació en Nanociència i Nanotecnologia (CIN2) (CSIC-ICN), Spain

The visualization of water layers adsorbed on surfaces at ambient conditions with probe force microscopies can be achieved either by protecting such layers with graphene layers [1] or by the use of perturbation-free non-contact amplitude-modulation modes at the free air-water interface [2]. In addition to such protective character, graphene coatings are wetting transparent: they do not significantly disrupt the intrinsic wetting behavior of surfaces in absence of hydrogen bonding; only van der Waals interactions involved [3]. Here, we have confined water layers between freshly cleaved $BaF_2(111)$ surfaces, a known water-structuring surface with low lattice mismatch to hexagonal ice [4], and graphene at ambient conditions under different controlled humidity conditions. We observe that (i) water mono- and bilayers are formed upon confinement as observed in contact mode and (ii) water preferentially adsorbs on top of regions of the graphene layers for which ordered layers can be found below, as measured in non-contact amplitude-modulation mode.

[1] K. Xu, P. Cao and J. R. Heath, Science 329, 1188 (2010).
[2] S. Santos, A. Verdaguer, T. Souier, N. H Thomson and M. Chiesa, Nanotechnology 22, 465705 (2011).
[3] J. Rafiee et al. Nature Materials 11, 217 (2012).
[4] M. Cardellach, A. Verdaguer, J. Santiso and J. Fraxedas, J. Chem. Phys. 132, 234708 (2010).

Structure and proton transfer dynamics of the liquid water-ZnO(10-10) interface

G Tocci and A Michaelides

University College London, UK

Despite the widespread interest in proton transfer at liquid water-solid interfaces, a detailed understanding of the dynamics involved in proton transfer is lacking. Studies at well defined solid surfaces provide the opportunity to understand the intimate details of proton transfer, in so-doing revealing insight that may be relevant to other more complicated systems (e.g. fuel cells or bio-membranes). Here, we report first principles molecular dynamics simulations of the liquid water-ZnO(10-10) interface which show that proton transfer occurs on a picosecond time-scale. We first illustrate that the structure of the liquid water film has a pronounced layering shown as oscillations in its density profile. We then investigate the relation between hydrogen bonding and proton transfer. We find that if a water molecule is a hydrogen bond donor it is energetically favourable in the intact state, whereas if it is an acceptor it is favourable in the dissociated state. Analysis of the physical origin of this effect implies that the correlation between hydrogen bonding and proton transfer observed here is likely to be of importance to other water-solid interfaces where proton transfer occurs.

Electron traps at the ice surface

M Bockstedte[1] and A Michl[2]

[1]Universitaet Erlangen-Nuernberg, Germany, [2]TU Hamburg-Harburg, Germany

Water, water clusters and ice possess the fascinating ability to solvate electrons. On the surface of water cluster [1] and thin crystalline ice layers deposited on a metal substrate [2] long-living solvated electron states were observed that derive from pre-existing surface traps. In the experiments [2], the solvated electron state was found to evolve in a thermally activated process characterized by an enhancement of its binding energy. The identification of initial electron-traps provides important insight into the electronic structure of the water surface, ice layers on metals and the dissociative interaction of electrons with adsorbates. The reconstruction of the electron trap during the solvation dynamics is crucial to understand the long lifetime.

Theoretical models [2] based on the bilayer terminated Ih-(0001) surface related such traps to orientational defects. At these traps with low formation energy, the electron attaches to the local dipole moment of dangling OH-groups. Other models suggest surface vacancies with dangling OH-groups [4]. Yet, also more complex surface structures may act as electron traps. In fact, recent high resolution STM-experiments [5] gave evidence for other surface terminations than the bilayer, characterized by hexagon adrows and admolecule superstructures. So far, a conclusive microscopic model of the electron traps at the surface of water structures on metals is not available, in particular as the theoretical description is based on rather approximate methods.

Here we address the electronic structure of the ice surface and candidate electron traps theoretically within the framework of density functional theory and many-body perturbation theory in the G0W0 approximation. While hybrid functionals consistently improve the description of insulator band gaps, the G0W0 approximation furthermore guarantees a proper description of the asymptotic decay of exchange-correlation interaction into the vacuum. This is pivotal for a correct description of the vertical electron affinity of electron traps, which is overestimated by hybrid functionals.

Among the investigated electron traps we identify a hierarchy of traps with increasing vertical electron affinity, ranging from water admolecules and hexagon adrows via clusters of orientational defects to vacancy related traps.

[1] K. R. Siefermann and B. Abel, Angew. Chem. Int. Ed., 50, 5264 (2011).
[2] U. Bovensiepen et al., J. Chem. Phys. C 113, 979 (2009).
[3] V. Buch et al., PNAS 105, 5969 (2008).
[4] A. Hermann et al., J. Phys. cond. matter, 20, 225003 (2008).
[5] M. Mehlhorn and K. Morgenstern, Phys. Rev. Lett. 99, 246101 (2007).

Surface structure 1

(invited) Interaction across metal-organic and heterorganic contacts: Adsorption of organic molecules on noble metal surfaces

C Kumpf

Forschungszentrum Jülich, Germany and Jülich-Aachen Research Alliance (JARA) – Fundamentals of Future Information Technology, Germany

The properties of functional materials and electronic devices are dominated by their surfaces and interfaces. This is particularly true for organic thin films and adsorbate systems as they are frequently used in the field of organic electronics. While recently interfaces between organic layers and metals were investigated intensively, only very few studies focus on the interface between different organic materials.

Model systems in this context are copper-II-phthalocyanine (CuPc) and perylen-tetracarboxylicacid dianhydride (PTCDA) on Ag, Au and Cu(111) surfaces, which we have studied intensively using complementary techniques. The hetero-epitaxial system CuPc/PTCDA [1] is of particular interest since it combines two molecules exhibiting very different structure formation mechanisms: While PTCDA forms well-ordered island on the Ag(111) surface, caused by an attractive intermolecular interaction, CuPc molecules repel each other after adsorption and form dilute phases [2]. I am going to give an overview of recent experiments on these model systems using high resolution low energy electron diffraction (SPA-LEED), photoelectron spectroscopy (PES), x-ray standing waves (XSW) and scanning tunneling microscopy (STM).

[1] B. Stadtmüller et al., Phys. Rev. Lett. 108, 106103 (2012).

[2] C. Stadler et al., Nature Physics 5, 153 (2009); I. Kröger et al., New J. Phys.12, 083038 (2010); B. Stadtmüller et al., Phys. Rev. B83, 085416 (2011).

Chemical identification of atoms in surface alloys with nc-AFM

M Ondracek, P Mutombo, Z Majzik, M Setvin and P Jelinek

Academy of Sciences of the Czech Republic, Czech Republic

Single-atom chemical resolution in scanning-probe microscopies is a long-standing problem, seriously limiting their applications for chemical purposes. Probably the most promising method so far is that of Sugimoto et al. [1], who used a non-contact atomic force microscope (nc-AFM) to distinguish different atoms in a semiconductor surface alloy, based on the maximum of the attractive short-range force measured on the atoms. However, the range of applicability of this method needs to be investigated further.

Here we will discuss two different cases: (i) 1-D metallic chains on Si(100) surface and (ii) metal surface alloys. In the first case, we used a combination of nc-AFM and extensive DFT simulations to distinguish between different chemical species and their chemical state within the atomic chains. In particular, the site-specific atomic force spectroscopy (i.e. measuring the distance dependence of the short-range force at different atomic sites) enabled a reliable distinction between In and Sn atoms. Moreover, it revealed the presence of Si impurities within the 1-D chain, which had been completely omitted in previous STM-based studies. As the second case, we will deal with a theoretical prediction concerning the possibility to distinguish among atoms of platinum-group metals, namely Pt, Pd and Rh, on a surface of their alloy. Our simulations show that all three elements may be distinguished unambiguously provided that the atomic force measurement is supplemented with known hysteresis of the force-distance curves (detected as the dissipation signal in nc-AFM).

[1] Nature 446, pp 64-67 (2007)

Structure and characters of Co-2x2 nanoislands on Ag/Ge(111) surfaces

T-Y Fu, A Tomaszewska and X-L Huang

NTNU, Taiwan

With the use of scanning tunneling microscope (STM) technique we have investigated the evolution of Co-2×2 islands grown on the Ag/Ge(111)surfaces. We have found that the evolution proceeds from formation of compact structures with atomic arrangement which has differences in inner inter-row distances. As the Co-2×2 islands grown to higher and higher due to the greater Co coverage or temperature trigger, the island shape transforms from hexagonal into stripe-like. These behaviors are explained in terms of the predominance of either Co-Co or Co-substrate interaction during the growth, and simple structural models for islands with different type of atomic arrangement are proposed.

(invited) Visualizing the configurations of a molecular switch by means of atomic force microscopy

N Pavlicek

University of Regensburg, Germany

Unambiguously determining configurational changes of individual molecules is challenging in scanning tunnelling microscopy (STM) [1]. This, of course, is because STM probes local density of states as opposed to geometry. Recently, Gross et al. [2] have demonstrated the role of tip-functionalization in atomic force microscopy (AFM) by resolving the chemical structure of pentacene molecules. In such combined STM/AFM setups based on the qPlus sensor [3] the AFM channel enables access to truly complementary information to the STM data.

After an introduction to the topic, investigations of dibenzo[a,h]thianthrene molecules adsorbed on ultrathin layers of NaCl will be presented. These nonplanar molecules exist in two stable adsorption configurations. The STM tip can be used to switch between both configurations by inelastic current. However, only AFM measurements with submolecular resolution directly reveal the configurational change. From AFM data and taking the chirality of the molecules into account, we could unambiguously determine the pathway of the change.

[1] T. A. Jung et al., Nature 386, 696 (1997).
[2] L. Gross et al., Science 325, 1110 (2009).
[3] F. J. Giessibl, Appl. Phys. Lett. 76, 1470 (2000).

Theory and modelling 2

Size dependence of the propulsion velocity for catalytic swimmers

M-H Tu[1] and R Golestanian[2]

[1]University of Sheffield, UK, [2]University of Oxford, UK

Recently the locomotion of Janus particles that asymmetrically catalyse a chemical reaction on the surface to achieve autonomous propulsion is fully characterized both theoretically and experimentally. The results of both the experimental data and the theory demonstrate the propulsion velocity of the Janus particle is inversely proportional to the size at the large size limit, and the 1/R behaviour is expected to saturate for smaller sizes of swimmers. In order to get insight into the mechanism, arbitrary angular patterns with asymmetrical catalyst coated onto the surface of a spherical swimmer have been considered. We also use a diffusion-reaction model and assume that the kinetic route for the chemical reaction is a two-step process to study the effect of size on the propulsion velocity. Compared with Janus particles, our results show the similar behaviours of propulsion velocity for the smaller swimmers. However, the propulsion velocityof spherical swimmers with arbitrary angular patternsof catalyst exhibits decay with $1/R^2$ dependence at the large size limit. The extension of the theoretical model suggests strategies for designing artificial micro-swimmers. Such self-propelled colloids can be used for applications such as drug delivery and to understand the nature of the non-equilibrium phenomenon.

Malliavin Weight Sampling: Computing responses to perturbations in Brownian dynamics simulations

R Allen[1] and P Warren[2]

[1]University of Edinburgh, UK, [2]Unilever R&D Port Sunlight, UK

Responses to external perturbations are often computed as an important signature of a system's underlying physics. Knowing how a system's behaviour changes in response to internal perturbations (e.g. changes in intermolecular potentials) is important in optimising simulation parameters to fit empirical observations or experimental data. However, computing how a system responds to perturbations can be expensive. We present a simple method, Malliavin Weight Sampling, for computing response coefficients to external or internal perturbations without the need to simulate the perturbation explicitly. Our method relies on adding an auxiliary tracking variable to the system dynamics; this variable allows us to sample the derivative of the probability density with respect to the perturbation and hence to compute the sensitivity of an arbitrary function of the coordinates; the method works for equilibrium or nonequilibrium systems. We demonstrate its effectiveness and efficiency for a simple test case as well as for a cluster of interacting particles under shear.

Crystalline structure and vibrational properties of organic ferroelectric croconic acid : an investigation using density functional theory

S Mukhopadhyay, M Gutmann, D Jochym, K Refson and F Fernanndez-Alonso

STFC Rutherford Appleton Laboratory, UK

Croconic Acid ($C_5O_5H_2$) is the first organic molecule which shows room temperature ferroelectricity in its crystalline form [1] . The structure and vibrational properties of this crystal are important to understand its ferroelectric properties. Few structural studies have been done on Croconic Acid in its solid state form using X-ray diffraction [1] only. In this investigation, we employed state-of-the-art calculations based on plane wave pseudo potential density functional theory (DFT) to predict the structure, vibrational and polarizability properties of Croconic acid and compared with in-house experiments.

We investigated structures of Croconic Acid in both centro symmetric, space group Pcam, and non-centrosymmetric, space group $Pca2_1$, form using CASTEP code and Perdew-Burke-Ernerhof generalised gradient approximation (PBE-GGA) in DFT. The experimentally obtained structures were relaxed using BFGS method and the centrosymmetric structure was found to be unstable with respect to the non-centro symmetric structure. The calculated bond lengths were in agreement with neutron diffraction results within 3%. The calculated vibrational spectrum compared well with experimental infrared (IR) and Raman spectroscopic results.

The polarizability of the crystal was identified by the large anisotropy of the Born effective charge tensors [2] associated with the hydrogen ions, which also had directional properties. We predicted that these hydrogen ions had dominant role in the ferroelectric properties of the crystal.

[1] S. Horiouchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, Nature, 463, 789 (2010).
[2] A. Stroppa, D. D. Sante, S. Horiuchi, Y. Tokura, D. Vanderbilt, S. Picozzi, Phys. Rev. B, 84, 014101 (2011).

The influence of hydroxyl and oxygen on the spectral properties of PCBM

I E Brumboiu[1], O Eriksson[1], B Brena[1], A Dzwilewski[2], A Sofia Anselmo[2], K Svensson[2] and E Moons[2]

[1]Uppsala University, Sweden, [2]Karlstad University, Sweden

Organic semiconductors are promising candidates for flexible, portable and light-weight photovoltaic devices with reduced production cost [1, 2]. Phenyl-[6, 6]- C_{60} butyric acid methyl ester (PCBM) [3] is a fullerene derivative widely used as an electron acceptor in organic solar cells [4]. Understanding its electronic structure and spectral properties both from a theoretical and an experimental point of view is of great importance, leading to the possibility of better tuning the photovoltaic devices involving PCBM and making them last longer by finding stabilization strategies [1].

It has been observed that PCBM, similarly to C_{60}, is strongly affected by exposure to light, especially in the presence of oxygen. We believe, therefore, that quite a number of the spectra of PCBM presented in the literature are affected by unintentional light exposure.

In order to determine the causes of the PCBM photodegradation [1, 5, 6], we investigated by means of DFT two of the possible chemical changes in the molecule: the hydroxylation and, respectively, the oxygenation of the PCBM. We report the optimized geometries of several PCBM-OH and PCBM-O structures, as well as the calculated NEXAFS, XPS, Valence Band, Raman and IR spectra of the lowest energy configurations. Experimental data are provided where available for both exposed and unexposed PCBM.

[1] A. Rivaton, S. Chambon, M. Manceau, J.L. Gardette, M. Firon, N. Lemaître, S. Guillerez, S. Cros, Proc. Of SPIE, 7002, 70020I-1, 2008.
[2] S. Cook, H. Ohkita, Y. Kim, J.J. Benson-Smith, D. D.C. Bradley, J. R. Durrant, Chem. Phys. Lett., 445, 276, 2007.
[3] D. S. Germack, C.K. Chan, B.H. Hamadani, L.J. Richter, D.A. Fischer, D.J. Gundlach, D.M. DeLongchamp, Appl. Phys. Lett., 94, 233303-1, 2009.
[4] M. Passos Felicissimo, D. Jarzab, M. Gorgoi, M. Forster, U. Scherf, M.C. Scharber, S. Svensson, P. Rudolf, M.A. Loi, J. Mater. Chem, 19, 4899, 2009.
[5] A. Dzwilewski, T. Wågberg, L. Edman, J. Am. Chem. Soc., 131, 4006, 2009.
[6] M. O. Reese, A.M. Nardes, B.L. Rupert, R.E. Larsen, D.C. Olson, M.T. Lloyd, S.E. Shaheen, D.S. Ginley, G. Rumbles, N. Kapidakis, Adv. Func. Mater., 20, 3476, 2010.

Adsorption of metal free Phthalocyanine and Lutetium-Bis-Phthalocyanine

J Lüder[1], I Biedermane[1], N Shariati[1], N Witkowski[2], C Puglia[1], B Sanyal[1], O Erriksson[1] and B Brena[1]

[1]Uppsala University, Sweden, [2]Université Pierre et Marie Curie, France

Molecular films of organic and metal-organic molecules on metallic and semiconductor surfaces are a field of growing interest since they offer interesting and promising applications in electronic devices such as gas sensors and solar cells. Determining the electronic properties is an important step to understand the adsorption process, surface-molecule interaction and the assembly of the molecular film. Combining experimental results and Density Functional Theory (DFT) calculations, we have studied the adsorption behavior of metal free phthaloycyanine (H2Pc) molecules on the Au(111) surface [1] and of Lutetium-Bis-Phthalocyanine (LuBisPc) molecules on Si(001) surface. For the double decker molecule we have compared thin and thick molecular films. We have modeled photo electron spectroscopy (PES) and near edge x-ray absorption spectroscopy (NEXAFS) for both systems. The theoretical calculations were compared with the experimental results. The electronic states and the adsorption orientation of the molecules with respect to the surface could be determined.

[1] M. N. Shariati[a], J. Lüder, B. Brena, I. Bidermane [a,b], S. Ahmadi[c], E. Göthelid[a], P. Palmgren[a] , B. Sanyal, O. Eriksson, M. N. Piancastelli[a] and C. Puglia, to be submitted.

Break down of one-dimensional free fermion picture on equilibrium crystal shape for sticky steps II: non-universal form of vicinal surface free energy

N Akutsu

Osaka Electro-Communication University, Japan

In the case of vicinal surface with sticky steps, an inhomogeneous structure, including `step droplets'[1,2] which are locally merged steps, is formed at low temperature in equilibrium. The mean size of the step droplets <n>, the mean number of elementary steps merged in a step droplet, increases as the surface slope increases[2]. Due to the step droplets, one-dimensional free fermion or Gruber-Mullins-Pokrovsky-Talapov (GMPT) picture on the vicinal surface breaks down[2].

We derive non-GMPT vicinal surface free energy[2] assuming that <n> depends on the surface slope. Using the non-GMPT vicinal surface free energy, we calculate an equilibrium crystal shape (ECS), which is a shape of a crystal particulate with the least surface free energy, and anomalous shape exponents near (001) facet. We show the slope dependence of <n> by using the Monte Carlo method on a restricted solid-on-solid model with point-contact type step-step attraction (p-RSOS model)[2,3].

[1] N. Akutsu, Y. Akutsu and T. Yamamoto, Phys. Rev. B 67 (2003) 125407.
[2] N. Akutsu, J. Phys.: Condens. Matter 23 (2011) 485004.
[3] N. Akutsu, Appl. Surf. Sci. vol. 256 (2009) 1205; J. Cryst. Growth, 318 (2011), 10.

Multihydrogen complexes in InGaN alloys from a theoretical standpoint

F Filippone[1], G Mattioli[1], G Ciatto[2], E Fonda[2], F Boscherini[3], L Amidani[3], A Polimeni[4], M Capizzi[4] and A A Bonapasta[1]

[1]CNR-ISM Istituto di Struttura della Materia, Italy, [2]synchrotron SOLEIL, France, [3]University of Bologna, Italy, [4]University of Roma "La Sapienza", Italy

InGaN alloys have an enormous potential for application in optoelectronic devices thanks to their direct band gaps spanning the spectrum from infrared to ultraviolet. If Ga-rich alloys are already widely exploited in technology, the same is not true for In-rich ones, that are characterized by a huge unintentional n-type conductivity. Nitrogen vacancies and unintentional impurities, such as oxygen and interstitial hydrogen,[1] have been proposed as possible causes.

In the present study, we have focussed on the hydrogen impurity and performed an extensive Density Functional Theory investigation on the local structure and energetics of isolated H and H complexes in InN, GaN and InGaN alloys. We resorted to Hubbard U corrections in order to reproduce correctly the band gaps of the materials.[2] Our results indicate that H clustering can occur provided that a suitable H concentration is reached during the hydrogenation procedure. In particular, multi-hydrogen complexes involving four H atom surrounding In or Ga atoms can form in InN and InGaN alloys. The structural features of such complexes are in good agreement with N [3] as well as In [4] K-edge EXAFS data. These novel multi-H complexes permit the achievement of quite high H concentrations in InGaN alloys. They can play, therefore, a crucial role for understanding the optical and transport properties of the InGaN alloys.

[1] A. Janotti and C.G. van de Walle, Appl. Phys. Lett. 92, 032104 (2008).
[2] F. Filippone et al., Phys. Rev. Lett. 107, 196401 (2011).
[3] L. Amidani, private communication.
[4] G. Ciatto, private communication.

Atomic scale simulations of α-, γ-, κ- and θ-alumina from a transferable tight-binding variable-charge model

N Salles, R Tetot and E Amzallag

CNRS Université Paris, France

Alumina thin films are used for protection against friction and corrosion, in optical and micro electronic devices and as dielectric to prevent electrical shorting. Al_2O_3 presents a complex polymorphism: the most stable phase, α-Al_2O_3, formed of AlO_6 octahedron and metastable phases, such as γ-, k- or θ-Al_2O_3, containing both AlO_6 octahedron and AlO_4 tetrahedron. The structural and mechanical characteristics of the films depend on the phases formed at the earliest stage of oxidation of aluminium. So, it is of great interest to be able to describe all these structures. In this work we shall present a new transferable variable-charge model [1] aimed at describe heterogeneous environments in oxides. In this model, the metal-oxygen covalent bonding energy is obtained thanks to a tight-binding analytical description [2]: $E_{cov}=-\xi\sqrt{Z}\{(-2-Q_o)(2n_0/m+2+Q_o)\}^{1/2}$, where ξ is the hopping integral between oxygen $2p$ and metal orbitals. Z and Q_o are the coordination number and the oxygen charge respectively, n_0 is the number of coupled electronic states between metal and oxygen sublattices. The equilibrium charges are obtained by a modified QEq formalism [3]. Results on energetic and structural properties of α-, θ-, κ- and γ-alumina as well as for several α-alumina surfaces will be presented. These results will be compared with experimental data and ab initio calculations performed with the CRYSTAL09 code.

[1] A. Hallil, E. Amzallag, S. Landron, R. Tétot, Surf. Sci. 605, 738 (2011).
[2] J. Goniakowski, C. Noguera, Surf. Sci. 319, 81 (1994).
[3] A. K. Rappé, W. A. Goddard III, J. Phys. Chem. 95, 3358 (1991).

Oxides and oxide surfaces 3

Growth of ultrathin aluminium oxide films on the (110) surface of the gamma-Al_4Cu_9 complex metallic alloy

S Le Moal[1], M Wardé[1], J Ledieu[2], L Serkovic[2], M Hérinx[1], M-C de Weerd[2], V Fournée[2] and M-G Barthés-Labrousse[1]

[1]Institut de Chimie Moléculaire et des Matériaux d'Orsay, France, [2]Institut Jean Lamour, France

Complex metallic alloys (CMAs) are intermetallic compounds whose crystallographic structure differs from that of usual alloys. In particular, their unit cell contains from several tens to a few thousands atoms, which are typically arranged into highly symmetric clusters. They are usually considered as stable approximants of quasicrystals. Al-based CMAs offer great opportunities in the field of catalysis, including flexible chemistry thanks to the huge variety of CMA compositions and tuning of d band centre by selection of CMAs composition and structure.

In this work, X-ray Photoelectron Spectroscopy (XPS), Low Energy Electron Diffraction (LEED) and Scanning Tunnelling Microscopy (STM) have been used to investigate the first oxidation stages of the γ-Al_4Cu_9(110) surface. When oxidation is carried out at room temperature (RT), only aluminium is oxidized, copper remaining in the metallic state. The decomposition of the O1s photopeak shows the presence of two different Al-O bonds. No preferential site for oxygen adsorption can be identified from the STM images. At saturation in oxygen, the surface is covered by a uniform disordered aluminium oxide film, 8.5 Å in thickness. A subsequent annealing at 650°C of this disordered oxide layer leads to the formation of crystalline aluminium oxide islands, which exhibit a peculiar rectangular structure (a’=18.2 Å, b’=10.8 Å) called sixton. This sixton structure is similar to that previously reported for ultrathin alumina films grown on various metallic substrates, as for instance NiAl(110) and Ni(111). Its unit cell comprises 92 atoms arranged in an interfacial $Al_{24}O_{28}$ plane and a surface $Al_{16}O_{24}$ plane.

Writing with atoms: Oxygen adatoms on the MoO_2/Mo(110) surface

O Lübben[1], S Krasnikov[1], S Bozhko[2], B Murphy[1] and I Shvets[1]

[1]Trinity College Dublin, Ireland, [2]Russian Academy of Sciences, Russia

Nanoscale writing using oxygen adatoms on the MoO_2/Mo(110) surface is demonstrated by scanning tunneling microscopy (STM). The oxidation of metal surfaces can produce a variety of ordered oxide nanostructures and two-dimensional surface oxides, which are of great significance for heterogeneous catalysis. High-temperature oxidation of the Mo(110) surface results in a strained bulk-like MoO_2(010) ultra-thin film with an O-Mo-O tri-layer structure. Due to the lattice mismatch between the Mo(110) and the MoO_2(010), the latter consists of well-ordered molybdenum oxide nanorows separated by 2.5 nm. The MoO_2(010) structure observed by STM is confirmed by density functional theory calculations. Further oxidation results in perfectly-aligned double rows of oxygen adatoms, imaged by STM as bright protrusions. These adatoms can be removed from the surface in a controlled fashion by the STM tip. Tip movement along the surface can be used for controlled lithography (or nanoscale writing), with a minimum feature size of just 5 nm. By moving the STM tip in a controlled fashion, information can be written, read and erased by applying specific biases between the surface and the tip. Furthermore, oxygen adatoms on the MoO_2/Mo(110) surface can be used to create other oxide nanostructures. As shown by STM, deposition of Fe on the oxygen-rich MoO_2/Mo(110) surface leads to the formation of well-ordered Fe oxide nanowires with a zigzag shape.

(invited) Exploring low dimensional transport in $SrTiO_3$–based heterostructures

C Bell

Stanford University, USA

At low temperatures bulk $SrTiO_3$ is on the border of ferroelectricity, and can be doped to create a low density superconductor with high electron mobility. These fascinating properties have motivated the recent interest in low dimensional $SrTiO_3$ heterostructures. The conductivity at the asymmetrically confined $LaAlO_3/SrTiO_3$ interface [1], and in particular its control with a field effect gate [2, 3], is one example where we can explore novel low dimensional physics. At the same time, studies of symmetrically confined 2D superconductivity and 2D quantum oscillations in Nb:$SrTiO_3$ [4, 5] offer additional control and insights into this fascinating quantum material. I will compare and contrast these two different ways of constraining the electrons.

I will also present data from our collaborative efforts using real space imaging of the superfluid density by scanning SQUID microscopy, which have provided an extremely powerful complementary tool to transport studies, revealing the relationship between the superconductivity and the magnetism in these fascinating systems [6].

[1] A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2004).
[2] A. D. Caviglia et al., Nature456, 624 (2008).
[3] C. Bell et al., Phys. Rev. Lett. 103, 226802 (2009).
[4] Y. Kozuka et al., Nature 462, 487 (2009).
[5] M. Kim et al., Phys. Rev. Lett. 107, 106801 (2011).
[6] J. Bert et al., Nature Phys. 7, 767 (2011).

Ab-initio study of tin dioxide surfaces: stability and electronic structure

S Küfner[1], S André[2], B Höffling[3] and F Bechstedt[3]

[1]Institut für Festkörpertheorie und -optik, Germany, [2]Lawrence Livermore National Laboratory, USA, [3]Friedrich-Schiller-Universität, Germany

SnO_2 as an transparent conducting oxide is an interesting material for application in transparent circuits and photovoltaic or optoelectronic devices.

Despite the importance of the oxide, the electronic structures as well as the relative stability of different orientations and terminations of SnO_2 surfaces are not well known.

We apply the density functional theory to calculate the atomic geometries of the low-index surfaces (001), (100), (110), (111) of rutile tin dioxide. From a comparison of the approximate LDA-1/2 bulk band structure to the quasiparticle bulk result we conclude that the LDA-1/2 method is sufficiently accurate enough while it demands significantly lower computational costs. Therefore, we use the LDA-1/2 to predict surface bands inside the fundamental band gap.

Using the minimization of the surface free energy depending on the oxygen chemical potential, we find the oxygen-terminated (100) and (110) surfaces to be most stable, in accordance with experimental and other ab-initio results. We show that the tendency to fill oxygen 2p states with two electrons to lone pairs and to form Sn2+ ions in the surface region leads to insulating surfaces. We derive characteristic energies such as the ionization energy and the electron affinity and discuss them versus orientation and termination of the surface.

Influence of Mo doping on the Au-binding and O_2-dissociation behavior on CaO thin films

Y Cui, X Shao, N Nilius and H-J Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Doping is a versatile approach to tailor the physical and chemical properties of oxide thin films. By means of scanning tunnelling microscopy, we demonstrate that small amounts of Mo embedded in a CaO matrix are able to alter the growth behaviour of gold. While 3D deposits form on the pristine oxide, strictly 2D growth prevails on the Mo-doped films. The crossover in particle shape is driven by an electron transfer from localized Mo d-states in the oxide band gap towards the Au islands. Similar charge transfer processes modify also the adsorption characteristic of O_2. In presence of the dopants, the cross section for O_2 dissociation via electron injection from the STM tip becomes enhanced. The reason is a partial occupation of the anti-bonding p-orbitals of O_2 due to an electron donation from the Mo-impurities, as suggested from electron spectroscopy data. Even spontaneous O_2 dissociation might occur along the electron-rich perimeter of the 2D Au islands on the Mo-doped CaO. Doping the oxide support thus opens new routes to modify and improve the properties of a supported metal catalyst.

Scanning tunneling microscopy investigation of the interfacial electronic properties between YBCO and LCMO

B-C Huang[1], J-C Wang[1], Y-C Huang[2], V T Tra[3], J-Y Lin[3], Y-C Chen[2], Y-P Chiu[1] and Y-H Chu[3]

[1]National Sun Yat-Sen University, Taiwan, [2]National Cheng Kung University, Taiwan, [3]National Chiao Tung University, Taiwan

Direct measurements of the interfacial electronic structures in YBCO/LCMO hetero-structures have been performed using cross-sectional scanning tunneling microscopy (STM) and spectroscopy (STS). Both scanning tunneling spectroscopy and analysis of the local electronic states across the interface of YBCO/LCMO reveal the evolution of the energy-band structures. Closely examining the recognition of the electronic structure by the unique combination of STM and STS reveals the direct information on the local interaction between superconductivity and magnetism in this work. The results show how the electronic property of YBCO is interacted by LCMO near the interface. In addition, the temperature dependent electronic properties between YBCO and LCMO are also investigated in the work.

Organic layers and polymers 7

(invited) New directions in electrochemical imaging: structure-activity at the nanoscale

P Unwin, S C S Lai, K McKelvey, A G Güell, N Ebejer, A N Patel, M E Snowden, M A O'Connell, H V Patten, K E Meadows, J V Macpherson, R A Lazenby, M Peruffo, B D B Aaronson, C Chen and A W Colburn

The University of Warwick, UK

Electrochemical imaging methods, such as scanning electrochemical microscopy (SECM) have had a significant impact in electrochemistry and interfacial chemistry, allowing reactions and fluxes to be measured and mapped locally.[1] However, despite considerable effort such methods have largely remained stuck with a resolution at the several µm scale at best. At Warwick, we have recently developed new techniques for electrochemical imaging, notably scanning electrochemical cell microscopy (SECCM),[2] intermittent contact (IC)-SECM,[3] and related methods, which allow us to examine electrochemical and surface reactions with unprecedented spatial resolution. This talk will introduce these methods and show how they can be used to probe electrochemical reactions at individual features at electrode surfaces, including steps, terraces and single nanoparticles. A particular focus of our work is new forms of carbon such as graphene and nanotubes, where our novel methods provide considerable new insights on the intrinsic activity and allow key textbook models to be examined in detail.

[1] Amemiya, S.; Bard, A. J.; Fan, F. R. F.; Mirkin, M. V.; Unwin, P. R. Annu. Rev. Anal. Chem., 2008, 1, 95.
[2] (a) Ebejer, N.; Schnippering, M.; Colburn, A. W.; Edwards, M. A.; Unwin, P. R. Anal. Chem. 2010, 82, 9141. (b) Lai, S. C. S.; Dudin, P. V.; Macpherson, J. V.; Unwin, P. R. J. Am. Chem. Soc. 2011, 133, 10744. (c) Lai, S. C. S.; Patel, A. N.; Macpherson, J. V.; Unwin, P. R. Angew. Chem. 2012, in press.
[3] McKelvey, K.; Edwards, M. A.; Unwin, P. R. Anal. Chem. 2010, 82, 6334.

Detection on the agglomerated silver nanoparticles in sea urchins

S Piticharoenphun[1], L Siller[1], M-L Lemloh[2], B Mendis[3], U Bangert[4], N Poolton[4], B Horrocks[4], F Brummer[3] and D Medakovic[5]

[1]Newcastle University, UK, [2]University of Stuttgart, Germany, [3]Durham University, UK, [4]The University of Manchester, UK, [5]Boskovic Institute, Croatia

The progress in surface science provides the tools to detect the presence of nanomaterials in the biological sample. Herein, we use photoluminescence technique (PL) to measure silver nanoparticles (AgNPs) agglomerated in exposed sea urchin larvae (Paracentrotus lividus). The mobile luminescence end-station (MoLES) was used to collect the emission spectra of synthesized AgNPs. Then, the submicron images of agglomerated AgNPs in exposed larvae were obtained by Chemistry, Luminescence and Structure of Surface via micro-Imaging X-ray adsorption (CLASSIX) instrument in order to locate the position of agglomerated AgNPs in sea urchin larvae.

In MoLES instrument, the results showed that synthesized AgNPs can provide emission spectra around 450 nm at room temperature (300 K), using a 404 nm laser excitation source. The emission spectra at 450 nm can be observed in exposed sea urchin larvae by CLASSIX instrument. Additionally, the submicron images identified the location of agglomerated AgNPs around the oral region and likely on the ectoderm of sea urchin larvae. We suggested that the intake pathway might take place via mouth after the mouth organ was completely developed. In conclusion, photoluminescence is a potential and practical technique that can be used to detect the presence of nanomaterials in biological sample.

(invited) Photoinduced water splitting with oxotitanium porphyrins

A L Sobolewski

Institute of Physics of the Polish Academy of Sciences, Poland

Oxygenic photosynthesis in cyanobacteria and green plants provides the proof that the photocatalytic conversion of sunlight into useful chemical energy is possible. The goal of artificial photosynthesis is to mimic the energy conversion processes with photochemical or photoelectrochemical systems which are much simpler than the blueprints of nature.

The extensive current research efforts towards solar water splitting are based on two main strategies. In the photoelectrochemical approach [1], electrons and holes generated by the absorption of light in a semiconductor are used to neutralize protons and OH^- anions in an electrochemical cell. In an alternative approach, supramolecular structures have been devised which consist of an organic chromophore, an electron donor and an electron acceptor [2,3]. The absorption of a photon by the chromophore results in a charge-separation process which oxidizes the electron donor and reduces the electron acceptor, which will eventually neutralize hydroxide anions and protons, respectively.

In the work presented here, we have explored a third strategy, which aims at the direct photoinduced homolytic cleavage of H_2O molecules into $H^\bullet$ and $OH^\bullet$ radicals by a photocatalytically active chromophore. We propose and investigate a model which may potentially be suitable for these purposes: oxotitanium porphyrin (TiOP). While the porphyrin moiety (P) serves as the antenna for visible light, the TiO group exhibits the redox properties needed for the oxidation of water.

[1] A. Fujishima and K. Honda, Nature, 1972, 238, 37.
[2] M. R. Wasielewski, Chem. Rev., 1992, 92, 435.
[3] A.L. Sobolewski, W. Domcke, J. Phys. Chem. A, 2008, 112, 7311.

Selective detection of phospholipid in model cell membrane by AFM with probe-protein-conjugated tips

T Yamada, T Wang, H Shogomori, M Hara and T Kobayashi

RIKEN, Japan

We performed selective detection of sphingomyelin (SM), a ubiquitous kind of phospholipids contained in multi-component model cell membranes supported on mica substrate. For this purpose we used an atomic force microscope installed with a SiN tip modified with lysenin, a kind of hemolytic protein that binds SM specifically [1]. Lysenin is therefore called a “probe protein” for SM [2]. We covered the tip surface with lysenin using siloxane-thiol-amide linkage. The target model cell membranes, containing phosphatidylcholines (DOPC or DPPC) and cholesterol as well as palmitoyl sphingomielin (PSM), were deposited on mica as double layers by LB/LS method and placed in a Hepes/NaCl solution. AFM images in general demonstrated smooth bilayers of pure PSM and PSM+cholesterol. The PSM+DOPC and PSM+DOPC+cholesterol areally separated into two phases in the sub-micron scale. Regardless the phase separation, we repeated recording approaching-retracting force curves by lysenin-conjugated tips. Nearly 90% of the force-curve cycles, no attractive force was observed. In the rest 10% cases, we observed fairly constant adhesion forces ~ 170 pN for the bilayers containing PSM. This value of adhesion force is less than one tenth of the force to remove a phospholipid molecule out of bilayer [3], and therefore recognized as the lysenin single-molecular bonding force with a PSM cluster. We never observed attractive forces on pure DPPC or DOPC bilayers, which do not bind lysenin selectively. Lysenin-conjugated tips were active for averagely 1000 approaches to PSM containing membranes. Some tips were never active, probably depending on the configuration of the lysenin molecule fixed near the tip apex. We attempted to plot the adhesive forces over the two phases seen on the PSM+DOPC(+cholesterol) bilayers. In one of two phases, the adhesive forces ~ 170 pN were observed, and in the other phase, no adhesive forces were seen. The phase condensation of PSM was apparently demonstrated by the distribution of force curves. The bilayer lipid phase containing PSM and cholesterol corresponds to the “raft” structure (diameter < 100 nm) on the real cell membranes. The raft structure is anticipated to be instrumental in cellular signaling as well as virus infection. Our present technique will be applicable for direct observation of the raft on real live cell membranes.

[1] T. Wang et al., *Biochemistry* 51 (2012) 74.
[2] A. Yamaji et al., *J. Biol. Chem.* 273 (1998) 5300.
[3] R. M. Sullan et al., *Langmuir* 25 (2009) 7471.

(invited) Structure and dynamics of solutions of entangled ring polymers. Biological applications.

A Rosa[1] and R Everaers[2]

[1]Sissa, Italy, [2]Ecole Normale Superieure Lyon, France

Topological constraints (or, "entanglements") dominate the visco-elastic behavior of semi-dilute and dense polymer solutions [Doi & Edwards, "The Theory of Polymer Dynamics"]. Entanglements in systems of linear chains can be suitably accounted for by the so-called "reptation theory" [De Gennes, J. Chem. Phys. (1971)], which relies upon the observation that chains in melt relax from their original conformations via the motion of their ends. Unfortunately, much less is known about solutions of unlinked, circular (ring) polymers: rings have no free ends, topological constraints are permanent, and they are expected to behave differently than linear chains. For these reasons, ring polymers represent one of the major remaining challenges in theoretical and experimental Polymer Physics.

Here, we present novel theoretical and computational results concerning the structure and dynamics of ring polymers in dense solution, and we discuss their connection to theories which were proposed in the past. Furthermore, we show that systems of entangled ring polymers

(invited) Structure and dynamics of solutions of entangled ring polymers. Biological applications.

A Rosa[1] and R Everaers[2]

[1]Sissa, Italy, [2]Ecole Normale Superieure Lyon, France

Topological constraints (or, "entanglements") dominate the visco-elastic behavior of semi-dilute and dense polymer solutions [Doi & Edwards, "The Theory of Polymer Dynamics"]. Entanglements in systems of linear chains can be suitably accounted for by the so-called "reptation theory" [De Gennes, J. Chem. Phys. (1971)], which relies upon the observation that chains in melt relax from their original conformations via the motion of their ends. Unfortunately, much less is known about solutions of unlinked, circular (ring) polymers: rings have no free ends, topological constraints are permanent, and they are expected to behave differently than linear chains. For these reasons, ring polymers represent one of the major remaining challenges in theoretical and experimental Polymer Physics.

Here, we present novel theoretical and computational results concerning the structure and dynamics of ring polymers in dense solution, and we discuss their connection to theories which were proposed in the past. Furthermore, we show that systems of entangled ring polymers provide a detailed, minimalistic model of chromosome organization in eukaryotes.

(invited) Modelling DNA organisation in confined geometries: hints from topology

E Orlandini[1], C Micheletti[2] and D Marenduzzo[3]

[1]University of Padova, Italy, [2]SISSA, Italy, [3]The University of Edinburgh, UK

Nanodevices are increasingly used to investigate the impact of spatial restraints on the statics and dynamics of polymers and biopolymers. DNA is ideally suited for such studies both for its applicative potential (nanoconfinement can be used to sort, sieve and sequence DNA) and because its elastic properties can be exploited to elucidate issues of primary interest in polymer science. In fact, the width of presently available confining nanodevices (a channel, a slit, a pit etc.) can be set to compete with one or more of the characteristic lengths of a DNA molecule and hence allow for probing different physical regimes. Natural questions that may arise in this context are the following: Which are the effects of geometrical confinement on the metric and topological properties of linear and circular DNAs? Is there any relation between the topology-based features of the confined DNA and the multiple scaling regimes (de Gennes, Odjik) conjectures for its average extension?

Here we present a theoretical study of several aspects of DNA under confinement. This is based on a suitable mesoscopic model of dsDNA which can be studied by advances Monte Carlo simulations and scaling analysis. The results obtained either for nano-slits and nano-channels reveal an interesting characterization of the metric crossover behaviour in terms of knotting probability and complexity of the knot population.

Finally we show that the topological properties of the DNA molecules confined into nano-slits and nano-channles have two major differences compared to three-dimensional confinement as viral capsids. Firstly, the overall knotting probability is nonmonotonic for increasing confinement and can be largely enhanced or suppressed compared to the bulk case by simply varying the slit or channel trasversal dimension. Secondly, the knot population consists of knots that are far simpler than for three-dimensional confinement.

The results suggest that nanoslits and nanochannels could be used in nanofluidic setups to produce DNA rings having simple topologies (including the unknot) or to sevie DNA rings according to their knotted state.

Immobilization of molecularly imprinted polymer nanoparticles by photochemical conjugation

S Chaudhary, T kamra, K M Ahsan Uddin, J Schnadt, L Montelius, M Yan and L Ye

Lund University, Sweden

Our goal is to develop label-free nanosensors which are aimed at sensing specific targets. For sensing we intend to exploit the high stability and selectivity of molecularly imprinted polymers (MIPs). A critical step in the nanosensor preparation is to immobilize the MIPs on a suitable surface in a reliable and straightforward way.Here we study for model supports how the immobilization can be achieved by photoactivated nanoparticle conjugation. MIP nanoparticles in the 100 nm size range and specific for propranolol as a target were synthesized by precipitation polymerization [1]. The involved perfluorophenylazide (PFPA) has two different reactive centers, the fluorinated phenylazidecapable, which can form stable covalent bonds, and a functional group R [2]. Our approach is to attach the PFPA to the surface – a glass slide treated with (3-aminopropyl)-trethoxysilane (APTES) – so that the azido group points outwards and can couple to the MIP nanoparticles. In this particular case we used perfluorophenylazideN-hydroxysuccinimide (PFPA-NHS) as agent. The MIP nanoparticles were then drop-casted on the PFPA modified slide and irradiated with UV light at ambient temperature. Both the nanoparticle-coated slides and different control slides were characterized by fluorescence microscopy, FTIR, AFM and synchrotron-based XPS.

The condition for silinization of the glass substrate with APTES was optimized by fluorescence microscopy. Using a concentration of 6% of APTES in toluene we obtained an even coverage of the terminal amines on the glass slide with minimal formation of APTES aggregates. XPS confirmed the successful attachment of PFPA on the amine-modified slides. AFM inspections proved that the photo-conjugation was effective to immobilize the MIP nanoparticles on surface.

We find that we have established optimized conditions for surface modification to introduce terminal amines on a glass substrate and attachment of the photo-active reagent PFPA-NHS. Using photoactivated conjugation, unmodified MIP nanoparticles have been immobilized successfully on the flat substrate in a single step. The method developed in this work should be very useful for construction of various sensor platforms using MIP nanoparticles for selective molecular recognition.

[1] Changgang Xu and Lei Ye, Chem. Commun., 2011, 47, 6096–6098.
[2] Keana, J. F. W., and Cai, S. X., J. Org. Chem., 1990, 55, 3640–3647.

The adsorption geometry and chemical state of glycine on Ni {110}

S Baldanza[1], J Ardini[1], D Watson[2] and G Held[1]

[1]University of Reading, UK, [2]University of Surrey, UK

One of the great challenges in heterogeneous catalysis is to develop catalysts for asymmetric synthesis, promoting the reaction for only one of the enantiomers. Stereochemical control can be induced on non-chiral metal surfaces by the adsorption of chiral modifiers, and Ni catalysts show substantial enantioselectivity in the hydrogenation of β-ketoesters after modification with alanine [1]. In this work we studied the adsorption of the smallest, non-chiral amino acid glycine on Ni{110} by XPS and NEXAFS as a model system to characterise the bare interaction between amino acids and more open metal. At room temperature, glycine was found to adsorb in its anionic form, in a similar way to what is observed for other amino acids on Ni and Cu surfaces [2,3], with both oxygen atoms of the carboxylate group and the nitrogen atom bonded to Ni atoms. Analysis of layers at different coverages does not show differences in the chemical state of the molecule for coverages lower than a chemisorbed layer. Multilayers with glycine in both anionic and zwitterionic states are observed after high exposures at 250 K. Temperature-Programmed XPS shows that the multilayers disappear at 350 K, the remaining chemisorbed layer is unchanged up to 400 K. Angular dependent NEXAFS spectra indicate that the O-C-O plane is tilted with respect to the metal surface.

[1] C. J. Baddeley, Topics in Catalysis, 2003, 25(1-4), 17-28.
[2] C. J. Baddeley, G. Held, Elsevier Academic Press: Amsterdam, 2010, 105-133.
[3] S.M. Barlow, R. Raval, Surface Science Reports 2003, 50, 201–341.

Carbon, graphene 5

(invited) Spin physics in carbon nanotube double quantum dots

M Buitelaar

University of Cambridge, UK

I will discuss recent measurements in which we investigate spin blockade and Kondo physics in carbon nanotube double quantum dots. Spin blockade is observed in weakly coupled double quantum dots when electron transitions between the dots are forbidden by spin conservation. As such, this phenomenon is of considerable importance in spin-based quantum information processing schemes as a way to convert the spin degree of freedom to a much easier detectable charge state or current. The ability to control the tunnel couplings in the nanotube devices also allows us to investigate carbon nanotube double quantum dots which are more strongly coupled to their leads. In this case, we observe pronounced Kondo features. Of particular interest here is the competition between Kondo correlations and exchange coupling between the spins, when both quantum dots contain an odd number of electrons. These effects have been studied as a function of tunnel coupling, temperature and magnetic field and will be discussed during the second part of the talk.

Giant Rashba effect on Dirac fermions in graphene on various substrates

D Marchenko[1], A Varykhalov[1], M Scholz[1], G Bihlmayer[2], E Rashba[3], J Sánchez-Barriga[1], A Rybkin[4], A Shikin[4], T Seyller[5] and O Rader[1]

[1]Helmholtz-Zentrum Berlin, Germany, [2]Forschungszentrum Jülich and JARA, Germany, [3]Harvard University, USA, [4]St. Petersburg State University, Russia, [5]Erlangen University, Germany

The low instrinsic spin-orbit interaction in graphene can be strongly enhanced by an extrinsic effect. We measure a giant Rashba-type spin-orbit splitting of ~100 meV for graphene in contact with Au directly by spin- and angle-resolved photoemission. The splitting is constant with binding energy and extends up to the Fermi energy in slightly p-doped graphene which is created by intercalation of Au between graphene and Ni(111). We compare this result to Ir(111), on which two different graphene moiré phases are prepared and only the R0 phase shows a giant Rashba splitting of ~50 meV. We characterize a new rotated graphene phase by ARPES and STM and show that it leads to a reduced interaction and a reduced Rashba splitting. Finally, we discuss the intercalation of Au between graphene and SiC and the prospects of a giant Rashba splitting in graphene on an insulating substrate.

The optical properties of undecyl nanodiamond

Y Astuti[1], N Poolton[2] and L Siller[1]

[1]Newcastle University, UK, [2]The University of Manchester, UK

Due to their potential optical properties, nanodiamonds hold great interest in a variety of applications, such as biolabels, photonics, etc. These properties are correlated with surface modification, presence of impurities and presence of defects (contained either on their surface or within the crystal structure). Undecyl-nanodiamonds produced by attachment of 1-undecene onto the nanodiamond surface could be a good candidate as a luminescent marker in the future; therefore, understanding of their optical properties with regards to factors mentioned above is essential. In this work, the optical properties of two samples, acid-purified nanodiamonds and undecyl-nanodiamonds, have been determined by Surface Enhanced Raman Spectroscopy (SERS) and photoluminescence spectroscopy. The SERS samples were prepared by mixing the samples with silver nanoparticles. Analysis of the SERS sample was performed using LabRAM HR800 with the 514.5 nm line from an Ar ion laser; whereas a 30 mW semiconductor diode laser emitting at 445 nm equipped with appropriate laser clean-up filters, was used as an excitation source in photoluminescence analysis. The results demonstrated that the characteristic Raman signal at 1330 cm^{-1} was still observed after chemical surface modification;[1] while the absence of signal at ~1600 cm^{-1}, attributed to graphite bands; that specify agglomerated nanodiamond, shows the presence of isolated nanodiamonds. The photoluminescence emission in the range 500-800 nm which is characteristic for isolated nanodiamonds with diameter 5 nm[2, 3] is observed and the peaks became sharper with attachment of undecene as compared to the sample without surface functionalisation. The observed emission could be related with structural disorder on the nanodiamond surface.

[1] Ferrari, A.C. & Robertson, J. Resonant raman spectroscopy of disordered, amorphous, and diamondlike carbon. Phys. Rev. B 64, 754141-7541413 (2001).
[2] Chung, P.-H., Perevedentseva, E., Cheng, C.-L. The particle size-dependent photoluminescence of nanodiamonds Surf. Sci. 601, 5 (2007).
[3] Smith, B.R. et al. Five-nanometer diamond with luminescent nitrogen-vacancy defect centers. Small 5, 1649-1653 (2009).

Investigation of the electronic structure of multilayer graphene on Ni(111) with respect to possible application in spin-filter devices

M Weser[1], R J Koch[2], E Voloshina[3], A Generalov[4], H Vita[5], T Seyller[2], K Horn[1] and Y S Dedkov[5]

[1]Fritz-Haber Institute, Germany, [2]Universität Erlangen-Nürnberg, Germany, [3]Freie Universität Berlin, Germany, [4]Technische Universität Dresden, Germany, [5]Specs Berlin, Germany

Among the many intriguing properties and envisaged applications of graphene, its use as a spin filter in the emerging “spintronics” has received considerable attention. Karpan et al. [1] have predicted that a stack of graphene layers on top of Ni(111) may serve as a fully spin-polarized current injector, because the graphene states overlap only with the Ni minority bands at the Dirac point. However, due to the tunneling of electrons and the fact that the first monolayer exhibits a strong interaction with the Ni bands, a sizeable spin filter effect only occurs for several graphene layers. Here we report on a procedure to overcome the passivation effect of the first graphene layer, which avoids the catalytic growth of subsequent layers on the Ni surface. This procedure permits the growth of graphene in a multilayer structure. Core and valence level photoemission spectroscopy is used to characterize the growth process and the electronic band structure of such epitaxially grown samples. Two different rotational domains are observed, and their influence on the spin-filter effect is analyzed. We also study the intercalation of Au in order to decouple the first strongly bound layer, and to restore the Dirac cone throughout the graphene stack.

[1] Karpan et al. Phys. Rev. Lett. , 99, 176602, (2007).

(invited) Title and abstract not available

F Jelezko

Ulm University, Germany

Fabrication and characteristics of fullerene embedded Si(111) surfaces

M-S Ho[1], C-P Huang[1], W-S Su[2], C-C Su[1] and M-F Chang[3]

[1]National Chung Hsing University, Taiwan, [2]National Center for High-Performance Computing, Taiwan, [3]National Tsing Hua University, Taiwan

The supramolecular nanostructures of the Si(111) surfaces with embedded self-assembled C_{84} were studied using UHV-STM. Such a system not only has advantages over conventional silicon carbide devices but also has none of the porous defects. This investigation also determined the electronic density of states and the optoelectronic properties of the Si(111) surfaces with embedded C_{84} from the I-V characteristics, in which a traditional detection system and UHV-STM were drawn. The electron field emission was stable for a period, revealing a stable interaction between fullerene molecules and the silicon substrate. The magnetic properties of Si surfaces with embedded C84 molecules examined using a MFM and a SQUID were demonstrated to be ferromagnetic. Calculations from the first-principles method agreed closely with experimental results. The results of this study can help to improve, and even lead to a breakthrough in, the fabrication of optoelectronical device and a replacement for semiconductor carbide.

[1] C. P. Huang, C. C. Su, W. S. Su, C. F. Hsu and M. S. Ho, Appl. Phys. Lett. 97, 061908 (2010).
[2] W. S. Su, T. C. Leung, B. Li and C. T. Chan, Appl. Phys. Lett. 90, 163103 (2007).

C_{60} molecules embedded in SiO_2 for memory applications

D Beckmeier, T Stimpel-Lindner and H Baumgärtner

Universität der Bundeswehr München, Germany

The goal of this work is to produce a memory structure containing Fullerene (C_{60}) molecules as floating gate. For this, C_{60} molecules were embedded in a SiO_2 layer. Around this layer a metal oxide semiconductor diode structure was defined to study the charge and discharge of electronic states caused by the molecules.

The structure was formed by evaporating five percent of a monolayer of C_{60} molecules onto a cleaned {100} p^-(B) wafer followed by in situ overgrowth of the molecules with amorphous silicon. A part of the wafer was covered using a shadow mask during C_{60} evaporation for reference measurements.

These samples were then oxidized in a wet atmosphere at 710°C for 150 minutes to achieve a complete encapsulation of the C_{60} molecules by the thermal oxide without destroying the molecules. Aluminium contacts were defined on top of these layers.

To charge and discharge the molecules, DC voltages on these contacts were swept in positive and negative directions and the resulting current was detected. To analyze the amount of stored charge, CV measurements were performed. Negative voltage sweeps resulted in a flatband voltage shift to more negative voltages, while positive voltage sweeps caused a shift back to its more positive starting value. This shows that the molecules could be discharged and recharged with electrons reversibly. The IV data show a Fowler-Nordheim behaviour for negative directions. For positive directions, currents start at lower fields and have a smaller slope. This can be explained by trap-assisted tunneling injection from semiconductor into oxide.

Determining the orientations of a surface absorbed fullerene and a fullerene molecule acting as a functionalised tip

A Lakin, C Chiutu, A Sweetman, P Moriarty and J Dunn

University of Nottingham, UK

Recent advances in scanning probe microscopy, triggered by the pioneering work undertaken by Gross et al. [1], have centred around the functionalisation of the scanning probe tip through deliberate absorption of atomic or molecular species. In the theoretical modelling of the STM images obtained using this technique, density functional theory is used almost exclusively. However, when the associated systems become too complicated, as is often the case when a functionalised tip is considered, it can become too cumbersome to use in an investigative manner. In these cases an alternative would be beneficial.

The work presented here provides a simple and speedy theoretical alternative, based on Hückel molecular orbital theory, that allows for the analysis of dynamic STM images obtained when a C_{60} functionalised tip is allowed to interact with a second C_{60} molecule on the surface. In doing so the molecular orientation of both molecules can be obtained, and the relevant molecular orbitals associated with the tunnelling process elucidated. By itself, this provides valuable information on the system, which could be of particular importance in conductance type experiments, while also providing important information that may then be used as a start point to simplify any further DFT calculations on the system.

[1] L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer. Science, 325(5944): 1110--1114, 2009.

Reactions on surfaces 7

(invited) Extending the concept of semiconductor defect chemistry to electrochemistry

M Todorova and J Neugebauer

Max-Planck-Institut für Eisenforschung, Germany

All materials processes are complex phenomena, but the prominent role which the solid/liquid interface plays in electrochemical systems further enhances this complexity. Since the predominant part of relevant process steps takes place at this interface our understanding of key steps, yet alone their interplay is incomplete. This makes improvement of a targeted functionality often a question of trial and error approaches, largely based on empirical observations rather than sound theoretical understanding.

The ability to predictively characterise the interface will enhance our understanding, but investigations by ab-initio calculations is challenging, not least because of the need to account for the electrode potential and environmental conditions, which influence the state of the system. A method linking first-principles calculations quite naturally to experimental observables, which determine and characterise the electrochemical system, will be presented. Being similar to the approach used in defect chemistry of semiconductors [1] the approach utilises thermodynamic concepts and is based on the formation energies of ions in solution. It allows the identification of a region of water stability, the pH-scale and the electrode potential. The capabilities of the approach will be demonstrate and discuss by the construction of E/pH diagrams, an important and valuable tool in corrosion science and various areas of electro-chemistry, for Zinc and Iron.

[1] C.G. Van de Walle and J. Neugebauer, J. Appl. Phys. 95, 3851 (2004).

Dehydrogenation of simple hydrocarbons and oxygenates on Pt/ceria model catalysts

Y Lykhach[1], A Neitzel[1], V Johánek[2], M Vorokhta[2], N Tsud[2], T Skála[3], K C Prince[3], V Matolín[2] and J Libuda[1]

[1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany, [2]Charles University, Czech Republic, [3]Sincrotrone Trieste SCpA, Italy

Ceria-based materials are used in many catalytic applications which involve dynamic oxygen uptake and release. The related oxygen storage processes generally involve electron transfer, altering the oxidation state of cerium between Ce^{4+} and Ce^{3+}. The redox state of ceria can also be employed as an indicator for many elementary processes on the catalyst surface. In this contribution, we will focus on the adsorption and reaction of simple hydrocarbons and hydrocarbon oxygenates upon reaction with ceria-based model catalysts.

Resonant Photoemission Spectroscopy (RPES) is employed as one of the most sensitive methods to determine the surface oxidation state of cerium cations.[1, 2] We use RPES in conjunction with high-resolution Synchrotron Photoelectron Spectroscopy (SRPES) to identify decomposition pathways of small molecules such as H_2, C_2H_4, H_2O as well as HCOOH, and CH_3COOH on the surfaces of single-crystal based ceria model catalysts. We use stoichiometric CeO_2(111) films on Cu(111), partially reduced CeO_{2-x}/Cu(111) and Pt/CeO_2/Cu(111). For each case, all surface intermediates and related reaction pathways have been investigated. Simultaneously, spillover processes involving hydrogen, oxygen, and hydrocarbon fragments between Pt and CeO_2 support are identified. [3-5]

[1] A. Trovarelli, Catalysis by Ceria and Related Metals, Imperial College Press, London, 2002.
[2] V. Matolín, I. Matolínová, L. Sedláček, K. C. Prince, T. Skála, Nanotechnology 2009, 20.
[3] G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G. P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K. C. Prince, V. Matolín, K. M. Neyman, J. Libuda, Nature Materials 2011, 10, 310-315.

[4] Y. Lykhach, T. Staudt, N. Tsud, T. Skála, K. C. Prince, V. Matolín, J. Libuda, PCCP 2011, 13(1), 253-261.

[5] Y. Lykhach, T. Staudt, M. Vorokhta, T. Skála, V. Johánek, K. C. Prince, V. Matolín, J. Libuda, J. Catal. 2012, 285 (1), 6-9.

Comparative study of the preferential oxidation of CO over Ir and Pt surfaces

L Piccolo, S Nassreddine and F Morfin

IRCELYON, France

The preferential oxidation of CO in the presence of hydrogen (PROX) is a promising way to purify hydrogen for possible use in PEM fuel cells [1]. Numerous works on PROX over supported Pt-based catalysts have been reported [1], but only one on model surfaces [2]. Moreover, although a few studies on H_2-free CO oxidation over Ir surfaces have been published [3-5], nothing has been reported to date on PROX.

In this work, CO oxidation, with or without hydrogen, has been studied on Ir(111), Ir(112), Pt(111) and Pt(112) single-crystal surfaces, in the pressure range 0.4-15 kPa [6]. Iridium appears more active in CO oxidation, and more active and selective in PROX than platinum, under both oxidative and stoichiometric $CO:O_2$ conditions. Moreover, the (112) stepped surfaces are more active than the (111) flat surfaces. It will be shown that these results are not consistent with a mechanism in which CO desorption would determine the reaction rate [4], if only the CO-surface adsorption energy is considered.

Besides, a promoting effect of low-content H_2 on the CO oxidation rate is evidenced both for Ir and Pt. This effect is shown to originate neither from water formation, nor from adsorption-induced surface restructuring.

[1] Park et al., Catal. Today 139 (2009) 280.

[2] Dupont et al., J. Catal. 278 (2011) 239.

[3] Ivanov et al., J. Catal. 48 (1977) 269.

[4] Engel and Ertl, Adv. Catal. 28 (1979) 1.

[5] Berlowitz et al., J. Phys. Chem. 92 (1988) 5213.

[6] Piccolo et al., Catal. Today, doi:10.1016/j.cattod.2012.02.046.

Real-time observation of thermal oxidation process on high-index silicon surfaces by means of photoemission spectroscopy with synchrotron radiation

S-Y Ohno[1], S Abe[1], R Kanemura[1], A Yoshigoe[2], Y Teraoka[2], S Ogata[1], T Yasuda[3] and M Tanaka[1]

[1]Yokohama National University, Japan, [2]Japan Atomic Energy Research Agency, Japan, [3]National Institute for Advanced Industrial Science and Technology, Japan

The initial oxidation on high-index silicon surfaces with (001), (113), (120) and (331) orientations at 340-920 K has been investigated by real-time X-ray photoemission spectroscopy (Si 2p and O 1s) using 687 eV photons. In the present study, we investigate oxidation kinetics in monolayer regime at the thickness of about 0.4 nm at most. Based on the study of Si(001), it has been shown that O 1s state can be decomposed into two components, low-binding-energy component (LBC) and high-binding-energy component (HBC) [1]. Analysis of the O 1s state indicated that the O atom in the strained Si-O-Si structure in the vicinity of the Si^{4+} states contribute to LBC, although this state was assigned to the suboxide components ($Si^{+,}$ $Si^{2+,}$ Si^{3+}). Temperature dependence of the ratio of LBC and HBC further indicated that relaxation of the interface strain at the SiO_2/Si interface occurs above a certain critical temperature except Si(113). In other words, interface strain should be quite large on Si(113), because strain relaxation due to formation of the point defect by removing surface Si atoms is prohibited [2]. We observed an abrupt change of the Si^{4+} intensity above the temperature of 820 K for the case of Si(120). The results obtained with LEED suggest that no surface reconstruction occurs on this surface, indicating that growth mode changes due to instability of the surface structure. Based on these observations, we summarize orientation dependence of the oxide growth mode, oxidation kinetics and interface strain, which are of great importance for device application.

[1] S. Ogawa, A. Yoshigoe, S. Ishidzuka, Y. Teraoka, and Y. Takakuwa, Jpn. J. Appl. Phys. 46 (2007) 3244.
[2] H.-J. Mussig, J. Dabrowski, K.-E. Ehwald, P. Gaworzewski, A. Huber, U. Lambert, Microelectron. Eng. 56 (2001) 195.

Reduction behavior of oxidized Pd(100) and $Pd_{75}Ag_{25}$(100) Surfaces

V Fernandes[1], L Erik Walle[1], S Blomberg[2], M Helene Farstad[1], J Gustafson[2], H Grönbeck[3], J Andersen[2], E Lundgren[2] and A Borg[1]

[1]Norwegian University of Science and Technology, Norway, [2]Lund University, Sweden, [3]Chalmers University of Technology, Sweden

Palladium exhibits high selectivity and permeability for hydrogen and is thus a suited material for hydrogen separation membrane applications. Upon exposure to hydrogen palladium is susceptible to embrittlement due to the formation of hydride phases [1]. Alloying with 23 wt% silver has shown to improve the performance of Pd-based membranes [2,3]. Furthermore, heat treatment in air has been reported to enhance the hydrogen permeation [4,5].

Inthe presentcontribution, we address the oxidation and reduction behavior of the $(\sqrt{5}\times\sqrt{5})R27^\circ$ surface oxides formed on the Pd(100) and $Pd_{75}Ag_{25}$(100) surfaces as model systems for PdAg membrane surfaces. The close similarities between the $(\sqrt{5}\times\sqrt{5})R27^\circ$ oxide structure at the two surfaces have been addressed through combining low energy diffraction (LEED), high resolution photoemission spectroscopy (HR-XPS) and scanning tunneling microscopy (STM) studies with density functional theory (DFT) calculations. The reduction behavior of the $(\sqrt{5}\times\sqrt{5})R27^\circ$surfaceoxides as monitored by photoemission spectroscopy during exposure to CO and H_2 at different temperatures and pressures will be presented and the observed reduction behavior for the two surface oxides will be compared.

[1] G. J. Grashoff et al., Plat. Met. Rev. 27, 157 (1983).
[2] J. Rogal et al., Phys. Rev. Lett. 98, 046101 (2007).
[3] S. Uemiya et al., J. Membr. Sci. 56, 315 (1991).
[4] J. N. Keuler et al., J. Membr. Sci. 195, 203 (2002).
[5] A. L. Mejdell et al., J. Membr. Sci. 350, 371 (2010).

PdAg model catalysts under reaction conditions

S Blomberg[1], J Gustafson[1], N Martin[1], M Messing[1], K Deppert[1], V Fernandes[2], L Erik Walle[2], A Borg[2], H Grönbeck[3], Z Liu[4] and E Lundgren[1]

[1]Lund University, Sweden, [2]Norwegian University of Science and Technology, Norway, [3]Chalmers University of Technology, Sweden, [4]Lawrence Berkeley National Laboratory, USA

Due to economic reasons, the development of cheaper catalysts is of high priority in the catalyst industry and in the society as a whole, providing that the catalyst is at least as efficient as a more expensive one. One way to realize this is to dilute the well-known oxidation catalyst Pd with a less costly material. This, however, requires that the Pd stays at the surface in the presence of the reactant gases, which may be possible to achieve by alloying it with a noble metal such as Ag. Previous studies have shown that Ag segregates to the surface [1] when the alloy is heated in UHV, but little is known about the segregation behavior in the alloy during industrial like reaction conditions.

In the present contribution we report on an in situ study of the CO oxidation over a $Pd_{75}Ag_{25}(100)$ single crystal using High Pressure X-ray Photoemission Spectroscopy (HPXPS) and Surface X-ray Diffraction (SXRD). Further, 10 and 17 nm PdAg particles have also been studied in an attempt to bridge the material gap. These particles are produced by an aerosol particle technique yielding a very narrow size distribution of the particles [2]. The results from the PdAg studies will be compared to results from CO oxidation over a pure Pd(100) single crystal and Pd particles.

[1] Wouda et. al, Surf. Sci. 417, (1998) 292.
[2] M. E. Messing et al, J. Phys. Chem. C. 114(2010) 9257.

Methane adsorption on PdO(101)

N Martin, E Lundgren, J Gustafson and E Erdogan

Lund University, Sweden

Pd is an important catalyst for different oxidation processes such as the oxidation of methane, hydrocarbons and CO in automotive exhausts. While the exact nature of the active site in CO-oxidation over Pd has been extensively debated during the last few years [1-3], less attention has been paid to the active site for the methane oxidation over Pd. In a recent publication we have shown, based on in situ SXRD experiments and DFT calculations, that the PdO(101) has a high activity for the oxidation of methane [4]. In particular, the calculations suggested that the oxygen undercoordinated Pd atoms at the PdO(101) surface provides the lowest dissociation barrier for the extraction of the first hydrogen atom from the methane. In order to elucidate the reactivity of PdO(101) we conducted a surface science study of methane adsorption on a PdO(101) thin film in ultra high vacuum conditions following the preparation methods described in references [5-6] to produce a high quality PdO(101) film. We have studied the film by a combination of High Resolution Core-level Spectroscopy (HRCLS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED), and confirm previous structural observations. We show that our HRCLS measurements provide resolution to separate between the Pd atoms at the PdO(101) surface coordinated to 3 or 4 oxygen atoms. Armed with this information we studied the adsorption of methane on the PdO(101) in UHV at liquid nitrogen temperatures. Our measurements strongly suggest that the methane adsorbs/dissociates on the Pd atoms coordinated to 3 oxygen atoms, supporting our previous assignment of the active site.

[1] B. L. M. Hendriksen et al., Surf. Sci. 552 (2004) 229.
[2] F. Gao et al., J. Phys. Chem. C, 113 (2009) 174.
[3] R. van Rijn et al., Phys. Chem. Chem. Phys., 13 (2011) 13167.
[4] A. Hellman et al., J.Phys.Chem. Lett in press.
[5] H. H. Kan and J. F. Weaver, Surf. Sci. 602 (2008) L53.
[6] H. H. Kan and J. F. Weaver, Surf. Sci. 602 (2008) L53.

Collision effect on the laser induced thermal desorption of Xe

A Ikeda, M Matsumoto, S Ogura, K Fukutani and T Okano

The University of Tokyo, Japan

Time-of-flight (TOF) measurements of desorbed molecules provide us with the insight into the desorption dynamics. When adsorbed molecules are thermally desorbed, the TOF is described by a Maxwell-Boltzmann (M-B) distribution [1]. At an intense desorption flux, however, the post-desorption collisions are not negligible, leading to the modification of the TOF [2]. To clarify the collision effects, we carried out a quantitative investigation of the laser induced thermal desorption of Xe by varying the initial Xe coverage Θ on a Au surface.

At Θ = 0.3 ML, the TOF of Xe was well analyzed with a Maxwell-Boltzmann distribution with a temperature of 310 K, which is consistent with the temperature rise estimated by a simulation [1]. At Θ > 0.5 ML, on the other hand, the TOFs of Xe fitted well only to a shifted Maxwell-Boltzmann distribution (SMB) that employs the stream velocity *u*, indicating the presence of the post-desorption collisions. With increasing Θ, *u* increased from ~0 to 140 m/s, and saturated at 140 m/s at Θ > 5 ML. Assuming a model of the Knudsen layer formation at the vicinity of the surface where a significant number of collisions occurs, the saturated stream velocity was analyzed to be 135 m/s, which is consistent with the present experimental result. Furthermore, the model quantitatively reproduces the experimentally observed relation between *u* and *T* at an intermediate Θ.

[1] A. Ikeda, M. Matsumoto, S. Ogura, K. Fukutani and T. Okano, Phys. Rev. B 84, 155412 (2011).
[2] J. P. Cowin and D. J. Auerbach and C. Becker and L. Wharton, Surf. Sci. 78, 545 (1978).

Chemometric and multivariate statistical analysis of ToF-SIMS spectra from complex Cu-Fe sulfides

S Harmer-Bassell and Y Kalegowda

University of South Australia, Australia

ToF-SIMS spectra of mineral samples are complex comprising of large mass ranges and many peaks. Consequently, characterization and classification analysis of these systems is challenging. In this study, different chemometric and statistical data evaluation methods, based on monolayer sensitive ToF-SIMS data have been tested for the characterization and classification of copper-iron sulfide minerals (chalcopyrite, chalcocite, bornite and pyrite) at different flotation pulp conditions (Feed, Conditioned feed and Eh modified). The complex mass spectral data sets were analyzed using the following chemometric and statistical techniques: principal component analysis (PCA); principal component-discriminant functional analysis (PC-DFA); soft independent modeling of class analogy (SIMCA); and k-Nearest Neighbour (k-NN) classification. PCA was found to be an important first step in multivariate analysis, providing insight both into both the relative grouping of samples and the elemental/molecular basis for those groupings. For samples exposed to oxidative conditions (at Eh ~ 430 mV), each technique (PCA, PC-DFA, SIMCA and k-NN) was found produce excellent classification. For samples at reductive conditions (at Eh ~ -200 mV SHE), k-NN and SIMCA produced most accurate classification. Phase identification of particles that contain the same elements but a different crystal structure in a mixed multi-metal mineral system has been achieved. These results prove ToF-SIMS can be used to track the surface chemistry of an individual particle throughout complex minerals processing procedures.

Neutron diffraction 2

(invited) Electron Ptychography: a route towards less than 50 picometre imaging resolution

J Rodenburg

The University of Sheffield, UK

The resolution of transmission electron microscopy is bounded by the properties of magnetic lenses (even if aberration-corrected). Ptychography is a method of diffractive imaging in which a number of diffraction patterns are recorded from adjacent areas of an object. Because of redundancy in the resulting data, it becomes possible to solve for the phase of the diffraction patterns, and thus calculate the complex transmission function of the object at a resolution determined by the effective numerical aperture of the synthetic lens created by the angular size of the detector, as subtended at the specimen plane. For electron ptychography, we use a condenser lens to bring the electron flux to within a reasonably localised illumination spot (which can be many times larger than the final reconstruction resolution). In this way, a poor lens can be used to generate a very high resolution image – in theory limited only by the electron wavelength (0.0025nm at 200keV), although of course in practice the scattering and vibrational properties of the atoms themselves will restrict meaningful resolution. Because ptychography uses self-referential interference (diffraction), it is relatively immune to instabilities in power supplies, etc, that also impair conventional lens imaging methods.

To date, ptychography has enjoyed most success in the field of soft and hard X-ray imaging. Electron ptychography has previously encountered various experimental difficulties which have only recently been overcome. However, because the scattering cross-section of interaction for electrons is so much higher than that of X-rays (by about a factor of 10^4), it is only with electrons that true sub-atomic scale imaging will be possible.

This talk will present electron ptychography results obtained in a converted scanning electron microscope (SEM) operating at 30keV. The lens employed has a nominal resolution of about 1.2nm. By phasing all the scattering k-vectors captured by the detector, the resolution improvement over that of the lens itself is a factor of 5, leading to 0.23nm resolution. Extending the same concept to higher energies should eventually deliver sub-Angstrom resolution imaging beyond that achievable with complex lens aberration correction technology. Expanding the method to incorporate tomography could deliver 3D atomic images at less than 50 pm resolution of the solid state. The principal limitation (especially for soft matter) will be radiation damage effects.

How to make vortex lattice diffraction patterns prettier and more accurate with Bayes' theorem

A Holmes

University of Birmingham, UK

Small Angle Neutron Scattering (SANS), has been a highly successful method for the study of vortex lattices in type-II superconductors for many years. The usual method for producing a diffraction pattern is to apply a field close to the beam direction, and rock the field and sample together (and hence vortex lattice) over a few degrees with respect to the neutron beam. Different reciprocal lattice points will fulfil the Bragg criterion at different rocking angles, producing spots on the 2D detector. A sum of intensities over the entire rock gives the complete diffraction pattern. This method is not optimal, however, as most parts of the detector sample regions of reciprocal space which contain no reciprocal lattice points, so the rocking sum contains large amounts of noise that could safely be ignored.

An appropriately weighted sum is one way to handle this, however for regions which have never fulfilled the Bragg criterion, such a sum will attempt to extrapolate a small noisy signal by a very large multiplication factor. A Bayesian approach removes these pathological features, and gives a much more realistic diffraction pattern, especially for weak and noisy data. This method can be integrated into existing 2D SANS analysis software such as GRASP.

Complex new crystal structure type in high-pressure europium

R Husband, M McMahon, I Loa and G Stinton

The University of Edinburgh, UK

Unlike their trivalent lanthanide neighbours, europium (Eu) and ytterbium (Yb) are both divalent at ambient conditions, and both have a significantly larger atomic volume and compressibility than would be expected to be consistent with the general trend observed within the lanthanide series. In addition, Eu and Yb do not fit in with the general trend of structural phase transitions observed in the trivalent lanthanides.

Although the structures adopted below 18 GPa are well known, previous x-ray diffraction studies have found that the diffraction pattern of Eu becomes much more complex at 18 GPa [1,2]. This was attributed to a transition to a new phase, Eu-III. The structure of this phase remained unknown until Biet al.recently reported a series of phase transitions in Eu up to 92 GPa [3].

We will present the results of extensive high-resolution angle-dispersive powder x-ray diffraction experiments on Eu up to a pressure of 50 GPa, performed at the SRS, ESRF and Diamond synchrotrons. We find that the complex diffraction patterns at 18 GPa are not due to a phase transition in Eu, but instead are due to pressure-induced changes of a contaminant phase that appears to have been present in previous studies. In our samples we did not observe the contamination peaks, and our high-resolution data enabled us to identify two new phase transitions: at 32 and 38 GPa. We will present a new, complex structure that gives an excellent fit to the patterns observed between 32-38 GPa; the first of this type to be observed in the lanthanide series.

[1] K .Takemura and K. Syassen, J. Phys. F: Met. Phys., 15, 543 (1985).
[2] T. Krüger, B. Merkau, W. A. Grosshans and W. B. Holzapfel, High Press. Res. 2, 193 (1990).
[3] W. Bi et al., Phys. Rev. B. 83 104106 (2011).

The high-pressure thermal properties of magnesium

S MacLeod[1], S Mehta[1], G Stinton[2], D Errandonea[3], Y Meng[4] and M McMahon[2]

[1]Atomic Weapons Establishment (AWE), UK, [2]The University of Edinburgh, UK, [3]Universidad de Valencia, Spain, [4]Carnegie Institution of Washington, USA

The simple electronic structure of Mg makes it attractive as a test case in obtaining a full understanding of the high-density behaviour of the low-Z group I and II elements. Mg is hcp at ambient conditions and melts at around 922 K at ambient pressure (AP). It is the only Group I or II metal that does not melt from the bcc phase at AP [1]. However, the high-pressure high-temperature (HP-HT) structural sequence in Mg is still uncertain. Calculations predict an hcp-bcc phase boundary with a negative slope, meeting the melt curve at a triple point in the region of 4 GPa and 1200 K [1-5]. An energy-dispersive X-ray diffraction study found evidence of a HT dhcp phase above 7.5 GPa [6], and the new hcp-dhcp phase boundary was estimated to intercept the melt curve at around 7.5 GPa and 1350 K. It is then possible that at high P, the hcp → dhcp transition occurs at 300 K, before the stability of the bcc phase is reached, or that an hcp-dhcp-bcc triple point exists in the solid at a temperature below melting [6]. We have performed new calculations and conducted a number of HP-HT experiments using diamond anvil cells, angle-dispersive X-ray diffraction, and double-sided laser heating at the high-pressure beamline 16-IDB at the Advanced Photon Source synchrotron in Chicago. For the first time, our studies reveal the nature of the solid to liquid transformations in Mg and provide unequivocal evidence for the structural sequence in Mg at HP-HT.

[1] J. D. Althoff et al, Phys. Rev. B 48, 13253 (1993).
[2] S. Mehta et al, J. Chem. Phys. 125, 194507 (2006).
[3] F. Jona and P. M. Marcus, J. Phys.: Condens. Matter 15, 7727 (2003).
[4] Q. Liu et al, J. App. Phys. 105, 123505 (2009).
[5] G. V. Sin'ko and N. A. Smirnov, Phys. Rev. B 80, 104113 (2009).
[6] D. Errandonea et al, J. Phys.: Condens. Matter 15, 1277 (2003).

Structure of liquid potassium under pressure

E McBride, G Stinton and M McMahon

The University of Edinburgh, UK

Anomalous melting has been observed in the alkali elements, first in Rb and caesium Cs[1], then more recently in Na[2], Li[3] and K[4]. At extreme compressions all the alkali elements transform to open-packed complex structures, such as the incommensurate host-guest structure observed in Na, K and Rb[5,6]. Na has a remarkable melting curve; it rises to a maximum of 1000 K at 35 GPa, before decreasing to a minimum of ~300 K at 118 GPa. The melting temperature then increases rapidly above this pressure.

Raty et al.[7] have shown from ab initio calculations that this unusual behaviour in the melting temperature arises from a sequence of structural and electronic transitions in the liquid. Confirmation of this would require a structural study at pressure and temperature conditions at the extreme limit of current capabilities. However, the striking similarity of the melting curves of K and Na[2,4] indicate that K is an ideal model system for studying this phenomenon, but at more experimentally accessible pressure and temperature conditions.

We have conducted an in situ x-ray diffraction study utilising diamond anvil cells and external resistive heating to study the change in co-ordination number of liquid-K with increasing pressure. Our results indicate that structural changes are occurring in the liquid, similar to those in the underlying solid, but at lower pressures.

[1] Boehler & Zha, Physica B+C, 139-140, 233, (1986).
[2] Gregoryanz, et al., Phys. Rev. Lett., 94, 185502 (2005).
[3] Guillaume, et al., Nature Physics 7, 211 (2011).
[4] Narygina, et al., Phys. Rev. B, 84, 054111 (2011).
[5] Gregoryanz, et al., Science, 320, 1054 (2008).
[6] McMahon & R.J. Nelmes, Chem. Soc. Rev. 35, 943 (2006).
[7] Raty, et al., Nature, 449, 448 (2007).

Metal hydrides at extreme conditions: A review

T Scheler, C Guillaume, R Howie and E Gregoryanz

The University of Edinburgh, UK

The application of extreme conditions offers a general route for the synthesis of materials under thermodynamic equilibrium. By finely tuning the thermodynamic variables of pressure and temperature one can manipulate matter on an atomic scale, creating novel compounds or improve the properties of existing materials. In particular, the study of hydrogen and hydrogen alloys has attracted the attention of researchers in the past. Although hydrogen reacts readily with many materials at ambient conditions, a significant "hydride hole" is apparent in the periodic table covering most of the transition metals between the chromium and copper group elements. At elevated pressures however, the chemical potential of hydrogen rises steeply and the hydrogen molecules eventually overcome the dissociation barrier on the metal surface. Atomic hydrogen diffuses into the metal to occupy available interstitial sites, forming a binary metal hydride and significantly altering the material's physical properties. Effects include increased toughness, structural phase transitions accompanied by drastic changes in the microstructure and hydrogen mediated superconductivity. Most of the d-metals have been found to exhibit hydride phases under certain conditions. However, besides rhenium, the 6th row metals between tungsten and gold, as well as silver, have long eluded the formation of a bulk hydride.

Here, we present a review of our most recent advancements and discoveries in the field of metal hydrides at extreme conditions. Synchrotron based in-situ x-ray diffraction techniques were used to study novel structures, their equation of state and, in combination with transmission electron microscopy, microstructure. Particular emphasis will be on the discoveries of the elusive hydrides of the 6th row elements.

Low temperature physics 4

Angular dependence of the flux lattice phase diagram in $YBa_2Cu_3O_7$ up to 17 T

A Cameron[1], E Forgan[1], A Holmes[1], E Blackburn[1], J White[2] and T Loew[3]

[1]University of Birmingham, UK, [2]Paul Scherrer Institut, Germany, [3]Max Planck Institut, Germany

The intrinsic vortex lattice (VL) structure in $YBa_2Cu_3O_7$ has recently been established as a function of field up to 16 T[1], for applied field perpendicular to the CuO_2 plains. The field dependent VL distortions and phase transitions that have been observed [2] are clearly being driven by underlying anisotropies in the material. However,it is not fully evident whether it is mainly Fermi surface or d-wave gap anisotropy that is responsible. Furthermore, the field dependence of superconducting states arising from the Cu-O chains remains unclear. By rotating the angle of the applied field away from the parallel configuration with the c-axis we have changed the anisotropy experienced by the VL in a controlled fashion, providing much more information about the driving force behind the structural changes of the VL.

We found the behavior of the rhombic phase with the field applied at angles up to 45 degrees to the c-axis to be analogous to the behavior with B applied parallel to c – the structural evolution of the rhombic phase continues up to 16 T, passing through a square structure with no sign of a lock-in transition. However, the precise structural configuration is seen to be different, with the structure of the VL distorting as a function of angle between the c-axis and applied field. This highlights the angle dependence of the anisotropies that govern the structure of the VL.

[1] A. S. Cameron et al., “High Field SANS measurements of the structure and melting of the Vortex Lattice in $YBa_2Cu_3O_7$”, submitted to Phys. Rev. Lett. (2012).

[2] J. S. White et al., Phys. Rev. B 84, 104519 (2011).

Vortex imaging and flux penetration in mesoscopic Sr_2RuO_4 structures

P Curran[1], W Desoky[1], S Bending[1], A Gibbs[2], S Lee[2] and A Mackenzie[2]

[1]University of Bath, UK, [2]University of St Andrews, UK

Superconductivity in nearly all known conventional and unconventional materials involves electrons with spin singlet (S=0) pairing. The search for spin triplet (S=1) superconductors has been the subject of intense research activity for many years, with the hope that this could lead to a better understanding of the microscopic mechanisms giving rise to superconductivity. In recent years a wide range of experiments on strontium ruthenate single crystals has strongly indicated that it is a spin triplet superconductor with an exotic chiral order parameter [1]. Here we present scanning Hall probe investigations of mesoscopic disks, fabricated on the surface of high quality single crystals. Such structures are expected to provide suitable conditions for the formation of spontaneous edge supercurrents, predicted by current theory as a signature of chiral pairing. We find no evidence for such spontaneous supercurrents in our samples, in direct contradiction with current expectations, but we do observe several highly anomalous magnetic behaviours. The mesostructures dominate the observed vortex patterns, with complete disruption of the square vortex lattice seen previously in this material [2] leading to vortex ring formation inside the largest mesas. In fact, first penetration of vortices into the mesoscopic structures occurs at surprisingly large fields and we also continue to see very strong diamagnetic screening up to remarkably high fields where magnetic contrast would normally be lost. The implications of the spontaneous supercurrent null result and all the unusual new magnetic features will be discussed.

[1] Mackenzie A P and Maeno Y, Rev. Mod. Phys. 75, 657 (2003).

[2] Curran P J *et al*. Phys. Rev. B. 84, 104507 (2011).

Orbital magnetization and the Berry curvature in the superconducting triplet state of $\mathrm{Sr_2RuO_4}$

M Gradhand, J F Annett and B L Györffy

University of Bristol, UK

The strong experimental evidence of spin triplet pairing in the superconducting phase of $\mathrm{Sr_2RuO_4}$ prompts an interest in a detailed material dependent study of orbital magnetization in this exotic superconductor.[1] The spontaneous breaking of time reversal symmetry in the superconducting state will cause new contributions to the Berry curvature. As has been shown recently, such curvatures plays an important role in the orbital magnetization of normal metals. Here we are exploring its consequences for the corresponding phenomena in superconductors.

We present first principles as well as tight binding calculations of the Berry curvature in the normal state of $\mathrm{Sr_2RuO_4}$. The spin-orbit coupling is an essential ingredient of the problem and will be considered in both approaches. [2] Furthermore, the tight-binding model is used to solve the Bogolubov-de Gennes equation [3] which accounts for the superconducting phase with triplet pairing. The new contributions to the Berry curvature arising from the k-dependent gap function will be discussed.

[1] Y. Maeno et al. Phys. Today 54 (1), 42 (2001).
[2] M. Gradhand et al. Phys. Rev. B 84, 075113 (2011).
[3] J.F. Annett et al. Phys. Rev. B 66, 134514 (2002).

Effect of charge order on the plasmon dispersion in transition-metal dichalcogenides investigated by electron energy-loss spectroscopy

A König[1], J van Wezel[2], R Schuster[1], M Knupfer[1], H Berger[3], J van den Brink[1] and B Büchner[1]

[1]IFW Dresden, Germany, [2]Argonne National Laboratory, USA, [3]Institut de Physique de la Matière Condensée, Switzerland

2H-$\mathrm{TaSe_2}$ is one of the various polytypes of the transition-metal dichalchogenides (TMDC) that show phase transitions to a charge-density wave (CDW) and to a superconducting state upon cooling. It is already proven for *2H*-$\mathrm{TaSe_2}$ [1] and a few other TMDCs that they show a negative dispersion of the bulk plasmon energy in the normal state and an even larger bandwidth of this negative dispersion in the CDW state, which is altogether not a behavior of a common metal.

We discuss the connection of the susceptibility to a CDW phase and of the negative plasmon dispersion by applying Electron Energy-Loss Spectroscopy (EELS) measurements in transmission on thin films of *2H*-$\mathrm{TaSe_2}$. Intercalation experiments with potassium that show a suppression of the CDW and a change of slope of the plasmon dispersion as well as a semiclassical Ginzburg-Landau approach [2] emphasize the connection of the different low temperature phases.

[1] Schuster et al., Phys. Rev. B 79, 045134 (2009).
[2] Van Wezel et al., Phys. Rev. Lett. 107, 176404 (2011).

Spin fluctuations and the Lifshitz transition in ferromagnetic superconductor $\mathrm{UGe_2}$

D Sokolov[1], R Ritz[2], C Pfleiderer[2], T Keller[3] and A Huxley[1]

[1]The University of Edinburgh, UK, [2]TUM, Germany, [3]FRM2, MPI Stuttgart, Germany

We present high resolution measurements of the lattice constants of $\mathrm{UGe_2}$ under pressure probed by a novel technique that utilizes Larmor precession of polarized neutrons to surpass the resolution of conventional scattering methods by an order of magnitude. At low temperature UGe_2 is ferromagnetic up to critical pressure p_c but superconductivity is peaked at a lower pressure p_x coinciding with a less understood transition within the ferromagnetic state [1]. At ambient pressure we observed sharp anomalies in the lattice parameters at the Curie temperature, T_{Curie}. At higher pressure sharp anomalies in the lattice parameters at both T_{Curie} and T_X (the characteristic temperature for the transition that occurs at p_x) shift to lower temperatures in agreement with the known phase diagram.

We show that the electronic part of the thermal expansion is dominated by the contribution due to the ordered moment in accord with the spin fluctuation theory at $p<p_x$, however at $p{\sim}p_x$ we identify an additional contribution to the thermal expansion due to fluctuating moment associated with the metamagnetic transition at T_X. At pressure near p_X and temperatures above T_{Curie} we observed positive contribution to the thermal expansion along the a and c axes of the orthorhombic structure of $UGe_{2,}$ most likely originating from the pressure driven Lifshitz transition[2] in the quasi-two-dimensional Fermi surface. We discuss the role of the Lifshitz transition and a plausible Kondo lattice scenario in stabilising superconductivity in ferromagnetic state.

[1] S. S. Saxena, et al., Nature 406, 587 (2000).
[2] I. M. Lifshitz, Sov. Phys. JETP 11, 1130 (1960).

(invited) Quantum magneto-transport of a 2DEG at a complex oxide interface

S Gariglio[1], A Fête[1], D Stornaiuolo[1], D Li[1], A D Caviglia[1], B Sacepe[1], A F Morpurgo[1], M Gabay[2], D Fontaine[3], P Ghosez[3], M Reinle-Schmitt[4], C Cancellieri[4], P Willmott[4] and J-M Triscone[1]

[1]University of Geneva, Switzerland, [2]Université Paris-Sud, France, [3]Université de Liège, Belgium, [4]Swiss Light Source, Paul Scherrer Institut, Switzerland

Interfaces between complex oxides are emerging as one of the most exciting systems in condensed-matter physics [1]. The interface between the band insulators $LaAlO_3$ (LAO) and $SrTiO_3$(STO) provides a remarkable illustration [2], displaying a two-dimensional electron gas (2DEG)[3] and superconductivity [4].

I will first discuss recent experiments aimed at determining the physical mechanism that induces the electron gas at the LAO/STO interface. Then I will present quantum magnetoresistance oscillations in devices exhibiting high electron mobility provided by recent progress in sample growth. I will conclude reporting on nanostructures where mesoscopic effects of phase-coherent transport have been observed. These progresses in carrier mobility and nanostructuring open the way to the observation of mesoscopic and 2D Landau-level physics in a new range of physical parameters (effective mass, g-factor, spin-orbit coupling, electron density).

[1] P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, J.-M. Triscone, Annu. Rev. Condens. Matter Phys. 2, 141 (2011).
[2] A. Ohtomo, H. Y. Hwang, Nature 427, 423 (2004).
[3] A.D. Caviglia et al., Phys. Rev. Lett. 105, 236802 (2010).
[4] N. Reyren et al., Science 317, 1197 (2007).

Determination of the electron-phonon coupling in ultra-thin Pb films with STM

M Schackert[1], F Frech[1], T Märkl[1], W Wulfhekel[1], S Ostanin[2], M Hölzer[2] and A Ernst[2]

[1]Karlsruhe Institute of Technology (KIT), Germany, [2]Max Planck Institute of Microstructure Physics, Germany

In conventional superconductors, Cooper pairs form due to electron-electron interaction via virtual phonon exchange. A central quantity in this process is the effective electron-phonon coupling, also known as Éliashberg function which determines the superconducting properties of the material. It can be measured by means of electron tunneling spectroscopy in the superconducting state and inversion of the Éliashberg equations or directly using inelastic tunneling spectroscopy (ITS) in the normal conducting state.

We used scanning tunneling microscopy (STM) at 720 mK in UHV to locally measure inelastic tunneling spectra of thin Pb films on different substrates in order to determine the effective electron-phonon coupling in dependance of the local Pb thickness. The films were prepared in situ with varying thickness up to 25 atomic layers. When the films are in the normal conducting state, for instance due to the proximity effect, STM-ITS reveals the expected shape of the effective electron-phonon spectrum and we find a good agreement with ab initio calculations.

Pb/Si nanoislands: structure and confined superconductivity

D Fokin[1], L Serrier-Garcia[2], T Cren[2], F Debontridder[2], S Bozhko[1] and D Roditchev[2]

[1]Joint Institute for High Temperatures RAS, Russia, [2]Universite Pierre et Marie Curie Paris, France

We report the study of the quantum confinement effects in superconductivity by means of the scanning tunnelling microscopy (STM) and spectroscopy (STS). The experiments were carried out in ultrahigh vacuum and on in-situ grown Pb-nanosized islands. The superconducting phase diagram of the nanostructures was probed at low and very low temperatures down to 280 mK and in the magnetic field up to 2 Tesla.

First, the growth of the nanometer size lead islands on the atomically clean surface of Si(111), and as well on vicinal Si(557), was studied in details. The STM data showed that while in general the growth at room temperature follows the Stransky-Krastanov scenario, the Pb-islands may have peculiar form and pancake-like layered structure that reflects the minimization of the total electron energy that includes the electron quantum confinement terms. The Pb electronic growth mode is realized in the case of homoepitaxy.

Second, the superconductive properties of individual Pb islands were probed by STM/STS at low temperature. Among many studied samples, the chosen island, of the lateral size L=110 nm, is in so called strong confinement regime: $L \sim 3\xi_{eff} << \lambda_{eff}$, where ξ_{eff} and λ_{eff} are respectively the effective coherence and penetration lengths. The STS data directly reveal that the superconducting phase diagram of such island in the magnetic field contains only three quantum states: a vortex-less (Meissner) state in low fields, a single vortex state in the intermediate fields, and the normal state at the fields above 0.5 T. Thus, the studied case corresponds to an interesting boundary in the phase diagram of confined superconductivity: The islands of a larger size accept the multi-vortex superconducting configurations, while the vortex state becomes energetically impossible for smaller islands, as we experimentally show.

Bulk thermodynamic signatures of topological transitions in superconductors

B Mazidian[1], J F Annett[1], J Quintanilla[2] and A D Hillier[3]

[1]University of Bristol, UK, [2]University of Kent, UK, [3]ISIS, UK

Superconductors which lack inversion often exhibit unconventional behaviour. This is thought to arise in such systems as a result of the admixture of singlet and triplet pairing on the superconducting gap via spin-orbit coupling (SOC). The available pairing symmetries for any superconductor can be classified by a group theoretical analysis of the crystal point group. Here we present the symmetry allowed order parameters for each irrep of the non-centrosymmetric (NCS) cubic group O. This point group describes the crystal structure of the superconductors $LiPd_xPt_{3-x}B$, where the strength of SOC, and therefore the degree of triplet admixture can be continuously tuned by doping, and the more recently discovered Mo_3Al_2C, whose pairing symmetry is at present unclear.

Furthermore, we present a detailed analysis of the possible gap-node topologies allowed by a triplet admixture with the full symmetry of the lattice. We find that 2 distinct point node topologies are possible, as well as related line nodes and fully-gapped states. There are topological transitions between these states. We compute the low temperature specific heat and find that some of these topological transitions are signalled by anomalous power-law dependencies.

Liquids and liquid interfaces 3

(invited) Electrolyte gating: In-situ STS and Raman Studies with single molecules and molecular ensembles

T Wandlowski

University of Bern, Switzerland

The electron transport through molecules has received great attention since organic structures have been considered as the active part in electronic nanoscale devices[1]. Different experimental set-ups allowed integrating single molecules and nanocrystals in electronic circuits. Examples are mechanically controlled break junctions (MCBJ) or scanning tunneling probes based break junctions which enabled basic investigations of correlations between molecular structures and transport properties on a single molecule level under UHV conditions at low and ambient temperatures, but also at electrified solid/liquid interfaces. The latter allow applying the concept of “electrolyte gating” in a transistor-analog configuration. These studies depend, among others, on parameters such as (i) the formation of a reproducible and stable contact between the tailored molecule and both metal electrodes, (ii) the structure and the conformation of the bridging molecule and (iii) the algorithms used for the analysis of the raw data[1,2].

In this talk we will focus on single molecule electron transport studies in Au│molecule (cluster)│Au junctions in an STM configuration under electrochemical conditions. Employing the concept of “electrolyte gating” we will describe four examples: orientational change[1], conformational change[3], redox-mediated electron transfer[4,5] as well as single cluster quantized charging[5]. The experimental data will be compared with simulations based on the phenomenological theory of electron transfer.

In an attempt to obtain structure information on nanoscale tunneling junctions we will also discuss our first results in combining gap-mode Raman spectroscopy[3,6] and single molecule electron transport experiments. The talk will conclude with a perspective outlook.

[1] C.Li, A.Mishchenko, Th.Wandlowski, Topics in Current Chemistry. 2012, 313, 121.
[2] C.Li, A.Mishchenko, I.Pobelov, Th.Wandlowski, Chimia. 2010, 64, 383.
[3] L.Cui, B.Liu, Th.Wandlowski, J. Am. Chem. Soc. 2011, 133, 7332.
[4] A.Mishchenko, M.Abdulla, A.Rudnev, Y.Fu, A.R.Pike, Th.Wandlowski, Chem. Commun. 2011, 47, 9807.
[5] Z.Li, Y.Liu, S.F.L.Mertens, I.Pobelov, Th.Wandlowski, J. Am. Chem. Soc. 2010, 132, 8187.
[6] B.Liu, Th.Wandlowski, ACS Nano, 2011, 5, 5662.

The early stage of corrosion of Cu_3Au alloy

J Zegenhagen[1], P Rajput[1], C Meneghini[2], A Gupta[3], G Sharma[3] and B Detlefs[1]

[1]ESRF, France, [2]Dipatimento di Fisica,Universita di Roma Tre, Italy, [3]UGC-DAE consortium, India

Metallic alloys are important in our daily life and in industry, but unfortunately highly susceptible to corrosion in wet environment. De-alloying is a particular type of corrosion, attacking alloys which are composed of metals of different “nobility”. When coming into contact with an electrolyte, the less noble metal may go into solution, typically causing crack formation and subsequent material failure upon stress. Potential controlled corrosion of a well ordered Cu_3Au crystal in sulfuric acid had been investigated in situ [1] showing that, far below the critical potential E_c, at which the alloy is massively dissolved, Cu goes into solution, leaving a ≈ 1 nm thick film of small, Au-rich clusters. Just below E_c, the surface is eventually covered with about 10-20 nm large gold islands with a thickness of 2-3 nm. The Au-rich surface protects the bulk of the alloy against further corrosion (unless E_c is exceeded).

We used, hard x-ray photoelectron spectroscopy (HAXPES), x-ray standing waves (XSW) and depth-selective x-ray absorption fine structure (XAFS) to investigate the very early stages of the corrosion of a more ‘realistic’, disordered CuAu binary alloy. Ultra-thin Cu_xAu films (2.5 nm, $x \approx 3$) were deposited on a Ru/B_4C multilayer to produce the XSW field. The XSW study provides detailed information about the concentration profile of Cu and Au upon de-alloying. HAXPES provides the binding energies (oxidation states) of Au and Cu and XAFS reveals the local atomic structure around Cu and Au.

The pristine Cu_3Au film appeared partially oxidized (CuO and Cu_2O). After de-alloying at 245 mV for 2 min in 0.1 M H_2SO_4, the partial Cu dissolution leads to the formation of a Au-rich film with $CuAu_3$-like composition. Quantitative XRF analysis showed that, surprisingly, even below $E_c$de-alloying leads to the loss of some Au as well.

[1] F. U. Renner, A. Stierle, H. Dosch, T. L. Lee, D. M. Kolb, J. Zegenhagen, Nature 439, 707 (2006).

Microstructure and magnetic properties of ultrathin Ni/Cu(100) fabricated in an electrolytic condition

J-S Tsay, C-L Lin, A-W Wu and Y-C Wang

National Taiwan Normal University, Taiwan

Microstructure and magnetic properties of ultrathin Ni/Cu(100) prepared by way of electrochemical approaches are investigated using STM and MOKE techniques. In a pure supporting electrolyte of hydrochloride acid, chloride anions form a highly ordered c(2x2)-Cl adlayer on Cu(100) [1]. After adding $NiCl_2$, the hydrogen evolution reaction (HER) is advanced to a more positive potential. No under potential deposition is found for the adsorption of Ni on Cu(100) [2]. The HER and the Ni deposition occur simultaneously on the Cu(100) electrode. Nickel atoms initially attach onto the steps and the surface shows single atomic steps. Straight step edges are observed in the STM image and it exhibits layer-by-layer growth. As the coverage of Ni increases, large amount of clusters form on the surface due to the condensation of Ni atoms. For Ni thinner than 2 ML, no magnetic hysteresis is observed due to the lowered Curie temperature for ultrathin overlayers. As the Ni coverage increases, the first hysteresis loop is observed around 2 ML with in-plane anisotropy of the films. In the presence of Pb^{2+} ions, the squareness of the magnetic hysteresis loops is enhanced and STM shows smoother interfaces of the Ni films confirming the surfactant effects of the Pb additives.

[1] S.L. Tsay, J.S. Tsay, T.Y. Fu, P. Broekmann, T. Sagara, and K. Wandelt, Phys. Chem. Chem. Phys. 12 (2010) 14950.
[2] P.Y. Yen, S.Z. Chen, H.L. Tu, H.L. Wu, S.L. Yau, and J.S.Tsay, J. Phys. Chem. C 115 (2011)23802.

Effect of alkali metal cations on the surface oxidation of Pt(111)

M Nakamura[1], Y Nakajima[1], N Hoshi[1] and O Sakata[2]

[1]Chiba University, Japan, [2]National Institute for Materials Science, Japan

Structure and physical properties of the electrical double layer at the solid liquid interface are attractive research subjects for fundamental electrochemistry and electrochemical industry. The spatial distribution of ionic species in the electrochemical double layer is different from that in the bulk phase remarkably. It was revealed that the cationic species in the outer Helmholtz plane (OHP) affect electrochemical reactions remarkably [1], but the structure and the potential dependence have been controversial for decades. Recently, we have successfully determined the detailed OHP structure of cationic layer above Ag(100) using surface X-ray diffraction [2]. In this study, we investigate the interface structure of Pt(111) in alkaline solution containing Cs and Li cations using X-ray diffraction.

X-ray diffraction measurements were performed with a multi-axis diffractometer at BL13XU (SPring-8). X-ray energy was 12.4 keV. Electrolyte solution was 0.1 M CsOH and LiOH. We measured the specular crystal truncation rod (CTR) of Pt(111) between 0.2 and 1.2 V vs RHE. Structural analysis indicates that Li^+ strongly protects surface flatness against oxidation. Although the OHP Cs^+ is localized at the nearest neighbor sites of adsorbed oxygen species (water, OH_{ad}, O_{ad}), the protective effect of Cs^+ is weaker than that of Li^+.

[1] D. Strmcnik et al. Nature Chem., 1 (2009) 466.
[2] M. Nakamura et al. ChemPhysChem, 12 (2011) 1430.

(invited) From Structure to function: Towards an atomistic understanding of the action of additives relevant for the Damascene and TSV copper plating

P Broekmann[1], A Fluegel[2], M Arnold[2], D Mayer[2], F Simona[1] and M Cascella[1]

[1]University of Bern, Switzerland, [2]BASF SE, Germany

Copper electrodeposition is of paramount importance for today’s fabrication of integrated circuits. The fill of small, nm-sized Damascene features and the fill of large, µm-sized Through Silicon Vias (TSVs) rely both on the super-conformal growth of copper involving an “accelerated” copper electrodeposition at the feature bottom with respect to the “suppressed” deposition at the wafer surface and the upper side walls of those features. Such non-uniformity in the local reaction velocity is typically achieved by the non-uniform distribution of suppressor additives and their specific antagonists inside and outside the feature. Transport and adsorption kinetics in combination with shape evolution phenomena at the feature bottom have been identified as physical origin for the required non-uniformity in the local additive surface coverage. Successful superfill is achieved only when the non-uniformity in the additive surface coverage is maintained over the complete fill process. Considering the different time-scales in the processing of sub-50nm Damascene features and mm-sized 3D-TSVs it appears crucial to take the time dependence of the structural stability of those suppressor ensembles into account.

It is the general aim of this contribution to discuss different strategies from chemistry and electrochemistry side in order to achieve such non-uniformity in the surface additive distribution tailored for different time scales. Suppressor concepts commonly used for Damascene processing are typically not well suited for 3D-TSV plating due to the temporal instability of the PEG/Cl suppressor ensemble. The time-scale of the PEG/Cl deactivation from electrolyte side is too short for the 3D-TSV plating. It is the particular aim of this contribution to discuss alternative plating routes towards superfill effects for 3D-TSV plating that rely on chemistries taking advantage of anion-cation pairing effects, hydrophobic interactions and Cu(I) coordination chemistry. A molecular scale understanding of the complex additive surface chemistry is achieved by a combination od in situ STM, XPS, chronopotentiometry, DFT and cross-sectional FIB.

A spectroelectrochemical study of the redox and photochemical functionality of the spiropyran-merocyanine molecular switch in solution and in self-assembled monolayers

O Ivashenko, J van Herpt, B Feringa, W Browne and P Rudolf

University of Groningen, The Netherlands

Photochromic and redox active spiropyran based systems undergo substantial changes in polarity and dipole moment upon switching and have found numerous applications in a wide range of novel smart materials, photonic devices and logic units. Under ambient conditions spiropyrans are in the ring-closed form (SP) in solution and as solids, with negligible amounts of the ring-open merocyanine (MC) form. The equilibrium between the states can be perturbed photochemically, electrochemically, thermally and by solvent or pH changes. Here we report a spectroelectrochemical study of the redox driven ring opening of the spiropyrans in solution and in SAMs on Au electrodes. Using cyclic voltammetry together with UV/Vis absorption and Raman/SERS spectroscopies we demonstrate the formation of intermediate ring-open (MC) species (e.g. (semi-)quinonodial) and propose a mechanism for oxidative SP-ring opening in solution. SAMs of spiropyrans formed on gold electrodes retain their photochromic and electrochromic properties and can be reversibly addressed electrochemically or with irradiation with UV/Vis light or via two photon absorption of NIR light. The spectroelectrochemical results obtained indicate that the solution chemistry of the SP/MC switching system is retained in SAMs and give insight into the properties of spiropyran and merocyanine forms and their response under light/potential stimuli. These results indicate opportunities for further utilization and development of this popular compound in smart materials.

An all-inorganic responsive surface: reversible electrochemical contact angle switching of hexagonal boron nitride nanomesh

S F L Mertens[1], S Muff[2], A Hemmi[2], R Küng[2], S De Feyter[1], J Osterwalder[2] and T Greber[2]

[1]KU Leuven, Germany, [2]Universität Zürich, Germany

The nanomesh superstructure formed by a monolayer of hexagonal boron nitride (*h*-BN) on Rh(111) holds great promise for supramolecular ordering [1] and other nanoscale phenomena. In this work, we have studied the dynamic contact angle at the interface between *h*-BN/Rh(111) and an electrolyte as a function of the electrochemical potential. We observe a strong effect on the contact angle in the potential region where hydrogen adsorption occurs on Rh(111) [2]. By analogy with observations in vacuum, we propose that this macroscopic effect is caused by nanotexture switching within the 3-nm unit cell of the nanomesh, as hydrogen intercalation flattens the sp^2 hybridized boron nitride layer [3]. The changes in dynamic contact angle of the electrolyte were observed *in situ* using a 3-electrode setup, and were fully reversible under electrochemical control. To our knowledge, this system represents one of the first all-inorganic responsive surfaces.

[1] Berner *et al. Angew. Chem. Int. Ed.* 2007, 46, 5115.
[2] Widmer *et al. Electrochem. Commun.* 2007, 9, 2484.
[3] Brugger *et al. Angew. Chem. Int. Ed.* 2010, 49, 6120.

To mix or not to mix: 2D crystallization and mixing behavior of saturated and unsaturated aliphatic primary amides

K Mali[1], B Van Averbeke[2], T Bhinde[3], A Brewer[3], T Arnold[4], R Lazzaroni[2], S Clarke[3] and S De Feyter[1]

[1]KU Leuven, Germany, [2]Université de Mons, Belgium, [3]University of Cambridge, UK, [4]DIAMOND Light Source Ltd., UK

Physisorbed monolayers based on relatively weak noncovalent interactions serve as excellent model systems for understanding crystallization of materials in reduced dimensionality. We have employed a combination of scanning tunneling microscopy (STM), differential scanning calorimetry (DSC) and computational modeling to reveal two dimensional (2D) crystallization and mixing behavior of saturated and unsaturated aliphatic primary amides. STM reveals, at sub–molecular resolution, the adsorption as well as the two-component 2D phase behavior of these molecules at the liquid–solid interface. Saturated and trans–unsaturated amides exhibit random mixing in view of their size and shape complementarity. Binary mixtures of linear saturated and bent cis–unsaturated amides on the other hand, display unprecedented mixing behavior. These molecules are found to mix surprisingly better at the liquid–solid interface than might have been expected on account of the dissimilarity in their shapes. Strong, directional hydrogen bonding interactions and the relative stabilization energies of the adlayers are responsible for such unusual mixing behavior. Computational modeling provides additional insight into the possible interactions in 2D assemblies and their impact on stabilization energies of the supramolecular networks. This study provides a model for understanding the effect of nanoscale cocrystallization on the thin film structure at interfaces and demonstrates the importance of molecular geometry and hydrogen bonding in determining the coadsorption behavior.[1]

[1] To Mix or Not to Mix: 2D Crystallization and Mixing Behaviour of Saturated and Unsaturated Aliphatic Primary Amides K. S. Mali, B. Van Averbeke, T. Bhinde, A. Y. Brewer, T. Arnold, R. Lazzaroni, S. Clarke and Steven De Feyter ACS Nano 2011, 5, 9122.

Surface structure 2

(invited) Quantitative adsorbate structure determination v. STM imaging; some examples

P Woodruff

The University of Warwick, UK

STM images of adsorbate systems can provide invaluable information on local ordering and possible structural models, yet they can also be very misleading if not interpreted with extreme caution, and can rarely (if ever) provide quantitative surface structure determination. A few examples of these problems, as well as of the positive complementarity of STM and true quantitative structural methods, will be given, comparing the quantitative information provided by scanned-energy mode photoelectron diffraction (PhD) with information contained in STM images. Examples include the structure of the C-induced surface reconstruction on Ni(100) and of the methoxy species, CH_3O-, on Cu(110). The importance of adsorbate-substrate bondlength information, not accessible in STM, will also be stressed. Finally, the role of quantitative structure determination in understanding water dissociation on the perfect rutile TiO_2(110) surface will be discussed.

Oxygen-induced Structural Changes in the Chiral Pt{531} Surface

C Nicklin[1], A Cornish[2], R Nicklin[2], J Rawle[1], I Robinson[3] and G Held[2]

[1]Diamond Light Source Ltd, UK, [2]University of Reading, UK, [3]University College London, UK

A possible route to enantioselective heterogeneous catalysis is the use of chiral surfaces as catalysts. Such surfaces have been shown to exhibit enantioselectivity [1] although they are also relatively unstable and likely to reconstruct [2]. Their interaction with simple adsorbates can be dramatically different to that with non-chiral, low Miller index surfaces on which the majority of surface science investigations focus [3]. Here, we present a study focusing on the structural modifications that occur on a Pt{531} surface in the presence of a simple adsorbate, oxygen.

The oxygen induced restructuring of the chiral Pt{531} surface was studied using surface X-ray diffraction (SXRD) at Beamline I07 of Diamond Light Source. The intensities along several crystal truncation rods (CTRs) were measured whilst the Pt{531} sample was held inside a small ultra-high vacuum (UHV) chamber. The sample was exposed to pressures of oxygen in the 10^{-7} mbar range and CO was used to remove the reconstruction.

The intensity at positions away from the bulk Bragg peaks show large variations depending on the sample surface morphology; which can be explained by a roughening transition ultimately resulting in facets, when the Pt{531} is annealed in oxygen. Annealing in a CO environment acts to smooth the surface. We will present fits to the data from a variety of models that establish the surface roughness and relaxation that occurs during this reordering of the surface. Additional data using low energy electron diffraction and X-ray photoelectron spectroscopy will be presented to provide complimentary evidence of the state of the surface.

[1] G. Held and M.J. Gladys. Top Catal, 48 (2008) 128.
[2] S. R. Puisto, G. Held, and D.A. King. Phys Rev Lett, 95 (2005) 036102.
[3] G. Held, L.B. Jones, E.A. Seddon, and D.A. King, J. Phys Chem B. 109 (2005) 6159.

Strategies for improving the precision and accuracy of LEED-IV structural analysis

Z V Zheleva and G Held

University of Reading, UK

LEED-IV structural analysis is one of the most powerful tools for surface structural analysis but, with a few exceptions [1,2], so far it is limited to adsorption structures of small molecules or atoms with small unit cells. While in the early days of LEED-IV analysis this limitation was imposed by the available computer power, the main limitations now are the size and quality of the experimental data set. We will discuss strategies of improving the data set and modifications to the standard LEED codes that are necessary in order to make full use of these improvements. The size of the data set can be increased by either extending the energy range to higher kinetic energies or by collecting data at multiple angles of incidence. The latter approach has the advantage that the symmetry is reduced at most off-normal angles and, hence, the data set of independent IV curves is additionally increased [3,4].

Improving the quality, i.e. signal-to-noise, of experimental IV curves is often hampered by the fact that molecular adsorbates are easily damaged by the electron beam and poorly ordered. Low-current LEED systems are a major improvement for beam-sensitive adsorbates. In some cases, the local structure of poorly ordered systems can be determined by only using the integer-order beams for the analysis. The limitations of this approach will be discussed.

[1] H.I. Li et al., PRL 103, 056101 (2009)
[2] Moritz et al., PRL, 105, (2010).
[3] Z. V. Zheleva, et al. J. Phys. Chem. C 116, 618 (2012)
[4] S. Karakatsani, et al. Surf. Sci. 606, 383 (2012).

Atomically precise adsorption site determination of trithiolate on Cu(111): A combined quantitative low-energy-electron-diffraction and density functional theory study

T Sirtl[1], J Jelic[1], J Meyer[1], W Moritz[2], W M Heckl[3], K Reuter[1] and M Lackinger[4]

[1]Technical University Munich, Germany, [2]Ludwig-Maximilians-Universität, Germany, [3]Technical University and Deutsches Museum, Germany, [4]Deutsches Museum, Germany

The facile structure determination of surface-supported organic structures in real space by STM is intriguing due its simplicity, especially for larger molecules, whose footprint can clearly be recognized. However, this widespread method is not capable of revealing precise structural details as adsorption sites, atomic heights above the substrate, or molecular deformations. This shortcoming is ideally overcome by the combination of quantitative LEED studies that provide contentful experimental data and state of the art DFT calculations. Detailed comparison allows not only to deduce structural details, but also to evaluate recent developments in DFT simulations.

We present a study of the aromatic trithiol molecule 1,3,5-tris(4-mercaptophenyl)benzene on Cu(111). Previous STM experiments revealed a long-range ordered trigonal $(3\sqrt{3}x3\sqrt{3})R30°$ superstructure with a lattice parameter of 1.30 nm. Both the submolecular STM contrast and chemical intuition indicate covalent anchoring through the three peripheral thiolate groups, yet further atomistic details are not accessible. Based on the STM data and symmetry of the LEED pattern, six different adsorption sites that are consistent with the experimentally known molecular orientation were considered and optimized by both quantitative LEED and DFT studies. Both methods independently and consistently yield the same adsorption site and structural model. This perfect agreement justifies a discussion and interpretation of structural details.

(invited) Recent advances in cathode lens microscopy

R M Tromp

Leiden University, The Netherlands

The key characteristic of Low Energy Electron Microscopy (LEEM) and Photo Electron Emission Microscopy (PEEM) is the use of a cathode objective lens in which the sample is immersed in a strong electric field to extract the low energy electrons from the sample into the image forming electron optical column. Traditionally, the spatial resolution has been limited by the combination of chromatic and spherical aberrations of this cathode lens. In most PEEM experiments (in particular when performed with synchrotron radiation) chromatic aberration dominates, while in LEEM spherical aberration is more important. Recently, the correction of these leading aberrations by combination of the cathode lens with a catadioptric system (electron lens + electron mirror) has been demonstrated experimentally, setting a record resolution in LEEM below 2 nm, just a few times the electron wavelength. In PEEM, 5 nm resolution has been achieved. The most advanced microscopes also incorporate an imaging electron energy filter that allows for spectroscopic imaging, as well as angle- and energy-resolved electron spectroscopy from micrometer-sized selected sample areas. Thus, these new instruments open up new areas of research, in particular when combined with powerful new light sources. In this talk, I will review these recent advances, and discuss the potential for additional future developments, including cryogenic capability down to 10K, as well as novel electron detection systems.

Elucidating the equilibrium states of C_{60} molecules on Ag(111) and Au(111)

K Pussi[1], H Shin[2], H I Li[2], L N Serkovic[3], A Shukla[3], V Fournée[3], J Ledieu[3], G Schull[4], R Berndt[5], L L Wang[6], G M McGuirk[2], K E Marino[2], S Su[2], A Schwarze[2], S E Rauterkus[2] and R D Diehl[2]

[1]Lappeenranta University of Technology, Finland, [2]Penn State University, USA, [3]Institut Jean Lamour, École des Mines, France, [4]Institut de Physique et Chimie des Matériaux de Strasbourg, France, [5]Christian-Albrechts-Universität zu Kiel, Germany, [6]The Division of Materials Sciences and Engineering (DMSE), USA

The properties of fullerenes at surfaces depend strongly on their local geometries, but the relatively weak interaction of C_{60} molecules with Ag(111) and Au(111) produces a structural complexity that makes it difficult to reliably characterize their properties. We have used a combination of STM, LEED and DFT to elucidate the nature of the most stable $(2\sqrt{3}\times2\sqrt{3})R30^\circ$ phases of C_{60} on Ag(111) and Au(111). To obtain the geometrical details of the mixtures of C_{60} molecules, we measured and analyzed LEED intensities at low temperature for both Ag(111)-$(2\sqrt{3}\times2\sqrt{3})R30^\circ$-$C_{60}$ and Au(111)-$(2\sqrt{3}\times2\sqrt{3})R30^\circ$-$C_{60}$. The measurement and calculation methods were described in an earlier paper [1], but in this new work we have optimized models that consist of mixtures of the different C_{60} configurations. To reduce the computational burden of testing all possible configurations, we limited the test models to those that are consistent with the STM images from each system. After applying the constraints provided by the STM and DFT results, we determined the final geometry for C_{60} on Au(111) to be an 80:20 mixture of molecules sitting at their hexagonal face on vacancy site and molecules sitting at their 6:6 bond on top site. For the case of Ag(111) the final geometry was a 60:40 mixture of molecules sitting at their hexagonal face on vacancy site and molecules sitting at their 6:6 bond on top site.

[1] Phys. Rev. Lett. 103, 056101 (2009).

Structure determination of pseudomorphic and close packed Ni overlayers on W(110)

J Ardini[1], T O Menteş[2], M A Niño[3], G Held[1] and A Locatelli[2]

[1]University of Reading, UK, [2]Sincrotrone Trieste, Italy, [3]Instituto Madrileño de Estudios Avanzados IMDEA Nanociencia, Spain

The epitaxy of fcc(111) or hcp(0001) overlayers on bcc(110) substrates motivated several studies investigating the growth of various metals on W and Mo, focusing in particular on the phase transition from the pseudomorphic (ps) regime to close packed (cp) superlattices.

In the case of Ni, two distinct (nx1) coincidence phases are formed, which relieve the large strain of the ps monolayer [1]. In the accepted view, the (nx1) phases consist of a distorted Ni(111) layer arranged in the Nishiyama-Wasserman orientation, showing pseudomorphism along <1-10>. The structure and formation of cp phases are understood in the frame of the misfit dislocation (MD) model [2], although a SXRD experiment proposed a more complex arrangement of the overlayer [3]. Motivated by this, we characterized Ni growth on W(110) using LEEM and micro-spot LEED. The crystal structure was determined using LEED-IV analysis, which shows that the Ni cp phases are relatively well-ordered quasi fcc structures, with oscillating chains of Ni adatoms aligned parallel to <001>, located midway between the dense <001> rows of the substrate atoms. The results confirm the MD model both for (7x1) and (8x1) structures, in excellent agreement with recent DFT calculations [4].

[1] C. Schmidthals et al., Surf. Sci. 417 (1998) 361.
[2] J. V. der Merwe et al., Phys.Rev.B, 49 (1994) 2127.
[3] H. Meyerheim, Phys. Rev. B 67 (2003) 155442.
[4] N Stojić and N Binggeli, J. Phys. Condens. Matter 24 (2012) 135001.

Nanostructures 5

(invited) nanoCathodoluminescence of Quantum Confined Nanostructures: working at the relevant scale

M Kociak

Laboratoire de Physique des Solides, France

In the recent years, many semi-conducting nanostructures including quantum confined elements (QCE) for controlled optical properties have emerged. Obtaining spectroscopic information at the scale of a nanostructure, or within the nanostructure itself is not straightforward because the required spatial resolution can be one or two order of magnitude smaller than the equivalent wavelength of light in the vacuum. Such information is however crucial for a full understanding. The techniques using photons alone thus tend to be very difficult to use. An obvious alternative would be to take benefit of the high spatial resolution of fast electrons by using spatially resolved Cathodoluminescence (CL) spectroscopy. However, while in principle perfectly suited for the study of QCE, the CL did not show for a long time enough spatial resolution to seriously compete pure optical methods.

In this talk, I will review recent results obtained in a Scanning Transmission Electron Microscope (STEM) on the nanometer-scale optical properties of quantum emitters.

I will show how an in-house high throughput and high spatial and spectral resolutions CL set-up can be used to probe optical properties of quantum emitters at the scale of the quantum confinement – typically few nanometers. I will also show how these optical properties can be directly related to the detailed structural analysis of the same system down to the single atomic plane. This will be exemplified with recent results on GaN/AlN composite nanowires and other systems like II-VI quantum dots and color centers in nanodiamonds.

Using chiral plasmonic nanostructures for ultrasensitive detection and characterisation of biomaterials

M Kadodwala

University of Glasgow, UK

We have developed a new paradigm for the spectrosocpic characterisation of the structure of molecular materials. We have significantly enhanced the capabilities of a spectroscopic measurement by using “sculpted” electromagnetic (EM) fields created using plasmonic nanomaterials. I will present proof of principle results [1], in which we demonstrate ultrasensitive (picogram) detection and characterisation of protein secondary structure; this level of sensitivity is a million times greater than is achieved by previously known spectroscopic phenomena. In recent work we have gone further than just amplifying sensitivity, and I’ll show that sculpted EM fields, applied in a technique we have named superpolarimetry, can be used to characterise an order of hierarchical structure of (bio)materials that is inaccessible with known spectroscopic phenomena, and can currently only be probed with microscopy. I’ll also discuss recent improvements in our understanding of the optical properties of hybrid chiral molecular – plasmonic material [2].

[1] E. Hendry, T. Carpy, J.Johnston, M. Popland, R.V. Mikhaylovskiy, , A.J. Lapthorn, S.M. Kelly, L.D. Barron, N. Gadegaard, , and M. Kadodwala, Nature Nanotechnology 5 783 (2010).

[2] N. A. Abdulrahman,. Z. Fan, T.Tonooka, S. M. Kelly, N.Gadegaard, E.Hendry, A.O. Govorov, and M. Kadodwala,. Nano Letters 12 977 (2012).

One-dimensional plasmons in arrays of monolayer silver wires on Si(557)

H Pfnür[1], U Krieg[2], Y Zhang[2], C Tegenkamp[2] and C Brand[2]

[1]Institut für Festkörperphysik, Germany, [2]Universität Hannover, Germany

An array of metallic stripes of monatomic height and up to 10 atoms wide was prepared on the (111)-oriented mini-terraces of vicinal Si (557) via self assembly. By characterization with spot profile analysis LEED (SPA-LEED), STM and finally by electron energy loss spectroscopy (EELS) with both high energy and momentum resolution, we demonstrate that a quasi one-dimensional system was prepared after adsorption between 0.5 and 1 monolayer (ML) of silver. Only stripes that show $\sqrt{3}\times\sqrt{3}R30°$ order turn out to be metallic with an almost linear dispersion of the plasmonic losses, detected by EELS, in the direction parallel to the steps. while in perpendicular direction the plasmonic losses do not disperse at all. Therefore, the wires within the array seem to be electronically decoupled. Due to the finite width, however, combined inter-subband-plasmon excitations become visible in the direction normal to the wires. The quantitative simulation of the plasmonic losses in the low momentum regime is compatible with a wire width of 3.6 nm which agrees well with the width of the (111) terraces of Si (557).

Interestingly, the electron concentration in the wires and thus the slope of the dispersion can be tuned in a wide range by doping these wires, making the Ag wires quite versatile for 1D conductance of plasmonic excitations.

Deep-ultraviolet plasmonic response of Al nanoparticles

G Maidecchi[1], F Bisio[2], R Moroni[2], A Giglia[3], C Vu Duc[4], S Nannarone[5], L Mattera[1] and M Canepa[1]

[1]Universitá di Genova, Italy, [2]CNR-SPIN, Italy, [3]IOM CNR Lab TASC, Italy, [4]Hanoi, Vietnam, [5]Univ Modena, Italy

Physical systems based on Aluminum nanoparticles (NPs) have for a long time been strong candidates for extending the plasmonic response of composite materials towards the deep-ultraviolet (DUV) range, with important fallouts in the fields of non-linear optical spectroscopies and high-sensitivity biosensing. Despite the expectation that Al NPs exhibit a localized surface plasmon resonance (L-SPR) in the DUV range, the metal's reactivity and the synthesis difficulties have strongly hampered the research in this direction.

Employing a strict control of the fabrication process, we realized 2-dimensional Al NPs arrays with DUV-frequency L-SPR supported onto self-organized nanopatterned LiF(110) surfaces. The arrays consist of ensembles of neighbouring, isolated Al_2O_3-Al core-shell nanoparticles aligned along the nanometric grooves of the LiF surface. Atomic-force microscopy showed that the NPs are ordered over large areas and exhibit a coherently-aligned ellipsoidal shape with narrow size distribution in the few tens-of-nm range. High-resolution X-ray photoemission data highlighted the presence of a metallic core surrounded by a few-nm thick shell of oxide. Polarized-light absorption measurements in the 3-12 eV range performed by synchrotron light at BEAR beamline at Elettra (Trieste) revealed the presence of the L-SPR at frequencies ranging between 5.8 eV and 3.9 eV depending on the NP mean size and the relative orientation of the polarization direction and the NP ellipsoids. The experimental data are compared with theoretical models for the L-SPR. The results show the suitability of the present method to fabricate DUV-plasmonic Al nanostructures.

(invited) Optical near-field control and nanoscale spectroscopy

W Pfeiffer

Bielefeld University, Germany

The combination of ultra-short laser excitation, adaptive pulse shaping and photoemission electron microscopy (PEEM) opens a new realm for the investigation of plasmonic and nanophotonic excitations. In this overview presentation coherent control of nanooptical excitations and a new type of nanoscale coherent spectroscopy is covered.

Polarization pulse shaping, i.e. the design of ultra-short laser pulses with continuously changing polarization state, allows nanoscale excitation switching in the vicinity of a metal nanostructure. The locally emitted photoelectrons are monitored with PEEM down to ~50 nm spatial resolution, revealing both adaptive control of localization and ultrafast spatio-temporal switching of the excitation.

Besides excitation control the locally recorded photoelectrons reveal the collective electron excitation in nanostructures via a modified coherent 2D spectroscopy scheme. As example long-living (150 fs) plasmonic resonances on a corrugated silver film are reported and explained in a model based on the hybridisation of bright antenna modes interacting with the far field and a dark mode composed of multiply scattered surface plasmon polaritons. The observation of long-lived coherent excitations on a metal surface has important implications for surface enhanced spectroscopies.

The prediction of separation phase-transitions in binary and ternary alloy nanoparticles

M Polak, L Rubinovich, H Tigger

Ben-Gurion University, Israel

Compositional structures of equilibrated Pt-Ir, Pd-Ir and Pt-Pd-Ir 923-atom cuboctahedron nanoparticles (CO-NPs) are predicted using the recently introduced DFT-based approach for deriving Coordination dependent Bond-Energy Variations [1], combined with the highly efficient statistical-mechanical Free-energy Concentration Expansion Method [2]. The minimization of the free-energy with respect to the NP 36 site concentration variables reveals sharp intra-particle nanophase transitions to partially-ordered structures for Pt-Ir NPs having “onion-like” structure [3] and Pd-Ir NPs with “core-shell” structure at lower temperatures. Additionally, convexities in the low-temperature mixing free-energy curves indicate tendency for inter-particle separation that disappears at a critical temperature signifying transition to a uniform system of solid-solution like NPs. The relationship between the two types of separation transitions as well as the role played by preferential strengthening of surface-subsurface inter-layer bonds are elucidated.

In Pt-Pd-Ir ternary CO-NPs (with 72 concentration variables!), at low temperatures an Ir inner core is surrounded by Pt, while Pd occupies edge and subsurface sites. At higher temperatures, preferential strengthening of Ir (111) surface-subsurface bonds favors partial replacement of subsurface atoms by Ir from the inner core via an intra-particle phase-transition, which shifts to lower temperatures and becomes sharper with decrease of the Ir core. The predicted novel phenomena are expected to affect significantly physical and chemical properties of the NPs.

[1] L. Rubinovich, M. Polak, Phys. Rev. B 80 (2009) 045404.
[2] M. Polak and L. Rubinovich, Surf. Sci. Rep. 38 (2000) 127.
[3] H. Tigger, L. Rubinovich and M. Polak, JPC C (to be published).

Photoluminescence of metal and metal-oxide nanostructures

Y-R Ma and J-H Lin

National Dong Hwa University, Taiwan

We explored the structural, electronic, and photoluminescent (PL) properties of Ta_2O_5 nanoblock stacks and 2D pure Zn-metal nanoplates.The Ta_2O_5 nanoblocks and 2D pure Zn-metal nanoplateswere synthesized by the hot filament metal-oxide vapor deposition (HFMOVD) and hot plate metal vapor deposition (HPMVD) techniques, respectively. The Ta_2O_5 nanoblocks are randomly arranged in large-area stacks, and most of themare21 nm wide.The2D pure Zn-metal nanoplates have an average diameter and thickness of ~520 and ~144 nm.X-ray photoemission spectroscopy (XPS) not only revealed the electronic structures and chemical compositions of the nanostructures, but also the Fermi levels of metal nanostructures. For example, in comparison with the bulk Zn metals, the Fermi levels of the 2D pure Zn-metal nanoplates are lowered.

Photoluminescence (PL) spectroscopy shows that the Ta_2O_5 nanoblocks have very strong green-light emissions, which emerged from the trap-levels of the oxygen vacancies within the Ta_2O_5 band gap. The PL intensities were linearly enhanced by increasing the laser power and excitation time. Also, PL spectroscopy reveals that the 2D nanoplates can provide a wide-range PL from ultraviolet (UV) to red light emissions at room temperature. The measured valence-band and the calculated band-structure of the 2D pure Zn-metal nanoplates verify that the UV and blue light arise from the 3d-sp interband transitions, while the green, yellow, and red light come from the valence-conduction interband transitions at a bandgap that is only present to the 2D nanoplates. Therefore, the 2D pure Zn-metal nanoplates possess not only metallic, but also semiconducting characteristics.

High density of site-controlled pyramidal quantum dots emitting polarization-entangled photons

G Juska, V Dimastrodonato, L O Mereni, A Gocalinska and E Pelucchi

Tyndall National Institute, Ireland

Entangled photons are of high relevance in the fields of quantum information processing and quantum cryptography. Quantum dots (QD) were recently demonstrated as sources of entangled photons [1]. However, the dominant self-assembled QD system suffers from asymmetry induced fine-structure splitting (FSS) which complicates the detection of entangled photons unless a particular FSS manipulation technique is utilized to reduce it, or a careful selection of ‘good’ candidates from the vast number of QDs is carried out, preventing the possibility of constructing vast arrays of emitters on the same sample. Here we show that our approach to site-controlled QDs grown in 7.5 μm pitch pyramidal recesses in (111)B GaAs substrate significantly overcomes FSS related problems, along with the random nature of self-assembled QDs, and opens way to the development of an efficient array of entangled photons.

$In_{0.25}Ga_{0.75}As_{1-\delta}N_{\delta}$QDs were grown by metalorganic vapour phase epitaxy (MOVPE) using unsymmetrical dimethylhydrazine as a source of nitrogen, which under certain growth conditions strongly modifies excitonic pattern and suppresses FSS under our resolution of ~4 μeV [2]. Results of polarization-sensitive cross-correlation measurements showed randomly selected areas containing up to 15% of nearby QDs emitting entangled photons. QDs with fidelity value as high as 0.72 were found. Quantum state tomography confirmed the entangled nature of photons.

[1] Stevenson, R.M., et al. Nature, 2006. 439(7073): p. 179; Akopian, N., et al. Physical Review Letters, 2006. 96(13): p. 130501; Mohan, A., et al. Nature Photonics, 2010. 4(5): p. 302.

[2] Dimastrodonato, V., et al. Applied Physics Letters, 2010. 97(7): p. 072115; Juska, G., et al. Nanoscale Research Letters, 2011. 6: p. 567.

Oxides and oxide surfaces 4

Local Raman spectroscopic study of mixed phase $BiFeO_3$ films with monoclinic symmetry

Y-C Huang[1], Y-C Chen[1], F-N Chu[1], W-I Liang[2], H-J Chen[2] and Y-H Chu[2]

[1]National Cheng Kung University, Taiwan, [2]National Chiao Tung University, Taiwan

Among the signle phase multiferroics, $BiFeO_3$ (BFO) has attracted great interests because possesses ferroelectric and antiferromagnetic couplings at room temperature. In a new-type morphotropic phase boundary driven by substrate strain, high piezoelectric coefficient and spontaneous ferromagnetic moments had been demonstrated for BFO epitaxial films grown on $LaAlO_3$ substrate. In this study, we used Raman spectroscopy to in-situ investigate the BFO thickness-dependent and temperature-dependent strained states, or phase transition by external electric fields. Tetragonal-like (T) and rhombohedral-like (R) monoclinic structures coexisted in the highly-strained BFO films, the transition from the T-BFO to R-BFO, and the ordering of the monoclinic structures could also be controlled by electric field. Phonons of two monoclinic structures could be easily distinguished by atomic force microscopy (AFM) equipped with on-axis Raman measurement.

Phonons of two monoclinic structures in different strained states were systematically studied. The crystal transformed from monoclinic to the rhombohedral symmetry in the relaxed film. When the temperature was increased, the Raman peak about 360 cm^{-1} disappeared around 150 °C, which correlated to the in-plane polarization rotation from [100] to [110]. Measuring different combinations of ordered monoclinic structures shows the peak near 360 cm^{-1} shifted to the higher frequency in the relaxed states. This study provided the basic physical insight of unique physical properties depending on distorted structures.

Scanning Tunneling Microscopy study of single-crystalline $Sr_3Ru_2O_7$

B Stöger[1], Z Wang[1], M Hieckel[1], F Mittendorfer[1], R Podloucky[1], J Redinger[1], D Fobes[2], Z Mao[2], M Schmid[1] and U Diebold[1]

[1]Vienna University of Technology, Austria, [2]Tulane University, USA

Perovskite oxides play an important role as cathodes in solid oxide fuel cells (SOFC) and in catalysis. Investigating surface defects such as oxygen vacancies and the adsorption of relevant molecules helps gaining more insight into the physics behind SOFCs and catalytic processes.

High-quality $Sr_3Ru_2O_7$ (SRO) single crystals were grown using the floating zone technique. The SRO samples were cleaved at 150 K under UHV conditions and subsequently investigated by STM at 78 K and 6 K. To determine which species are imaged in STM, doped SRO samples were investigated and STM simulations were performed.

Furthermore, we have characterized the defects that are present at the as-cleaved surfaces, and how reactivee they are if exposed to CO and O_2. CO binds to some defects at the surface and, possibly, also to apical oxygen atoms at the perfect surface. This work was supported by the Austrian Science Fund (FWF project F45).

Structure and stability of clean and Au-Rh containing titanate nanowires and nanotubes

J Kiss, D Madarász, G Pótari, B László, A Sapi, L Nagy, A Oszkó, Z Kónya and A Erdőhelyi

University of Szeged, Hungary

Au-Rh bimetallic nanoclusters were produced during the coadsorption of gold and rhodium on TiO_2 and high-aspect-ratio titanate nanotube (NT) and nanowire (NW) produced by hydrothermal conversion of sodium-titanate at 400 K. The catalyst's morphology was studied by TEM. The formation of ordered titanate nanoobjects depended on the time of conversion. Shorter time favoured hollow nanotube production, while during extended times the thermodynamically more stable nanowires were formed. The structure and stability of titanate nanocomposites were studied by XPS, LEIS, TEM, XRD and FTIR. The nanowire preserves its structure up to 850 K, while the nanotube starts to recrystallise from 600 K. FTIR measurements showed that the water and hydroxyl content gradually decreased with the rising of temperature in both cases. The OH content diminished around 850 K. XPS data revealed the existence of high binding energy, highly dispersed Au species besides metallic particles on both supports. The presence of highly dispersed Rh on Rh/NT and Rh/NW catalysts is possible. LEIS spectra evidenced the formation of Rh core – Au shell structures on the bimetallic nanosystem. Adsorption-induced morphological changes of Au-Rh nanoobjects were observed on titanate nanowire and nanotube. Adsorption of CO at 300 K may induce the segregation of Rh from core-shell to the titanate surface. Another scenario is that presence of CO leads to a significantly higher degree of wetting between metal nanocluster and titania, causing increased number of defects on topmost layer, and thus free Rh sites on core-shell structure. This behaviour is attributed to a chemisorption-induced surfactant effect.

Struture and Magnetism in $BaTiO_3$(001)-(2x1)

H Meyerheim[1], A Ernst[2], K Mohseni[2], I Maznichenko[3], S Ostanin[2], F Klimenta[2], N Jedrecy[4], W Feng[2], I Mertig[3], R Felici[5] and J Kirschner[2]

[1]Max-Planck-Institut, Germany, [2]MPI-Halle, Germany, [3]Martin-Luther-University Halle, Germany [4]UPMC-Sorbonne Universites, France, [5]European Synchrotron Radiation Facility, France

Using surface x-ray diffraction and ab initio calculations we present a model of the $BaTiO_3$-(001)-(2x1) surface structure, which has not been considered so far. While the crystal is terminated by two TiO_2 layers similarly to $SrTiO_3$(001)-(2x1), we find that one out of two surface layer Ti-atoms resides in a tetragonal pyramidal oxygen environment. Using the experimentally derived structure model the electronic and magnetic properties were calculated within the density functional theory (DFT) in the local density approximation using a Korringa-Kohn-Rostoker Green-function method, which is specially designed for semi-infinite layered systems. The structural motif of a Ti atom in a pyramidal environment involves symmetry breaking, localization of the electronic states and charge transfer to the central Ti-atom from surrounding oxygen atoms, the latter being directly related to the shift of the otherwise unoccupied 3d-states to the Fermi level. This leads to the metallization and magnetization with magnetic moments up to 2μB in magnitude located at the surface Ti-and O-atoms. Metallicity and large magentic moments are thus an intrinsic property of the surface. We infer that this metallization also contributes to the stabilization of the reconstruction related to the depolarization of the surface.

Atomic and electronic structure of the $SrRuO_3$ (001) surface: A combined STM and STS study

M Trautmann[1], D Hesse[2], I Vrejoiu[2] and W Widdra[1]

[1]Martin-Luther-Universität Halle-Wittenberg, Germany, [2]MPI of Microstructure Physics Halle, Germany

For applications in oxide-based electronic devices such as ferroelectric heterostructures and non-volatile ferroelectric random access memories the electrode material plays an important role. In this context $SrRuO_3$ has drawn significant attention due to its high conductivity and low lattice misfit with many functional perovskites.
In this study a 40 nm thick PLD grown film of orthorhombic $SrRuO_3$ on $SrTiO_3$(001) has been characterized by low energy electron diffraction (LEED) and scanning tunneling microscopy and spectroscopy (STM/STS). The as-grown film exhibits, also upon transfer through air, a well-ordered pseudocubic $SrRuO_3$(001)-(1x1) LEED pattern and STM shows large $SrRuO_3$(001) terraces which are separated by unit-cell high step edges. Upon heating to 300°C in oxygen the LEED pattern sharpens and reveals weak half-order spots [1]. Atomically resolved STM images indicate the beginning of a structural surface rearrangement with a superposition of c(2x2) and (2x1) reconstructions. Further annealing of the sample leads to an improved ordering of the surface with the appearance of small unit-cell deep vacancy islands as reported earlier [2]. The electronic structure of the $SrRuO_3$(001) surface is dominated by two well-resolved unoccupied density-of-states features at 1.2 eV and 2.7 eV above E_F as based on STS. These states are assigned to unoccupied Ru 4d states on the basis of DFT calculations [3].

[1] J. Shin, A. Y. Borisevich, V. Meunier, J. Zhou, E. W. Plummer, S. V. Kalinin and A. P. Baddorf, ACS Nano 4, 4190 (2010)

[2] H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau and D. H. Lowndes, Appl. Phys. Lett. 84, 4107 (2004)

[3] J. M. Rondinelli, N. M. Caffrey, S. Sanvito and N. A. Spaldin, Phys. Rev. B 78, 155107 (2008)

Vacancy induced surface band bending at the $SrTiO_3$(110) surface

Z Wang, M Schmid and U Diebold

Vienna University of Technology, Austria

The surfaces and interfaces of $SrTiO_3$ have attracted intense interest in diverse fields ranging from solid-state physics to surface chemistry and oxide electronics. In all these applications the structural and electronic surface properties are vital of importance, yet perovskite surfaces are notoriously complex and hard to control. We report an STM and XPS study of $SrTiO_3$(110). This polar surface tends to form a homologues series of (n × 1) (n = 4~6) reconstructions, which are well explained by models consisting of added TiO_4 tetrahedra. These tetrahedra are arranged in distorted rings with narrow and wide tetrahedral pairs. Such an arrangement breaks the mirror symmetry of surface along the [1-10] direction, and two degenerate anti-parallel (n × 1) domains are formed. Vacancies of $(Ti_2O_3)^{2-}$ and $(Ti_4O_5)^{6-}$ type are present at domain boundaries linked by wide and narrow TiO_4 tetrahedra rings, respectively. The relative ratio of these domain boundaries can be tuned judiciously by adjusting the oxygen pressure during annealing. XPS shows that the surface bands bends upward by 0.2 eV as the Ti_4O_5 vacancy density increases.

Oxygen-vacancy-induced electronic states on a $SrTiO_3$ surface and interaction with gas molecules

K Takeyasu, K Fukada, S Ogura and M Matsumoto

University of Tokyo, Japan

Perovskite-type transition metal oxides show attractive physical properties such as high electric permittivity, photo catalytic behavior and strong electron correlations. Generation of oxygen vacancies (Vo) on the surface and interaction of gas molecules with Vo are of fundamental interest and importance in understanding the surface reactions. While electron stimulated desorption (ESD) of oxygen occurs on the surface, the geometric and electronic structure of Vo due to ESD is yet to be elucidated. This paper reports properties of Vo on $SrTiO_3$(001) induced by ESD and their interaction with hydrogen.

Upon electron irradiation at 300–1500 eV on the $SrTiO_3$(001) surface, ultraviolet photoemission spectroscopy (UPS) revealed an apparent feature at 0-1.2 eV below the Fermi level, which can be ascribed to oxygen vacancies. With increasing electron dose, the conduction band bottom (CBB) was lowered across the Fermi level, which indicates a charge accumulation layer was formed at the surface. Oxygen exposure of 10 L decreased the intensity of the feature and the CBB got back above the Fermi level. The saturated density of the oxygen vacancy due to ESD was evaluated to be 7.1×10^{13} cm^{-2}. We discuss the saturation of oxygen ESD is caused by trapping of excited electrons in the vacancy-derived localized states, which prevents energy transfer to oxygen atoms. The structure of Vo and interaction with hydrogen molecules are also discussed.

Ge/$SrTiO_3$ heterogeneous system

B Gobaut[1], M El-Kazzi[2], J Penuelas[1], G Grenet[1], D Ferrah[1], A Benamrouche[1], A Chettaoui[1], Y Robach[1], C Botella[1], L Largeau[3], M Silly[2], F Sirotti[2], N Blanc[4], V Favre-Nicolin[4], G Renaud[4] and G Saint-Girons[1]

[1]Université de Lyon, France, [2]Synchrotron SOLEIL, France [3]Laboratoire de Photonique et Nanostructure, France, [4]SP2M, France

Recently, integrating III-V or IV-IV semiconductors on functional oxides has become a challenge in microelectronics because of the new functionalities such as ferroelectricity or piezoelectricity these oxides can offer [1]. However, engineering of an abrupt interface between semiconductor and oxide is chemically (due to semiconductor reactivity against oxygen) and structurally (due to difference in crystallography) difficult.

We used Soft-X-ray synchrotron-radiation photoemission at the beamline TEMPO at Soleil, to study the interface between Ge and $SrTiO_3$ (100). We have shown that Ge adsorption is strongly dependent on the SrTiO3 surface's initial composition: the richer the surface is in TiOx, the more Ge wets the STO surface [2]. The formation of Ge islands by annealing-promoted dewetting was monitored by soft-x-ray time-resolved photoemission. As temperature increases, the Ge^{2+}, Ge+ and Ge0 component evolution reveals that Ge adatoms, initially bonded to two (or more) oxygen atoms gradually aggregate to form Ge clusters.

The in-situ Ge growth on $SrTiO_3$ was studied by Grazing Incidence X-ray Diffraction at beamline BM32 at ESRF. The lattice mismatch is accommodated by a dislocation interfacial network which depends on the interface area between the Ge islands and the substrate. These results are complemented by others from RHEED, XRD, TEM and AFM which clearly show the competition that exists between interface energy (Ge-O bonds), cohesion energy (Ge-Ge bonds) and surface energies (Gefaceting) as a function of temperature.

[1] B. Gobaut et al., Appl. Phys. Letter 97, 201908 (2010).
[2] M. El-Kazzi et al., Phys. Rev. B 85, 075317 (2012).

Friday 7 September

Organic layers and polymers 5

(invited) Functional molecules on surfaces: polymerization and manipulation by STM

L Grill

Fritz-Haber-Institut, Germany

The investigation of functional molecules on surfaces is of fundamental interest for a detailed understanding of physical and chemical processes at the single molecule level as well as for future molecular nanotechnology, in particular in view of molecular machines, novel materials and molecular electronics. The scanning tunneling microscope is very a suitable tool to study such systems, because it can image with sub-molecular resolution and is also capable to manipulate individual molecules in a controlled way [1].

In this talk, various examples of single-molecule manipulations will be given, covering the entire range of mechanical, optical and electronic molecular functions. These are on the one hand molecular switches that can exist in various stable states with different properties [2] and it will be shown that the atomic-scale environment plays a fundamental role in the switching behavior [3]. The controlled covalent assembly of molecules on surfaces will be presented, leading to bottom-up fabricated networks of desired architectures [4], even in a hierarchical growth scheme [5]. Various molecular wires can be grown in this way and their conductance was measured by pulling single polymers off a surface [6]. Finally, the combination of inorganic with organic growth processes will be discussed [7].

[1] L. Grill, J. Phys.: Cond. Matt. 20, 053001 (2008).
[2] M. Alemani et al., JACS 128, 14446 (2006).
[3] C. Dri et al., Nature Nanotechn. 3, 649 (2008).
[4] L. Grill et al., Nature Nanotechn. 2, 687 (2007).
[5] L. Lafferentz et al., Nature Chem. 4, 215 (2012).
[6] L. Lafferentz et al., Science 323, 1193 (2009).
[7] C. Bombis et al., Ang. Chem. Int. Ed. 48, 9966 (2009).

Fullerene/porphyrin supramolecular and covalent networks on silver single crystal surfaces

F Sedona[1], M Di Marino[1], T Carofiglio[1], E Lubian[2], M Casarin[2] and M Sambi[2]

[1]Università degli studi di Padova, Italy, [2]Università di Padova, Italy

Fullerene and porphyrin chromophoric molecules spontaneously attract each other trough dispersion and donor-acceptor interactions both in solution and in the solid state. Relative few tentative of using this molecular affinity in order to obtain a supramolecular bidimensional self-assembling of C_{60} and porphyrin on a surface as been so far reported[1].

In this contribution we first show that 12 different multi-component supramolecular self-assemblies ordered nanostructures are obtained with the co-deposition of C_{60} and either pristine or variously aminated tetraphenylphenylporphyrins (i. e. TPP, TPP-NH_2, TPP-$(NH2)_2$ and TPP-$(NH_2)_4$) on Ag low-index surfaces followed by annealing[2].

Subsequently, we introduce a two step bottom-up approach to construct 2D long range ordered, covalently bonded fullerene/porphyrin binary nanostructures[3]. In the first place, reversible supramolecular interactions between C_{60} and either TPP-$(NH_2)_2$ or TPP-$(NH_2)_4$ are exploited to obtain very large domains of an ordered binary network; subsequently an addition reaction between fullerene molecules and the amino-groups on porphyrin units, triggered by thermal treatments, is used to freeze the supramolecular nanostructure with covalent bonds. In this approach, the preorganization step produces a supramolecular network wherein the MBU are linked to each other in a such a way that the subsequent covalent bond-formation implies minimal rearrangements in the superstructure, since substantial repositioning inevitably leads to a high level of disorder.These results show promising potential for the synthesis of highly ordered networks of surface-supported functional copolymers.

[1] D. Bonifazi, A. Kiebele, M. Stöhr, F. Cheng, T. Jung, F. Diederich, H. Spillmann, Adv. Funct. Mater. 2007, 17, 1051–1062.
[2] Di Marino, M.; Sedona, F.; Sambi, M.; Carofiglio, T.; Lubian, E.; Casarin, M.; Tondello E. Langmuir 2010, 26, 2466.
[3] Sedona, F.; Di Marino, M.; Sambi, M.; Carofiglio, T. ; Lubian, E.; Casarin, M.; Tondello, E. ACS Nano 2010, 4, 5147.

Construction of functionalised surface architectures by covalent coupling reactions on metal surfaces

C Baddeley, J Greenwood, H Fruchtl, S Jensen and F Grillo

University of St Andrews, UK

There has been considerable recent interest in the growth of 2-D supramolecular networks on metal surfaces utilising van der Waals, H-bonding and metal organic interactions. For many applications, there is a requirement for such 2-D networks to be thermally and chemically robust. Consequently, the controlled assembly of surface bound architectures via covalent coupling of adsorbed molecules has received much attention. We are particularly interested in the development of surface structures which could be exploited in the field of enantioselective heterogeneous catalysis so we have targeted porous networks whose walls are strategically functionalised in order to offer docking sites for pro-chiral reactants. We report surface confined reactions between amines and isocyanates to create urea linkages [1] and amines and acyl chlorides to create amide linkages[2]. Scanning Tunnelling Microscopy (STM), reflection absorption infrared spectroscopy (RAIRS) and high resolution electron energy loss spectroscopy (HREELS) are used to investigate the structure of the networks produced. We show that the ability to form ordered structures is strongly dependent on the specific choice of monomer species and metal surface [3] and the processing temperature.

[1] S. Jensen, H. Früchtl, C.J. Baddeley, Journal of the American Chemical Society 131 (2009) 16706-16713.
[2] S. Jensen, J. Greenwood, H.A. Fruechtl, C.J. Baddeley, Journal of Physical Chemistry C 115 (2011) 8630-8636.
[3] J. Greenwood, H.A. Früchtl, C.J. Baddeley, Journal of Physical Chemistry C 116 (2012) 6685-6690.

Evolution of the electronic structure during formation of a graphene nanoribbon in an on-surface synthesis

C Bronner[1], F Leyssner[1], S Meyer[1], M Utecht[2], A Haase[1], P Saalfrank[2], T Klamroth[2] and P Tegeder[1]

[1]Freie Universität Berlin, Germany, [2]Universität Potsdam, Germany

One-dimensional, flat graphene nanoribbons (GNRs) exhibit interesting electronic properties for use in nanotechnology applications, such as field effect transistors. In contrast to graphene, they exhibit a band gap which is tunable by varying the GNR width. Additionally their band structure is highly sensitive to the edge structure. Conventional fabrication techniques, using lithography or unzipping of carbon nanotubes, do not allow the production of atomically precise edge structures and GNR widths on the order of nanometers (where the band gap becomes technologically relevant). In contrast, a bottom-up technique has been developed [1] in which a molecular precursor undergoes a thermally assisted on-surface synthesis reaction: in a first heating step, a linear polymer is formed. This polymer undergoes a cyclodehydrogenation at higher temperature yielding a defect-free armchair GNR.

We use two-photon photoemission (2PPE) and high-resolution electron energy loss spectroscopy (HREELS) to follow this reaction in terms of the band structure. Both the intermediate non-aromatic polymer and the final aromatic product, the GNR, exhibit electronic bands which we follow in angle-resolved 2PPE. While the band structure in both phases is surprisingly similar, only the extended aromatic system of the GNR leads end states, which are a finite size effect of the experimentally realized GNRs.

[1] J. Cai *et al.*, Nature 466, 470-473 (2010).

Tailoring two-dimensional organic nanostructures on metal surfaces through a polymerisation reaction

T Cafolla[1], H Ling Lee[1], J-P Cunniffe[1], T Carpy[1], A Preobrajenski[2], N Vinogradov[2] and S Krasnikov[3]

[1]Dublin City University, Ireland, [2]Lund University, Sweden, [3]Trinity College Dublin, Ireland

Organic thin film systems have attacted attention in recent times due to their potential use in devices such as organic light emitting diodes (OLEDs) and solar cells. Thin film molecular assemblies also offer the potential to build electronic devices using a bottom-up approach. As such, ordered molecular arrays are of great potential interest. While networks can be formed via relatively weak interactions, such as hydrogen bonds[1] or metal-ligand bonds[2], covalent bonding offers desirable mechanical and thermal stability. In this study, the thermally initiated reaction between 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and 1,3,5 tris(4-aminophenyl)benzene (TAPB) on Ag(111) was investigated using scanning tunnelling microscopy (STM) and synchrotron based x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS). The molecules were thermally evaporated in a UHV chamber onto an atomically clean Ag(111) surface. STM showed that a 1 monolayer film of roughly 50% PTCDA and 50% TAPB formed a self assembled hydrogen bonded network at room temperature.

Subsequent annealing to successively higher temperatures results in the appearance of a number of different ordered structures, some involving TAPB-PTCDA-TAPB covalent units, until eventually, an extended disordered covalent network was formed at a temperature of 530K. This polymerisation reaction was accompanied by a 2.0 eV shift in the N 1S XPS spectra, and a 50% reduction in intensity in the C-O-C anhydride oxygen in the PTCDA. This agrees with the STM results, and suggests that imide formation is preferred over iso-imide formation.

[1] Theobald J.A., et.al. Nature, 424 (2003) 1029.
[2] L. Bartels, Nature Chemistry, 2 (2010) 87.

Comparison of covalent nano-structure formation on metal surfaces for two, three and fourfold-symmetrical brominated molecules

C Doyle[1], J-P Cunniffe[1], S Krasnikov[2], A Preobrajenski[3], N Vinogradov[3], N Sergeeva[2], M Senge[2] and A Cafolla[1]

[1]Dublin City University, Ireland, [2]Trinity College Dublin, Ireland, [3]University of Lund, Sweden

Covalently-bonded supramolecular nano-structures display features such as high thermal stability which are extremely useful for nanotechnological applications. Brominated porphyrins and polyaromatic molecules are excellent building blocks for such structures as bromine-carbon bonds can be dissociated at temperatures of approximately 450 K, enabling the molecular radicals to bond covalently at the former bromine sites. [1] 5,15-

dibromo-10,20-diphenyl porphyin (DBDPP), 1,3,5-tris(4-bromophenyl)benzene (TBPB) and 5,10,15,20-tetra(4-bromophenyl) porphyrin (TBrPP) [2] are brominated molecules exhibiting two, three and fourfold symmetry respectively. The self-assembly and thermally-induced covalent bonding of these molecules on Au(111), Ag(111) and Cu(111) have been studied using scanning tunnelling microscopy (STM) and synchrotron-based photoelectron spectroscopy (PES) and x-ray absorption spectroscopy (XAS). The molecules form well-ordered close-packed domains on room temperature deposition. STM data show that after subsequent annealing DBDPP forms nano-lines while TBPB and TBrPP form hexagonal and square nano-networks respectively. XPS measurements for TBPB and DBDPP show a 2 eV shift in the binding energy of the bromine after the initial annealing stage (370 K), suggesting that the bromine dissociates from the molecules but remains on the surface before being removed at higher temperatures. This is not the case for TBrPP, where the bromine is directly removed from the surface upon dissociation from the molecule. STM and spectroscopy results confirm that the nano-networks are recoverable following exposure to atmosphere, and are thermally stable up to 770 K.

[1] Grill et al., Nature Nanotechnology 2 (2007) 687.
[2] Krasnikov et al., Nano Research 4 (2011) 376.

An STM and XPS study of covalently bonded 2, 3, 6, 7, 10, 11 hexabromotriphenylene on Au(111), Ag(111) and Cu(111)

T Carpy[1], J-P Cunniffe[1], S Krasnikov[2], A Preobrajenski[3], N Vinogradov[3] and A Cafolla[1]

[1]Dublin City University, Ireland, [2]Trinity College Dublin, Ireland, [3]University of Lund, Sweden

The use of two-dimensional molecular networks to pattern surfaces is currently one of the most promising methods to produce architectures beyond the limit that is fundamentally possible with conventional lithography. This controlled assembly of nanostructures offers a number of powerful approaches for the development of molecule-based devices, possessing functions such as sensing, rectifying and switching. The production of nanometer scale molecular arrays has been achieved using hydrogen bonding and metal-organic interactions. However, these non-covalent bonding chemistries are inherently weak and the resulting networks lack the necessary mechanical and thermal stability required for many nanotechnological applications. In contrast, covalently bonded molecular systems show higher stability but are more difficult to control, and for this reason only a small number of studies exist. Here the self-assembly and temperature-assisted assembly of hexabromotriphenylene (HBTP) has been investigated by soft x-ray photoelectron spectroscopy (SXPS), x-ray absorption spectroscopy (XAS) and scanning tunneling microscopy (STM). Following Grill et al [1], network formation is observed on Au(111), Ag(111) and Cu (111) surfaces. The thermal dissociation of the bromine-carbon bonds in these molecules produce active radicals that subsequently dimerise resulting in the formation of covalently bonded, pi-conjugated, molecular networks. These networks are observed to be stable up to 400°C. The ordering observed in the resulting structures is largely determined by the initial molecular coverage, substrate temperature and deposition rate. A statistical analysis is performed to quantify the network ordering [2].

[1] Grill et al., Nature Nanotechnology 2 (2007) 687.
[2] Ourdjini et.al . Phys.Rev B 84 (2011) 125421.

Carbon, graphene 7

(invited) CVD growth of graphene and its application in flexible electronics

J-H Ahn

Sungkyunkwan University, South Korea

The outstanding physical and chemical properties of graphene, a single atomic layer of carbon atoms, have attracted significant attention. One of the most important advantages of graphene in the field of electronics is its superb charge carrier mobility. The mobility of ideal exfoliated graphene spans an extraordinarily large range, from 10,000-15,000 $cm^2/V\cdot s$ on SiO_2 insulating substrates to 200,000 $cm^2/V\cdot s$ in suspended structures, suggesting that graphene may potentially outperform established inorganicmaterials in certain applications, such as high-frequency transistors. Although useful deviceshave been prepared based on exfoliated graphene,the tiny size of exfoliated graphene particles limits the practical utility of such graphene in electronics applications. Recent studies designedto address this issue haveexploredthe preparation of large-area high-quality graphene via epitaxial growth or chemical vapor deposition (CVD). Many research groups have reported the fabrication of graphene-based transistors via the epitaxial growth of graphene directly on rigid insulating silicon carbide (SiC) wafers. These transistors operate at high frequencies,up to 100 GHz. Other researchers have synthesized graphene on Ni or Cu catalystsusing CVD methods and have demonstrated the utility of device integration on a variety of substratesusing transfer techniques. The CVD approach is attractive because it permits fabrication over large areas and expands the applicability of graphene to flexible or fully stretchable devices on thin plastic or elastomeric substrates.

In this talk, I will discuss recent progress in graphene film preparation and its various applications in the field of flexible and stretchable electronics, focusing on techniques to integrate them into devices on compliant substrates. Although significant engineering challenges including band gap opening and improved reliability still exist, it could create interesting opportunities for developing future electronic applications because many basic aspects of technically feasible approaches are now emerging.

High pressure CO intercalation of Ir(111) supported graphene studied with high pressure X-ray photoemission spectroscopy and scanning tunneling microscopy

J Knudsen[1], E Graanäs[1], T Gerber[2], M A Arman[1], T Michely[2] and J N Andersen[1]

[1]Lund University, Sweden, [2]Universität zu Köln, Germany

Graphene is an attractive support material for catalytic nano-particles since it is chemically inert and has a high thermal stability. We lack, however, knowledge about the stability of pristine graphene at realistic gas pressures for catalytic processes.

In this contribution we discuss the stability of Ir(111) supported graphene in high pressures of CO. Using high pressure X-ray photoemission spectroscopy (HP-XPS) we show that CO intercalates the graphene layer already at room temperature at pressures close to 1 mbar. Further, we show that the XPS fingerprints of CO intercalation structures are identical to a $(3\sqrt{3}\times 3\sqrt{3})R30^\circ$ CO adsorption structure formed on clean Ir(111) upon CO exposure at high pressure. Based on this observation we conclude that the CO adsorption structure formed under the graphene film is identical to the structure that is formed on clean Ir(111). The presence of graphene reduces, however, substantially the speed for formation of the high pressure CO adsorption structure.

Once the CO intercalated structure is formed it is stable at UHV conditions and it is, therefore, possible to study CO-intercalated graphene with scanning tunneling microscopy at UHV conditions. CO-intercalated and pristine graphene are easily distinguished in STM topographs and we reveal that the phase boundaries between intercalated and non-intercalated graphene areas are sharp. Further, we find that the phase boundaries follow the directions of the graphene moiré structure indicating that the binding energy inhomogeneity of graphene on Ir(111) leads to predominant intercalation of specific areas within the moiré unit cell.

Morphology of prisitne and intercalated graphene: An XSW study

C Busse[1], S Runte[1], C Vo-Van[2], J Coraux[2], J Zegenhagen[3] and T Michely[1]

[1]Universität zu Köln, Germany, [2]Institut Néel, France, [3]ESRF, France

Epitaxial growth of graphene on metals is an established way to obtain samples of high quality [1]. Depending on the substrate, the binding varies between pure covalent (e.g. on Ni(111)) to almost pure van-der-Waals (e.g. on Pt(111)). For graphene/Ir(111), the C layer is weakly bound to the substrate, which is indicated by the long distance between C and Ir [2]. In this system also a large unit cell with varying local registries is found, leading to a local variation of the respective bond strength. Hence the graphene layer is not flat but significantly corrugated [2]. We performed X-ray Standing Wave (XSW) measurements for graphene/Ir(111) to determine the height distribution of the C atoms. The peak-to-peak corrugation for a fully closed film is 1 Å and about half this value for small graphene flakes. This can be rationalized by different strain states resulting from the cool-down from high growth temperatures under the infuence of different thermal expansion coefficients.

A versatile tool to taylor the properties of graphene is intercalation of atoms between the carbon sheet and the substrate. This may cause doping which is a key for usability of graphene for next generation electronics, and can also induce spin-splitting of the Dirac cone [3]. Furthermore it reduces the bonding to the substrate, thereby allowing mechanical exfoliation. We determined the binding type and strength using XSW in three model systems: 1) an electron acceptor O, 2) a weak electron donor Cs, and 3) a strong electron donor Eu, whose high magnetic moment makes it a good candidate to induce spin splitting.

[1] R. van Gastel et al., Appl. Phys. Lett. 95, 121901 (2009).
[2] C. Busse et al., Phys. Rev. Lett. 107, 036101 (2011).
[3] A. Varykhalov et al., Phys. Rev. Lett. 101, 157601 (2008).

Patterned intercalation under a graphene moiré

S Schumacher[1], D F Förster[1], T O Wehling[2] and T Michely[1]

[1]Universität zu Köln, Germany, [2]Universität Bremen, Germany

Scanning tunneling microscopy reveals that intercalation of Eu under graphene on Ir(111) at 720 K results in spectacular patterns. These are formed by arrangements of one dimensional stripes for small intercalated amounts, stripes and two dimensional compact islands over a broad intermediate range and finally by one dimensional vacancy channels in a nearly saturated Eu layer. All pattern elements are oriented along the graphene/Ir(111) moiré and quantized in size by its unit mesh.

We explain the mechanism of pattern formation by the interplay of two contributions: First, the chemically modulated binding of graphene to the substrate leads to the orientation along the moiré and a preference of one dimensional stripes. Second, epitaxial graphene is usually compressively strained due to its cool down from the growth temperature. This strain can be relaxed by increasing the graphene arc length under Eu stripe formation.

Oxygen intercalation and etching controlled by the mesoscopic structure of graphene

E Grånäs[1], J Knudsen[1], U Schröder[2], T Gerber[2], C Busse[2], M A Arman[1], K Schulte[3], J Andersen[3] and T Michely[2]

[1]Lund University, Sweden, [2]Universität zu Köln, Germany, [3]Lund University, Sweden

Intercalation of gases between epitaxial graphene and its substrate has become a topic of interest for studies due to, for example, the unique opportunities to modify the graphene-substrate interaction and the possibilities to perform chemistry under the graphene layer. Further, obtaining a profound knowledge about graphenes stability in gases at elevated temperatures is essential for, among other things, the correct interpretation of gas adsorption studies on graphene supported metal cluster arrays.

We have studied graphene/Ir(111) and compare the properties of a perfect, closed graphene layer with the one of graphene flakes when exposed to molecular oxygen at different temperatures. We find that, depending on the graphene morphology and temperature, distinct oxygen adsorption processes and reactions take place and a coherent picture of temperature dependent oxygen etching and intercalation is developed. Using X-ray photoemission spectroscopy (XPS) and scanning tunnelling microscopy (STM) we show that a perfect graphene layer is stable against etching and intercalation up to 700 K, whereas at higher temperatures etching, but no intercalation, takes place. A partial graphene coverage on Ir(111) enables dissociative oxygen adsorption on the bare Ir and subsequent intercalation underneath graphene flakes at 355 K and above. Intercalated oxygen remains stable up to a temperature of 600 K. Above this temperature it desorbs in the form of CO or CO_2. We have determined XPS and STM fingerprints for the intercalated oxygen structure and we unambiguous assign it to a p(2x1)-O structure similar to the one observed on clean Ir(111). The decoupling of the intercalated graphene film from the metal substrate is directly visualized through the inability to form well-ordered Pt cluster arrays on the O-intercalated areas of graphene on Ir(111). Further, we have identified the rate limiting step for oxygen intercalation to be unlocking of the graphene edge and propose that this takes place through bond breaking between graphene edge bonds and the Ir substrate.

First-principles investigation of lithium doped and lithium intercalated bilayer graphene and carbon nanotubes

O Gulseren and H Sener Sen

Bilkent University, Turkey

We have performed first-principles calculations based on density-functional theory for understanding of the structural and electronic properties of Li doped bilayer graphene and Li intercalated carbon nanotubes especially addressing the controversial charge transfer state between Li and C. We have checked the possible adsorption, substitution and intercalation of Li by using a bilayer graphene system both with AB stacking (12 different initial configurations) and AA stacking (8 different initial configurations). All calculations are repeated both with LDA and GGA exchange-correlation potential, even though the values of binding energies are different, their order and corresponding physical picture are same from both of the functionals as well as the stackings. In conclusion, we can summarize that Li prefers the hollow site adsorption geometry and it prefers intercalation but not the substitution. In these adsorption modes, almost 0.9 electron of Li atom is transferred to neighboring carbon atoms network leaving positively charged core behind.

Reactions on surfaces 8

The formation of superhydrogenated PAHs and their catalytic role in H_2 formation

J Thrower[1], B Jørgensen[1], E Friis[1], A Skov[1], A Cassidy[1], S Baouche[1], R Balog[1], M Andersen[1], B Hammer[1], V Mennella[2] and L Hornekær[1]

[1]Aarhus University, Denmark, [2]Istituto Nazionale di Astrofisica, Italy

Polycyclic aromatic hydrocarbons (PAHs) are found in a diverse variety of environments ranging from the soot formed in combustion processes to the interstellar medium (ISM). Density functional theory (DFT) calculations [1] have suggested that H addition to neutral PAHs can occur readily along with Eley-Rideal abstraction reactions in which H_2 molecules are formed. Such processes have important implications for the formation of H_2 under astrophysically relevant conditions where surface reactions are essential for H recombination [2]. We have investigated experimentally the interaction between atomic hydrogen and PAH molecules adsorbed on a graphite surface. We present a combination of mass spectrometric and infrared spectroscopic measurements [3] which, along with scanning tunneling microscopy results, reveal the formation of PAH molecules with extremely high degrees of superhydrogenation. The observed product mass distributions confirm that abstraction reactions involving superhydrogenated PAHs can provide an alternative pathway to H_2 formation. The reported measurements are supported by complementary DFT calculations on the stability of the superhydrogenated species formed. These investigations highlight the importance of routes to H_2 formation involving neutral PAHs that have in general been neglected in astrochemical models.

[1] E. Rauls and L. Hornekær, Astrophys J., 679, 531 (2008).
[2] D. Hollenbach and E. E. Salpeter, Astrophys J., 163, 155 (1971).
[3] V. Mennella, L. Hornekær, J. Thrower, and M. Accolla, Astrophys. J.,745, L2 (2012).

Adsorption and reactivity of halo-compounds on metal and semiconductor surfaces

C Panosetti[1], W A Hofer[1], K R Harikumar[2], I R McNab[3], J C Polanyi[2] and A Zabet-Khosousi[4]

[1]University of Liverpool, UK, [2]University of Toronto, Canada, [3]Seneca College, Canada, [4]Columbia University, USA

An overview on surface reactivity of halo-compounds on metal and semiconductor surfaces will be presented, focusing on three systems whose characterization was carried out in our group. First, J. Polany's group at University of Toronto found that chloropentane forms asymmetric (A) and symmetric (S) pairs on Si(100)-2×1 with different curvature of one pentane tail. This renders the rate of thermal reaction of A much greater than S in chlorinating room-temperature silicon. The energy threshold for electron-induced reaction is also different. We have used Density Functional Theory and Nudged Elastic Band tools to explain the features of this system [1]. Second, we have computationally modeled the adsorption of 1,3-diiodobenzene (m-DIB) on Cu(110) by means of Density Functional Theory including Grimme's van der Waals interaction correction. We have compared the adsorption energies and structures of 23 possible configurations of the physisorbed molecule. Furthermore, we have simulated STM images for the four most stable configurations using the Tersoff-Hamann approach at different bias voltages. We find that all the adsorption orientations have comparable energy and we discuss the relative probabilities of experimental observation. We find that the adsorption induces small distortions in the molecular structure of the adsorbate and in some cases an adsorption-induced symmetry breakdown occurs and we find evidence that the most stable arrangement is actually a bistable system [2]. Finally, knowing that single atoms can be site-specifically imprinted onto a surface, we have designed Cu-atom-Cu clusters using as an anchor Cl, I and S atoms and we investigate their properties.

[1] K. R. Harikumar, Iain R. McNab, John C. Polanyi, Amir Zabet-Khosousi, Chiara Panosetti and Werner A. Hofer, Chem. Commun., 2011, 47, 12101-12103.
[2] Chiara Panosetti and Werner A. Hofer, J. Comput. Chem., 2012 (in press).

New organic reactions at solid surfaces controlled by charge transfer

J Rodriguez Fernandez[1], C Urban[1], Y Wang[1], R Garcia[2], M Angeles Herranz[2], M Alcami[2], N Martin[2], F Martin[4], J María Gallego[3], R Otero[1] and R Miranda[1]

[1]Universidad Autónoma de Madrid, Spain, [2]Universidad Complutense de Madrid, Spain, [3]CSIC, Spain

Albeit polymerization reactions on solid surfaces have attracted enormous interest over the last few years, little is hitherto known about the atomistic and electronic processes involved in the formation of polymers from monomeric adsorbed species. In this work we show a combined experimental and theoretical approach that enables us to characterize all the steps in the oligomerization reaction of 15,15,16,16-tetracyano-6,13-pentacene-p-quinodimethane (TCPQ) adsorbed on Cu(100), both from the structural (Scanning Tunnelling Microscopy, STM), electronic and chemical (X-ray Photoelectron Spectroscopy, XPS) points of view. Our analysis distinguishes three main steps in such reaction: 1) conformational change due to the charge transferred from the surface upon adsorption; 2) thermally-induced cyano elimination to yield a surface-stabilized diradical species; and 3) surface diffusion of the diradicals to form the oligomeric end results. We believe that such charge-transfer processes between surface and adsorbate might be an essential ingredient to understand those polymerization reactions on surfaces that have no solution analogue

On-surface "Click Chemistry"

F Bebensee, C Bombis, S Vadapoo, J Cramer, K Gothelf, F Besenbacher and T Linderoth

Aarhus Univeristy, Denmark

The on-surface synthesis scheme for joining molecular building blocks by strong covalent bonds has received tremendous interest in the last few years: it promises a route to formation of advanced molecular surface nanostructures with enhanced chemical and thermal stability compared to structures prepared from conventional non-covalent self-assembly. [1-3] In this context, one challenge is to identify suitable organic chemical reactions that will readily proceed under UHV conditions with the reactants confined on a surface. As “click-chemistry” utilizes simple starting materials and proceeds by-product free, this class of reactions presents an interesting route for on-surface synthesis schemes.

We employed scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy to study the most common among the “click-reactions” – the copper catalyzed 1,3-dipolar Huisgen cycloaddition – between terminal alkyne (9-ethynylphenanthrene) and azide (4-azidobiphenyl) molecules on a Cu(111) surface. We chose Cu(111) as the substrate in our experiments in order to mimic the Cu-catalyst employed in standard procedures to run this reaction (in solution). We find evidence that the reaction proceeds under these restrictive conditions. Interestingly, our data suggest the presence of more than one single conformer of the product, despite reports that solid copper catalyzes the reaction [4] and thus should yield only a single regio-isomer.

[1] G. Franc, A. Gourdon, PCCP, 2011, 13, 14283.
[2] S. Weigelt, C. Busse, C. Bombis, et al., Angew. Chem. Int. Ed., 2008, 46, 9227.
[3] S. Weigelt, J.Schnadt, A. Tuxen, et al., JACS, 2008, 130, 5388.
[4] J. F. Stoddart, W. F. Paxton, J. M. Spruell, JACS, 2009, 131, 6692.

Surface-assisted homo-coupling of mono-substituted acetylenes

Y Zhang[1], N Kepčija[1], M Kleinschrodt[1], K Diller[1], J Björk[2], S Klyatskaya[3], F Klappenberger[1], M Ruben[3] and J Barth[1]

[1]Technische Universität München, Germany, [2]Linköping University, Sweden, [3]Karlsruhe Institute of Technology, Germany

Considerable attention has recently been devoted to the on-surface synthesis scheme for the fabrication of molecular nanostructures at interfaces through the joining of organic building blocks by covalent bonds [1]. This strategy is anticipated to result in improved thermal and chemical stability compared to non-covalent self-assembly, may lead to materials with novel electronic properties, and provides a route towards two-dimensional (2D) polymers [2]. Here we demonstrate through scanning tunneling microscopy measurements and first principles calculations the formation of covalent C-C bonds through a surface-assisted reaction between two acetylene endgroups, which is formally reminiscent of the Hay coupling reaction [3]. The homo-coupling reaction occurs under soft conditions on a noble metal (Ag(111)), whereby model calculations reveal a drastically reduced energy barrier for the required hydrogen abstraction. Different benzene derivative building blocks featuring acetylene units could be linked through this reaction to form dimers and open-pore organic networks. Our approach provides a new route to synthesize covalently bonded, conjugated 2D molecular nanostructures and layers.

[1] J. Méndez et al., Chem Soc Rev. 40 4578 (2011); G. Franc and A. Gourdon, Phys Chem Chem Phys 13 14283 (2011).
[2] J. Sakamoto, J. van Heijst, O. Lukin, and A. D. Schlüter, Angew. Chem. Int. Ed. 121, 1048 (2009).
[3] A. S. Hay, J. Org. Chem. 27, 3320, (1962).

Surface Chemistry of NH_3 on Co(0001) surface in relation to Fischer-Tropsch Synthesis(FTS)

A C Kizilkaya, K-J Weststrate and H Niemantsverdriet

Eindhoven University of Technology, The Netherlands

Fischer-Tropsch Synthesis (FTS) has regained interest in the last decades mainly due to increase in oil prices, backed up with environmental and political reasons. One of the key issues in FTS is the catalyst deactivation problem, especially when the catalyst of choice is the expensive Co metal. One of the deactivating types of compound in FTS is the nitrogen containing species, in particular, NH_3. Although it is known that NH_3 is a strong poison, atomic scale information about the elementary steps of the deactivation mechanism is lacking. We present the first study that utilizes a surface science approach for this important reaction in the deactivation of Co-FTS catalysts.

Our results indicate that after heating an ammonia covered Co(0001) surface to 630 K, we are left with some decomposition products on the surface. We checked desorption of ammonia and other nitrogen compounds, however only H_2 desorption was observed. The preliminary results indicate that NH_3 readily dissociates on the flat close-packed Co(0001) surface. The only decomposition product that is desorbed is H_2, meaning that surface is covered with NH_x species after decomposition. The further steps in the research will be the investigation of the effect of NH_X species on the adsorption and desorption characteristics of CO and H_2 which are the main reactants of the FTS.

Isotope effects in desorption kinetics and adsorption geometry of cyclohexane on Rh(111)

T Koitaya, K Mukai, S Yoshimoto and J Yoshinobu

University of Tokyo, Japan

C-H bond activation of saturated hydrocarbons by transition metal is a key step in the conversion to more valuable functionalized molecules as well as dehydrogenation. In the case of cyclohexane adsorbed on metal surfaces, the softened C-H stretching modes have been observed, and assigned to C-H bonds pointing to a metal surface.[1-6] The significant red-shift of the soft mode is due to the electronic interaction between unoccupied C-H orbitals and occupied metal states (C-H•••M interaction), which leads to facilitation of dehydrogenation. The C-H•••M interaction is analogous to the hydrogen bond (H-bond). The isotope effect in the H-bond is widely known as the Ubbelohde effect.[7] In this study, we observed novel isotope effects in the desorption kinetics and adsorption geometry of cyclohexane on Rh(111) by infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD), photoelectron spectroscopy (PES), and spot-profile-analysis low energy electron diffraction (SPA-LEED). The desorption energy of deuterated cyclohexane (C_6D_{12}) is lower than that of C_6H_{12}. In addition, the work function change by adsorbed C_6D_{12} is smaller than that by adsorbed C_6H_{12}. These results indicate that C_6D_{12} has a shallower adsorption potential than C_6H_{12}. The lateral geometric isotope effect was also observed in two-dimensional cyclohexane superstructures as a result of the different repulsive interaction between interfacial dipoles. The observed isotope effects originate from the isotopic difference in the C-H•••M interaction, which may be a consequence of the quantum nature of hydrogen nuclei in analogy with the typical H-bond.

[1] J. E. Demuth, H. Ibach, and S. Lehwald, Phys. Rev. Lett. 40, 1044 (1978).
[2] M. A. Chesters and P. Gardner, Spectrochim. Acta A Mol. Biomol. Spectrosc. 46, 1011 (1990).
[3] R. Raval, S. F. Parker, and M. A. Chesters, Surf. Sci. 289, 227 (1993).
[4] M. K. Weldon, P. Uvdal, C. M. Friend, and B. C. Wiegand, Surf. Sci. 355, 71 (1996).
[5] T. Koitaya, A. Beniya, K. Mukai, S. Yoshimoto, and J. Yoshinobu, Phys. Rev. B 80, 193409 (2009).
[6] T. Koitaya, K. Mukai, S. Yoshimoto, and J. Yoshinobu, J. Chem. Phys. 135, 234704 (2011).
[7] E. M. T. Robertson and A. R. Ubbelohde, Proc. R. Soc. A 170, 0222 (1939).

Organic layers and polymers 9

Electronic properties and coverage-dependent orientation of free-base porphine on the Ag(111) surface

K Diller, F Klappenberger, S Fischer, F Allegretti, A C Papageorgiou and J V Barth

TU München, Germany

Porphyrins are extremely versatile building blocks whose special electrochemical and photophysical properties promise the utilization in various applications, such as organic solar cells, single-site catalysis, sensing, or nanoelectronics. A key point for the control of the functional properties is to understand the role of each single porphyrin constituent, namely the tetrapyrrole macrocycle, the metal center and the meso-substituents.

The study of the simplest porphyrin, the free base porphine (2H-P), represents a fundamental reference system for the understanding of functional porphyrin nanoarchitectures and films. We present a systematic X-ray spectroscopy investigation of the 2H-P/Ag(111) system. The experimental X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy data are accompanied by density functional theory (DFT) calculations which allow the peak assignment of the NEXAFS spectra and the derivation of the electronic structure of the molecule. For coverages up to one monolayer angle-resolved NEXAFS shows that the porphine molecules bind in a flat geometry. Contrary to adsorbed 2H-P on Cu(110) [1] no substantial charge transfer from the substrate to the LUMO can be observed. With increasing layer thickness the molecules tilt away from the surface plane, in marked contrast to phenyl-substituted species on the same substrate.

[1] Dyer et al., ACS Nano, 2011, 5 (3), pp 1831–1838.

Photocurrent generation in metal-organic coordination polymer thin films

J Joyce, D N Buckley and C Silien

University of Limerick, Ireland

Trimesic acid (TMA) forms highly ordered monolayers on Au(111) modified by underpotential deposition of copper sulfate and exhibits at least one unbound carboxylic acid moiety, readily affording thus, with $Cu(OAc)_2$, layer-by-layer growth of metal-organic coordination polymer on a substrate [1]. Highly ordered metal-organic frameworks (MOF) of tetra(4-carboxyphenyl)porphyrin (TCPP), a proto-typical chromophore in photovoltaic applications [2], have also been assembled [3]. In keeping with the recently demonstrated possibilities of assembling MOF exhibiting zeolite-like porous structure [4], which could improve electrolyte access into photoactive films, and with the flexibility in mixing molecular species afforded by a layer-by-layer construction, we have studied the growth of and photocurrent generation in TCPP and TMA/TCPP metal-organic polymer assembled on copper modified Au and sol-gel TiO monolayer-modified ITO electrodes with methyl-viologen as electron acceptor. More specifically, we discuss the introduction of TMA as spacer minimizing the quenching in TCPP, without compromising TCPP film growth.

[1] Cebula I., et al. Angew. Chem. Int. Ed. 2010, 49, 6220-6223.
[2] Cherian S., et al. J. Phys. Chem. B 2000, 104, 3624-3629.
[3] Motoyama S., et al. J. Am. Chem. Soc. 2011, 133, 5640-5643.
[4] Wang, S., et al. J. Am. Chem. Soc. 2010, 132, 18038-18041.

Chiral wetting layers of oligo-aramides on an insulating surface

C M Hauke[1], P Rahe[1], M Kittelmann[1], C Storz[2], A F M Kilbinger[2] and A Kühnle[1]

[1]Johannes Gutenberg University Mainz, Germany, [2]University of Fribourg, Switzerland

Molecular self-assembly constitutes a versatile strategy for creating tailor-made functional surface structures [1]. So far, however, the majority of self-assembled molecular structures have been limited to conducting surfaces [2]. On prototypical insulating surfaces, such as KBr or NaCl, the comparably weak molecule-surface interaction largely hinders the formation of extended wetting layers and frequently results in molecular bulk growth and dewetting [3]. Only very recently, the natural cleavage plane of calcite has been demonstrated to constitute a most suitable insulating substrate for the formation of molecular wetting layers [4].

Here, we extended the present knowledge to chiral surface structures by investigating prochiral and achiral molecules from the class of oligo-aramides on the (10-14) cleavage plane of calcite. These molecules have been designed as versatile candidates for molecular self-assembly, constituting ideal building blocks for molecular rods [5]. All experiments were performed using non-contact atomic force microscopy (NC-AFM) under ultra-high vacuum conditions.

Upon deposition at room temperature, we observe highly ordered molecular islands that form extended wetting layers. The islands' structure and orientation as well as their binding strength to the surface can be tuned by rational variation of the molecular moieties. This way it is possible to positively influence the stability of wetting layers on this insulating substrate and create structures that are suitable for thermally induced molecular coupling [6].

[1] G. Whitesides, Science 254 (1991) 1312.
[2] J.V. Barth, Annu. Rev. Phys. Chem. 85 (2007) 375.
[3] S. Burke et al., J. Phys.: Condens. Matter 21 (2009) 423101.
[4] P. Rahe et al., Phys. Chem. Chem. Phys. (2012), DOI: 10.1039/C2CP40172J.
[5] C. Storz et al., Macromol. Rapid Commun. 32 (2011) 238-244.
[6] M. Kittelman et al., ACS Nano 5 (2011) 8420-8425.

Molecular interplay between substrate templating and intermolecular interactions on an insulating surface

M Kittelmann, P Rahe and A Kühnle

Universität Mainz, Germany

Molecular self-assembly on surfaces is governed by a subtle interplay between intermolecular and molecule-surface interactions [1]. In fact, when aiming at exploiting the structural variety of organic molecules for self-assembled structure formation on surfaces, it is important to balance these two interactions, which is frequently achieved for molecular self-assembly on metallic surfaces [2]. On insulating substrates and thin insulating films, however, molecule-surface interactions have been found to be considerably reduced as compared to metallic substrates. This reduced interaction is frequently resulting in molecular bulk crystal formation or molecular dewetting [3] instead of self-assembly of extended two-dimensional islands. So far, however, only very few examples exist demonstrating the formation of a molecular wetting layer on an insulating surface [4,5].

Here, we present a system that directly expresses the balance between intermolecular and molecule-surface interactions by the coexistence of two different molecular structures on an insulating surface. We study the molecular self-assembly of biphenyl-4,4'-dicarboxylic acid (BPDCA) on the most stable cleavage plane of calcite, $CaCO_3$(10-14), revealing two-dimensional, ordered islands at room temperature [6].

High-resolution non-contact atomic force microscopy images of the molecular islands unravel an ordered inner structure that is dominated by rows of molecules aligned side-by-side. Our results indicate that an excellent size match of the molecular structure with respect to the underlying substrate allows for increased binding of the BPDCA molecules to the surface. In between the rows, a different molecular structure is coexisting with the molecules aligning head-to-tail. This structure is explained by intermolecular hydrogen bond formation very similar to the BPDCA bulk structure.

The coexistence of the bulk-like structure with the row structure indicates that molecule-substrate and intermolecular interactions are of similar strength in the presented system.

[1] J. V. Barth Annu. Rev. Phys. Chem. 58 (2007) 375.
[2] A. Kühnle Curr. Opin. Colloid Interface Sci. 14 (2009) 157–168.
[3] M. Körner et al. Phys. Rev. Lett. 107 (2011) 016101.
[4] R. Pawlak et al. J. Phys. Chem. C 114 (2010) 9290–9295.
[5] P. Rahe et al., Phys. Chem. Chem. Phys. (2012), DOI: 10.1039/C2CP40172J.
[6] M. Kittelmann et al. submitted.

Matching the cage: Y-shaped molecules templated by a honeycomb network

B Karamzadeh[1], I Cebula[2], D Muñoz Torres[3], T Eaton[3], M Mayor[3] and M Buck[1]

[1]University of St Andrews, UK, [2]University of Wroclaw, Poland, [3]University of Basel, Switzerland

Self-assembly of organic molecules at surfaces offer a range of opportunities to access the bottom of the nanoscale. A particular interesting one is the use of molecular networks as templates to control the assembly of other molecular entities [1-3]. While the design of pore geometries through variation of the network components is one possibility, adsorption of additional molecules is another one.

Here we report on our studies on a series of Y-shaped molecules which are adsorbed from solution into the hexagonal pores of a bimolecular hydrogen bonded network consisting of 3,4:9,10-perylenetetracarboxylic diimide (PTCDI) and melamine. These molecules which are variants of 1,3,5-tris(biphenylethynyl)benzene (TBPEB) divide each pore of the network into three sub-pores. In addition to the threefold symmetry of the TBPEB molecules also sixfold symmetric patterns are seen in the STM images which are explained by a switch between two equivalent positions on a time scale fast compared to the imaging. This rotation is blocked upon adsorption of fullerene molecules. In contrast to the unmodified pore of the network which hosts seven close-packed molecules only up to three, well separated fullerenes fit into the modified pore.

[1] R. Madueno, M. T. Räisänen, C. Silien, M. Buck, Nature 454, 618 (2008).
[2] D. Kühne, F. Klappenberger, W. Krenner, S. Klyatskaya, M. Ruben, and J. V. Barth, PNAS 107, 21332 (2010).
[3] M. T. Räisänen, A. G. Slater, N. R. Champness, and M. Buck, Chemical Science 3, 84 (2012).

Low-energy scale excitations in the spectral function of organic monolayer systems

A Schöll, J Ziroff, S Hame, M Kochler, A Bendounan and F Reinert

Universität Würzburg, Germany

Using high-resolution photoemission spectroscopy we demonstrate that the electronic structure of several organic monolayer systems, in particular 1,4,5,8-naphthalene tetracarboxylic dianhydride and Copper-phthalocyanine on Ag(111), is characterized by a peculiar excitation feature right at the Fermi level. This feature displays a strong temperature dependence and is immediately connected to the binding energy of the molecular states, determined by the coupling between the molecule and the substrate. At low temperatures, the line-width of this feature, appearing on top of the partly occupied LUMO (lowest unoccupied molecular orbital of the free molecule), amounts to only ~ 10 meV, representing an unusually small energy scale for electronic excitations in these systems. We discuss possible origins, related e.g. to many-body excitations in the organic-metal adsorbate system, in particular a generalized Kondo scenario based on the single impurity Anderson model [1,2].

[1] J. Ziroff et al, PRB Rapid Comm. (in press).
[2] A. Schöll, et al., Science 329 303 (2010).

Assessing Density-Functional Theory with screened van der Waals interactions (DFT+vdW^{surf}) for model hybrid inorganic/organic systems

N Ferri and A Tkatchenko

Fritz Haber Institut, Germany

Hybrid inorganic/organic systems (HIOS) are widely investigated for usage in a large variety of new electronic devices e.g. electro-opto (LED) or photovoltaics devices. The interface geometry plays a crucial role in HIOS and its correct description is a requisite for predicting electronic properties. Here we study two model HIOS: diindenoperylene (DIP, C_3H_{16}) and C_{60} on coinage-metal surfaces (Cu(111), Ag(111) and Au(111)). The DIP molecule is an interesting support for its organic n-type semiconductor nature and the ability to form excellently ordered films on coinage-metal surfaces. On the other hand, molecular crystal and films based on fullerene molecules are of interest because of their very rich electronic properties (e.g. superconductivity).

These systems are used to test the recently developed PBE+vdW^{surf} approach, which accurately treats hybridization and long-range Coulomb screening, and includes interface polarization effects [1]. We show that for both systems (DIP and C_{60}, the PBE+vdW^{surf} approach yields average equilibrium adsorption positions in excellent agreement (about 0.1 Å) with experimental data. In the case of DIP, measurements have been performed using X-ray standing wave technique plus X-ray photoelectron spectroscopy (XSW+XPS) [2]. In the case of C_{60}, STM and LEED results are available [3].

Finally, we assessed the role of self-consistency of the vdW energy in the DFT+vdW^{surf} method, by adding the potential due to vdW energy to the DFT potential. We compared post-process and self-consistent results using a large variety of systems: from small dimers (e.g. diatomic dimers, water dimer) to the HIOS presented above, passing through intermediate systems of increasing size.

[1] V. G. Ruiz *et al.*, Phys. Rev. Lett. (2012) in print.
[2] C. Bürker *et al.*, http://ftp.esrf.eu/pub/UserReports/43789_A.pdf.
[3] H.L. Li *et al.*, Phys. Rev. Lett. 103, 056101 (2009).

Exploiting surface reactivity: Ni(II) diphenylporphyrin monolayers on Ag(111) and Ag/Si(111)

B Murphy[1], S Krasnikov[1], A Cafolla[2], N Sergeeva[1], N Vinogradov[3], J Beggan[2], O Lübben[1], M Senge[1] and I Shvets[1]

[1]Trinity College Dublin, Ireland, [2]Dublin City University, Ireland, [3]Lund University, Sweden

Due to their interesting physicochemical properties and conformational flexibility, porphyrins are widely used for the fabrication of complex supramolecular structures, which are utilized in many technological applications including light-harvesting arrays for solar energy generation, sensors, molecular optoelectronic gates, photo-inducible energy or electron transfer systems, nonlinear optics and oxidation catalysts. In this work, the room temperature self-assembly and ordering of (5,15-diphenylporphyrinato)nickel(II) (NiDPP) on the Ag(111) and Ag/Si(111) surfaces have been investigated using scanning tunnelling microscopy and low-energy electron diffraction. The self-assembled structures and lattice parameters of the NiDPP monolayer are shown to be extremely dependent on the reactivity of the substrate, and probable molecular binding sites are proposed. The NiDPP overlayer on Ag(111) grows from the substrate step edges, which results in a single-domain structure. This close-packed structure has an oblique unit cell and consists of molecular rows. The molecules in adjacent rows are rotated by approximately 17 degrees with respect to each other. In turn, the NiDPP molecules form three equivalent domains on the Ag/Si(111) surface, which follow the three-fold symmetry of the substrate. The molecules adopt one of three equivalent orientations on the surface, acting as nucleation sites for these domains, due to the stronger molecule-substrate interaction compared to the case of the Ag(111). The results are explained in terms of the substrate reactivity and the lattice mismatch between the substrate and the molecular overlayer.

Low temperature physics 5

(invited) Muon-spin rotation study of magnetic and superconducting properties of Fe-based superconductors

R Khasanov[1], A Amato[1], H Luetkens[1], M Bendele[1], K Conder[2], E Pomjakushina[2] and N Zhigadlo[3]

[1]Paul Scherrer Institute, Switzerland, [2]Laboratory for Developments and Methods, Paul Scherrer Institute, Switzerland, [3]Laboratory for Solid State Physics, ETH Zürich, Switzerland

We attempt to give a comprehensive discussion of studies performed to date by muon-spin spectroscopy (more precisely the relaxation and rotation technique, also know as μSR) on the recently discovered layered iron-based superconductors. On one side, μSR has been used to characterized the magnetic state of different families of layered iron-based systems. Similarly the subtle interplay of the magnetic state and the structural transition present in some families has been investigated. We will also discuss the information provided by this technique on the interaction between the magnetic state and the superconducting phase. Finally the μSR technique has been used to investigate the magnetic penetration depth of the superconducting ground state. The study of its absolute value, temperature and magnetic field dependence provides crucial tests for investigating possible unconventional superconducting states in such systems.

Effect of pressure on band structure, lattice and superconductivity in iron compounds

M Nunez-Regueiro[1], G Garbarino[2] and R Weht[3]

[1]CNRS, France, [2]ESRF, France, [3]CNEA, France

A systematic study on the effect of pressure on the superconducting properties, crystallographic lattice and electronic band structure has been performed on several iron superconductors. The correlation between the maximum superconducting transition temperature T_c and ideal tetrahedron was verified for Sr_2VO_3FeAs and $SmFeAsO_{1-x}F_x$. However, the analysis of both cases suggests that different mechanisms are at play and that there is no common picture for all iron superconductors as has been theoretically proposed. Namely, for Sr_2VO_3FeAs, the multiple nesting, that quenches antiferromagnetism and favours superconductivity, disappears as the tetrahedron is deformed. While in $SmFeAsO_{1-x}F_x$, a reversion of the doping near the ideal tetrahedron seems to be the cause of the maximum T_c . For the case of non-superconducting parent compounds CaFeAsF and SrFeAsF, we show that the structural distortion transition temperature T_0 and the antiferromagnetic transition T_N decrease with pressure at different rates, while superconductivity appears and increases concurrently. When T_N crosses T_0, there is a symmetry change of the low temperature phase, from orthorhombic to monoclinic, with the subsequent recovery of T_N and concomitantly decrease of T_c. This curious and previously unobserved behaviour can be explained within a Ginzburg-Landau approach.

Optical properties of Co-doped 122 iron-pnictides

L Degiorgi, A Dusza and C Mirri

ETH Zurich, Switzerland

The discovery of superconductivity in several families of closely related iron-pnictides has generated considerable interest, primarily because superconductivity is possible at high-temperature in materials without CuO_2 planes, and has also induced a frenetic search for possible common mechanisms between them and the superconducting cuprates. Furthermore, these materials provide an interesting arena in which to study the impact of electronic correlations with respect to the emergence of structural/magnetic and superconducting phase transitions. We report on a thorough optical investigation over a broad spectral range and as a function of temperature of the charge dynamics in $Ba(Co_xFe_{1-x})_2As_2$ compounds for Co-doping ranging between 0 and 18%. For the parent compound as well as for $x=0.025$ we observe the opening of a pseudogap, due to the spin-density-wave phase transition and inducing a reshuffling of spectral weight from low to high frequencies. For compounds with $0.051<x<0.11$ we detect the superconducting gap, while at $x=0.18$ the material stays metallic at all temperatures. Through spectral weight arguments, we give clear-cut evidence for moderate electronic correlations for $0<x<0.061$, which then crossover to values appropriate for a regime of weak interacting and nearly-free electron metals for $x>0.11$.

Magnetic fluctuations - a driving force for superconductivity. Neutron scattering investigations in Fe-based superconductors

A Taylor[1], R Ewings[2], T Perring[2], S Clarke[1] and A Boothroyd[1]

[1]University of Oxford, UK, [2]STFC, UK

One of the most exciting findings in investigations of High-Tc superconductivity has been the discovery of a magnetic resonance in the superconducting state, associated with a spin excitation with a characteristic position in wavevector and energy space [1]. This resonance has been investigated across the families of Fe-based superconductors with several common features observed such as the scaling of the resonant energy with Tc (Er ≈ 4.3 Tc in (Ba,K)Fe2As2 [1]) and the position of the resonance either at, or incommensurate about, the antiferromagnetic wavevector [1,2,3]. This work presents results of inelastic neutron scattering experiments on a broad range of Fe-based superconducting materials in order to address the question - are these features really common to all these materials? Results from the characteristic 122-arsenide family [4] are contrasted with LiFeAs [2], $Cs_xFe_{(2-y)}Se_2$ and phosphorus containing materials.

[1] A. D. Christianson et al., Nature 456, 930 (2008).
[2] A. E. Taylor et al., Phys. Rev. B 83. 220514(R) (2011).
[3] J. -P. Castellan et al., Phys. Rev. Lett. 107, 177003 (2011).
[4] R. A. Ewings et al., Phys. Rev. B 83, 214519 (2011).

Variation of the superconducting penetration depth in $Ba(Fe,Ni)_2As_2$ single crystals

K Hasselbach[1], Z Sheng Wang[2], T Klein[2], P Rodiere[1], H Luo[3], X Y Lu[3], H-H Wen[4] and C Marcenat[5]

[1]CNRS, France, [2]Université Joseph Fourier, France [3]Chinese Academy of Science, China, [4]Nanjing University, China, [5]SPSMS, France

We report on the concentration dependence of the absolute value of London penetration depth in $Ba(Ni_xFe_{1-x})_2As_2$ single crystals. Nano-SQUID scanning microscopy allowed us a precise measurement of the flux profiles of a large number of individual vortices. As the distance of the SQUID sensor from the sample surface is known, +- 40 nm, we can deduce the absolute penetration depth from the flux profile. The measurements were performed between 0.7 K and 2 K allowing us access to lambda(0) and to compare the absolute value and the temperature evolution of the penetration depth to the data obtained on the same crystals by tunnel diode oscillator, local magnetization and specific heat measurements. Our results are consistent with the results obtained by these techniques and support a power law scaling in both the underdoped and overdoped region of the phase diagram of lambda(0) in function of T_c.

Multigap superconductivity in Co-doped 122 Iron Pnictide superconductors investigated by Local Magnetic Imaging

W Desoky[1,2], S J Bending[1], S E Sebastian[3] and T Tamegai[3]

[1]University of Bath, UK, [2]Zagazig University, Egypt, [3]Cavendish Laboratory, University of Cambridge, UK, [4]University of Tokyo, Japan

High resolution scanning Hall probe microscopy and Hall magnetometry have been used to investigate the magnetic properties of single crystal samples of Co-doped Sr-122 and Ba-122 iron pnictide superconductors. We resolve rather disordered field-cooled vortex structures for all doping levels and at all values of magnetic field studied. We have made a quantitative analysis of the evolution of the profiles of well-isolated vortices as a function of temperature, and used a fitting procedure to extract the temperature-dependent magnetic field penetration depth, $\lambda(T)$. This, in turn, allows us to infer the temperature-dependent superfluid density which has been compared with model results for a two band superconductor. Fit parameters yield insights into the symmetry of the order parameter at the electron and hole pockets as well as the relative contributions of the bands to the superfluid density. Vortex imaging and 'local' magnetisation measurements, with a static Hall probe parked just above the sample surface, also yield important information about the strength of vortex pinning forces and the possible presence of material inhomogeneities in our samples. Results will be discussed in the context of recent experimental and theoretical studies of the microscopic origin of superconductivity in these materials.

Vortex pinning and quasi-particle scattering by point defects in $Ba(Fe_{1-x}Cox)_2As_2$

S Demirdis[1], C J van der Beek[1], M Konczykowski[1], P Gierlowski[2] and D Colson[3]

[1]CNRS UMR 7642 & CEA-DSM-IRAMIS, France, [2]Institute of Physics of the Polish Academy of Sciences, Poland, [3]L'Orme des Mérisiers, France

While chemical heterogeneity and subsequent spatial variations of the superconducting parameters, as well as crystalline disorder on the scale of several dozen nm determine strong vortex pinning in iron-based superconductors at low fields [1,2], at higher magnetic fields the critical current density J_c is determinedby quasi-particle scattering in the vortex cores. The latter leads to the mean-free path variation pinning mechanism due to the local fluctuations of the dopant atom distribution. Plausibly, the relevant scatterers are the dopant atoms themselves.

In order to test this hypothesis, we study the evolution of vortex pinning and creep in $Ba(Fe_{1-x}Co_x)_2As_2$ as function of dopant concentration x, using the magneto-optical imaging technique and Hall probe array magnetometry. We also study the surface resistance as a fuction of temperature for single crystalline $Ba(Fe_{1-x}Co_x)_2As_2$ across the phase diagram, using the cavity perturbation method. Finally, we evaluate the effect of the controlled introduction of atomic-sized point defects using high energy electron irradiation, with doses of 0-2.7 C/m^2. In all cases, the differential magneto-optical technique is used to reveal large-scale disorder, to discard single crystals with pathological defects, and to select use single crystals with a spatially homogenous distribution of T_c.
We find that electron irradiation leads, in $Ba(Fe_{1-x}Co_x)_2As_2$ single crystals, to a decrease of the critical temperature of ΔT_c= - 0 to -3 K. No further dramatic changes are observed in the $Ba(Fe_{1-x}Co_x)_2As_2$ system after electron irradiation.

[1] S. Demirdis et al. Phys. Rev. B 84, 094517 (2011).
[2] C. J. van der Beek et al., Physica B 11 407 (2012).

Liquids and liquid interfaces 4

(invited) Photoelectron spectroscopy studies of chemistry at the liquid/vapor interface

J C Hemminger

University of California, USA

We have utilized Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS), and Liquid-Jet X-ray Photoelectron Spectroscopy (LJXPS) to study the composition and chemistry at the surface of aqueous solutions. APXPS has been used to obtain XPS spectra from deliquesced alkali halide salts. These experiments show that the halide ion concentration of larger, more polarizable halide ions is enhanced at the liquid surface. We also show that organic surfactant molecules adsorbed at the aqueous solution surface modify the depth distribution of the ions. LJXPS experiments have been used to study a variety of solutes in aqueous solutions. The dissociation equilibrium of nitric acid at the interface and compared to in the bulk of the solution will be described in detail. Nitric acid is less dissociated at the interface and the enthalpy of the dissociation reaction is decreased by a factor of two as compared to the bulk solution. First principles molecular dynamics simulations of nitric acid aqueous solutions shed light on how the differences in solvation of molecular nitric acid and the nitrate ion determine the different behavior in the bulk of the solution and at the liquid/vapor interface. The spatial distribution of and associated reaction equilibria for a number of organic molecular solutes in aqueous solutions have been studied and will be described.

Probing the silica-aqueous interface with in situ XPS and XAS

M Brown and J van Bokhoven

ETH Zürich, Switzerland

We have recently extended in situ XPS[1] and XAS[2] to the silica (SiO_2) nanoparticle-aqueous interface using a liquid microjet in combination with synchrotron radiation. Our in situ XPS[1] measurements of 7 nm SiO_2 at pH 10 show two distinct electronic structures in the Si 2p region at 107.8 and 106.5 eV. Electron kinetic energy dependent measurements allow the two components to be assigned to the bulk of the nanoparticle, and to the surface of the nanoparticle that is in direct contact with solution, respectively. Our in situ XAS[2] measurements at the Si K-edge as a function of pH for nanoparticles of 7, 12, and 22 nm reveal a change in shape of the Si 1s – t_2 absorption brought about by changes in solution pH. Our results are consistent with the number of silanol groups changing protonation state being inversely correlated with SiO_2 nanoparticle size. The importance of in situ studies will also be discussed by comparing the XAS spectra of aqueous 7 nm SiO_2 with the same dehydrated sample in vacuum.

[1] M.A. Brown, R. Seidel, S. Thurmer, M. Faubel, J.C. Hemminger, J.A. van Bokhoven, B. Winter, M. Sterrer Electronic structure of sub-10 nm colloidal silica nanoparticles measured by in situ photoelectron spectroscopy at the aqueous-solid interface Physical Chemistry Chemical Physics 13, 12720 (2011).

[2] M.A. Brown, T. Huthwelker, A. Beloqui Redondo, M. Janousch, M. Faubel, C.A. Arrell, M. Scarongella, M. Chergui, J.A. van Bokhoven Changes in the silanol protonation state measured in situ at the silica-aqueous interface Journal of Physical Chemistry Letters 3, 231 (2012).

The interaction between water and solid surfaces studied with near-ambient pressure X-ray photoelectron spectroscopy (NAP XPS)

A Jürgensen, H Raschke and R Hergenröder

Leibnitz-Institut für Analytische Wissenschaften (ISAS), Germany

The interaction between water and solid surfaces is ubiquitous in nature and technology, and thus of fundamental interest in materials science. It is important for the understanding of surface processes such as corrosion, electrochemistry and heterogeneous catalysis. Water-surface interactions also play an important role in geochemistry, in atmospheric chemistry and in biological systems.

The adsorption of water is dependent on the physical and chemical properties of the surface, and it influences the reaction mechanisms and kinetics of chemical processes that occur, acting as a spectator, a reactant, a catalyst, a product, or an inhibitor of surface reactions. However, the actual processes involved are still not well understood. X-ray photoelectron spectroscopy (XPS) is one UHV technique that is used for surface analysis, providing information on the elemental composition of the surface. Recently, an XPS system has been developed that can operate at near ambient pressure, making it possible to use this method to study interactions between water and solid surfaces *in situ* under more realistic conditions. Moreover, by using a conventional laboratory source, it is possible to study the interaction of biomolecules and water on surfaces while minimizing radiation damage. Here, we present the interaction of water with several metal and metal oxide surfaces, part of an ongoing near ambient pressure XPS study of processes at interfaces.

Hectorite clay swelling monitored by Near-Ambient Pressure-XPS

H Tissot[1], J-J Gallet[2], F Bournel[2], A Naitabdi[2], R Benbalagh[2], F Rochet[2], V Marry[2], E Dubois[2], A Pietzsch[3] and J Schnadt[3]

[1]synchrotron SOLEIL, France, [2]Université Pierre et Maris Curie (UPMC), France [3]Lund University, Sweden

Natural clays are key materials in ecological engineering, from the geological storage of long half-time radioactive waste to CO_2 sequestration. With respect to these issues, it is crucial to establish a bridge between the microscopic scale (chemical bonding, ionic exchange, ion solvation, ion and matter transport) and the macroscopic scale (swelling, retention capacities). One fundamental question is the hydration behaviour of clays, which governs their properties and uses.

Hydration of clays has already been studied by several techniques: diffraction, infrared spectroscopy, several neutrons induced techniques; however their interpretations cannot lead, up to now, to a clear global view of the key parameters governing the interaction between water and clays. In fact, these experiments deal with bulk measurements. Near-Ambient X-ray photoelectron spectroscopy (NAP-XPS) is a surface sensitive technique; it enables the in situ study of clays hydration by following changes in the core-level binding energies of counterion, water and silicate oxygen as a function of relative humidity (RH) and provides an accurate description of the structure and dynamics of both water and hydrated counterions on clays surfaces. We present here high resolution XPS at the Na 2s and O 1s levels recorded in surface sensitive conditions, for relative humidity values of 5 and 60%. Strong modification of the Na 2s binding energy is observed when the relative humidity increases. This shift shows that water insertion into hectorite interlayer modifies the electrostatic potential felt by the counterion.

Influence of a local stress on the kinetics of dissolution of a mineral

J Colombani, E Pachon-Rodriguez and A Piednoir

Université Claude Bernard Lyon 1, France

Dissolution of minerals is involved in many environmental questions, often with large human consequences. One can cite the durability of mineral materials, the management of nuclear wastes, the sequestration of atmospheric CO_2 or the pollution of drinking water. Progresses have been made during the last decade in our understanding of dissolution, particularly concerning the nature of the reactive surface, the role of etch pits, the influence of the mineral history, ...

One of the remaining open problems is the influence of an elastic stress on the nature and rate of dissolution. For instance a large discrepancy still exists between experimental results and modelling of pressure solution creep, a plastic strain mechanism of minerals based on the dissolution enhancement by an external stress.

We present here a first experimental evidence of the influence of a local stress on a molecular elementary mechanism of dissolution. This was performed by atomic force microscopy observation of the migration of a molecular step on the surface of a single crystal of gypsum during dissolution in water, where the AFM tip is used alternatively to apply a stress and probe the surface. The kinetics of this atomic mechanism is seen to obey the same law of pressure solution as the corresponding macroscopic phenomenon. This experiment evidences also how AFM may disturb the quantity it probes.

Asymmetric transport behaviors of positive and negative ion defects in an ice film

H Kang and E-S Moon

Seoul National University, South Korea

The transport properties of positive and negative ion defects in ice are deeply related to some interesting electrical properties of ice, such as the thermoelectric effect and the freezing potential. It has long been conceived that the positive and negative ion defects may transport via the so called "mirror image" mechanisms with only the proton transfer directions reversed. This idea, however, has not yet been clearly proven or refuted by experiments. In this work, we measured the transport distances of the ion defects in an amorphous ice film at low temperature (< 100 K). H_3O^+ (or OH^-) was placed at the ice film surface, and NH_3 (or NH_4^+) was buried in the interior of the ice at a controlled distance from surface. The acid-base reaction between the proton donor and acceptor species was monitored by the methods of reactive ion scattering and infrared spectroscopies. The study showed that H_3O^+ travels a much longer distance than OH^- in ice. The different transport distances of H_3O^+ and OH^- are explained in terms of their different transport mechanisms. H_3O^+ can move via an efficient proton-relay mechanism in ice, which does not exist for OH^-.

In situ characterisation of the GaPN/Si(100) surface for photoelectrocatalysis

M May[1], O Supplie[1], H Döscher[1], H Stange[1], H-J Lewerenz[2] and T Hannapel[3]

[1]Helmholtz-Zentrum Berlin, Germany, [2]California Institute of Technology, USA, [3]Technische Universität Ilmenau, Germany

The dilute nitride $GaP_{1-x}N_x$ lattice matched to Si is a promising absorber structure for solar-driven hydrogen production. As a photoelectrolytical tandem, it provides sufficient voltage for water-splitting as well as an efficient exploitation of the solar spectrum and benefits simultaneously from the unique properties of the Si substrate.
A microscopic understanding of both morphological and electronic properties of the semiconductor-liquid interface helps to avoid corrosion or even to use it favourably: Photocorrosion was used to form a thin oxide layer enhancing

stability and current densitiy for the related material InP, which had been homoepitaxially prepared by metal-organic vapour phase epitaxy (MOVPE) [1]. We explore the possibility to transfer the concepts demonstrated for the InP half-cell to this GaP-derived material system.

To this end, we employed MOVPE to grow $GaP_{1-x}N_x$ on Si(100) under in situ control with reflection anisotropy spectroscopy (RAS). A contamination-free MOVPE to UHV transfer system was used to study the $GaP_{1-x}N_x$/Si(100) surface before and after contact with the electrolyte applying surface analysis tools like photoelectron spectroscopy and LEED in addition to ex situ AFM and XRD.

We present first results starting from the preparation of microscopically well-defined surfaces, benchmarked by in situ characterisation methods, and their subsequent electrochemically induced modification. Photocorrosion was monitored by in situ RAS and is interpreted in combination with photoelectron spectroscopy.

[1] HJ Lewerenz et al., Energy Environ. Sci. 3 (2010) 748.

Surface dynamics 3

(invited) Manipulation of hydrogen distribution in Pd by injection of ballistic electrons

M Blanco-Rey

Donostia International Physics Center (DIPC), Spain

Incoming current from a scanning tunnelling microscope (STM) tip can be used to induce vibrations and diffusion of not only adsorbed species, but also below the surface. In particular, Sykes et al. [1] used STM to extract the H diluted in a Pd sample, moving it from the bulk region towards subsurface sites. Subsurface H species were imaged by STM as bright features, proving that diffusion was undergoing. Crucially, the experimental H extraction rates for positive and negative bias voltages had similar magnitudes. This is counterintuitive, as the Pd bandstructure is asymmetric around the Fermi level. We have put together a model that describes the diffusion mechanism, using a truncated harmonic potential and quantum tunnelling for H in Pd. The vibrational states of H are excited via interaction with electrons until the atom gains enough energy to jump over the barrier or to attempt tunnelling. Density Functional Theory (DFT) provides us with bandstructures, diffusion pathways and electron-phonon coupling values to parameterize the model. Interestingly, the main ingredient in the model, which is suggested by the theory of ballistic electron microscopy, is the fact that H diffusion is driven by the s-band electrons only [2]. The proposed theoretical model explains the qualitative aspects of the experiment and also provides quantitative predictions of diffusion rates under different experimental conditions.

[1] E.C.H. Sykes, L.C. Fernandez-Torres, et al., Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 17907.

[2] M. Blanco-Rey, M. Alducin, J.I. Juaristi, P.L. de Andres, Phys. Rev. Lett. 108 (2012) 115902.

Nonadiabatic effects during the dissociative adsorption of O_2 at Ag(111)? A first-principles divide and conquer study

I Goikoetxea[1], J Meyer[2], J Iñaki Juaristi[3], M Alducin[3] and K Reuter[2]

[1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, [2]Technische Universität München, Germany, [3]Departamento de Física de Materiales and Donostia International Physics Center, Spain

Experimentally, the Ag(111) surface is known for being rather inert to atom and molecular oxygen uptake. In this study [1], we have performed adiabatic gas-surface dynamics calculations in order to determine whether electronic non-adiabatic effects are responsible for such low reactivity. We use a first-principles divide and conquer approach in which, first we construct an accurate, adiabatic potential energy surface from extensive density functional theory calculations that map the dependence of the energy on the position of the two oxygen atoms over the Ag(111) surface. Next, we use this potential energy surface to compute a sufficiently large number of molecular dynamics trajectories to quantitatively determine the very low initial dissociative sticking coefficient at this surface.

Interestingly, our adiabatic calculations reproduce the low dissociation probabilities observed in experiments. We find that the low reactivity on Ag(111) is indeed caused by large energy barriers of about 1.1eV existing close to the surface. When analyzing the scattered molecules, the good agreement obtained between theory and experiments further confirms the validity of the adiabatic calculation. We conclude that the need to invoke potential spin or charge nonadiabatic effects is at least questionable in this system.

[1] I. Goikoetxea, J. Beltrán, J. Meyer, J I Juaristi, M. Alducin, and K. Reuter, New Journal of Physics 14 (2012) 013050.

The lifetimes and energy redistribution of intramolecular vibrational modes of a surface adsorbate: methoxy on Cu(100)

P Uvdal[1], M Andersson[2], J Blomquist[3], A Fuentes[4] and M Persson[4]

[1]Lund University, Sweden, [2]University of Copenhagen, Denmark, [3]Malmö University, Sweden, [4]University of Liverpool, UK

The lifetimes of different vibrational modes in a set of different isotopes of methoxy adsorbed on a copper surface have been measured. The lifetimes are determined using infrared spectroscopy by measuring full width at half maximum (FWHM) of different vibrational modes. We show that the experimental line shapes are clearly Lorentzian and due to lifetime broadening. This is in contrast to the vast majority of the data found in the literature where the line widths are dominated by inhomogeneous broadening. In our experiments we measure line widths down to 0.36 cm^{-1} (0.043 meV) at ultra low coverage, 0.004 monolayers. The lifetime of high frequency methyl stretch modes, 2000 -3000 cm^{-1}, are dominated by intramolecular vibrational energy relaxation, 3 - 7 ps. In contrast there are two low frequency methyl bend modes, 900 – 1100 cm^{-1}, for which the lifetimes, $\leq$ 15 ps, are dominated by electron-hole pair damping. The observed electronic vibrational damping rates are consistent with density functional theory (DFT) calculations.

Competition between electron and phonon excitations in the dynamics of nitrogen atoms and molecules at metal surfaces

R D Muino[1], L Martin-Gondre[2], M Alducin[1], G A Bocan[3], K R Geethalakshmi[1] and J I Juaristi[1]

[1]Centro de Fisica de Materiales CSIC-UPV/EHU, Spain, [2]Donostia International Physics Center DIPC, Spain, [3]Centro Atómico Bariloche, Argentina

We investigate the role played by electron-hole pair and phonon excitations in the interaction of reactive gas molecules and atoms with metal surfaces. We present a theoretical framework that allows us to evaluate within a full-dimensional dynamics the combined contribution of both excitation mechanisms while the gas particle-surface interaction is described by an ab initio potential energy surface [1]. The model is applied to study energy dissipation in the scattering and adsorption of nitrogen atoms and molecules in different metal surfaces. In non-reactive scattering processes, our results show that phonon excitation is the dominant energy loss channel, whereas electron-hole pair excitations represent a minor contribution. We substantiate that, even when the energy dissipated is quantitatively significant, important aspects of the scattering dynamics are well captured by the adiabatic approximation. In atomic adsorption, the two dissipative channels play a different role during the dynamics: phonons are responsible for determining the adsorption probability but electronic excitations are relevant at a later stage to fix the atoms to the adsorption positions. We also discuss the role of exchange-correlation in the theoretical description of the adiabatic interaction when using density functional theory [2]. We show that the dynamics of scattering processes at surfaces can be used as a valuable tool to test methodological advances in this respect.

[1] L. Martin-Gondre, M. Alducin, G. A. Bocan, R. Díez Muiño, and J. I. Juaristi, 2012 Phys. Rev. Lett. 108 096101.

[2] K. R. Geethalakshmi, J. I. Juaristi, R. Díez Muiño, and M. Alducin, 2011, Phys. Chem. Chem. Phys. 13, 4357.

An STM Investigation into Molecular Switches: Azophenine on Cu(110)

G Simpson, S Hogan, H Früchtl, T van Mourik and R Schaub

University of St Andrews, UK

Molecular switches are molecules that display stability in two or more states and the use of such molecules as electronic devices has been the focus of many recent studies. They are seen as a possible replacement to silicon microelectronics which face limitations in performance and cost as component size decreases.
Focusing on switching molecules, a few striking examples in the literature include H tautomerisation in naphthalocyanine [1], metal-ligand complexation in Cu[PVBA]$_2$ [2] and cis-/trans- isomerisation in azobenzene and its derivatives[3]. We report on a similarly remarkable system: azophenine adsorbed on a Cu(110) substrate.
STM measurements are carried out at 5 K on N,N'-diphenyl-2,5-bis(phenylimino)-1,4-benzoquinone diimine (azophenine). When adsorbed on a Cu(110) surface, the molecule remains in one of two stable H-tautomeric states and can be made to switch between them, at will, by applying a bias exceeding a threshold voltage of approximately 0.3 eV. By recording many switch events the process is shown to be activated by inelastic electron excitations. The interaction between the molecule and the underlying substrate plays a crucial role in activating azophenine for switching thanks to a chelate effect between lone pairs of the molecule and surface copper atoms. Our DFT calculations support this claim.

[1] P. Liljeroth, J. Repp, G. Meyer, Science 317, 1203 (2007).
[2] R. Ohmann, L. Vitali, K. Kern, Nano Lett. 10, 2995 (2010).
[3] B.-Y. Choi, S.-J. Khang, S. Kim, H. Kim, H. W. Kim, Y. J. Song, J. Ihm, Y. Kuk, Phys. Rev. Lett. 96, 156106 (2006).

Employing a Ni cylindrical single crystal in elementary and overall chemical reactions at stepped surfaces

L Juurlink[1], C Hahn[1] and A Kleyn[2]

[1]Leiden University, The Netherlands, [2]University of Amsterdam, The Netherlands

It is well known that steps on atomically flat surfaces may strongly affect the adsorption dynamics of, e.g., hydrogen. Much less is known how surface chemical reactions are influenced by the width of adjacent terraces or the exact arrangement of atoms in the step. Recently, we have systematically investigated how dissociative adsorption of H_2 on Pt is affected by terrace width employing a series of flat single crystals[1]. This type of study is very time consuming and may be hampered by differences in quality between the individual disc-shaped single crystals.

Here, we show that is possible to use a hollow, cylindrical single crystal to study both the dynamics of elementary steps in gas-surface interactions and overall chemical surface reactions[2]. LEED studies of the curved outer surface of a Ni single crystal show a continuous range of stepped and atomically flat surfaces. We utilize a supersonic molecular beam to locally impinge molecules onto small identified surfaces areas. While the King and Wells-technique quantifies adsorption as absolute dissociation probabilities, desorption is studied using spatially-resolved temperature programmed desorption (SR-TPD). We show that results obtained from the cylindrical single crystal compare well to those obtained on flat crystals. In addition, we provide results of a detailed study of D_2 dissociation on nickel surfaces with (111), (110) and (100) terraces and varying step densities. Results are interpreted in terms of direct and indirect dissociation mechanisms previously proposed to explain step-density effects for Pt.

[1] I. M. N. Groot et al., Angew. Chem. Int. Ed. 2011, 50, 5174.
[2] C. Hahn et al., J.Chem. Phys. 2012, 136, 114201.

Hydrogen atoms on graphite: Eley-Rideal reaction and dimers formation from ab-inito molecular dynamics

S Casolo, G F Tantardini and R Martinazzo

Università degli Studi di Milano, Italy

Molecular hydrogen represents the most abundant molecule in the interstellar medium where it is believed to form onto the surface of carbonaceous dust grains. Details of this formation process are still being debated, despite the progress made in the last few years.

We present here the first *ab initio* molecular dynamics study of the Eley-Rideal (ER) hydrogen recombination on a model graphite surface. We included substrate motion and corrugation by modeling a 3x3 graphene unit cell initially a T=0 K. Importantly, competitive reaction channels such as formation of stable dimers were taken into full account in this *ab initio*, on-the-fly approach.

We find that steering of the projectile atom gives an important contribution to the reaction for E<0.1 eV and prevents dimer formation, despite the favorable (barrier-less) energetics. At higher energies, on the other hand, *para* and *ortho* dimers form abundantly at the expense of the reaction yield.

Computed ER cross sections and ro-vibrational H_2 populations are in reasonable agreement with existing thermal desorption and molecular beams studies, as well as with quantum results on simplified models, and thermal rate constants for ER reaction and dimer formation are given for T in the range 300-10000 K. At lower temperatures quantum effects may play an important role but cannot be captured by the adopted classical approach.

Theory and modelling 3

(invited) Two-dimensional polaronic behavior in the binary oxides m-HfO_2 and m-ZrO_2

K McKenna[1], M Wolf[2], A Shluger[2], S Lany[3] and A Zunger[3]

[1]The University of York, UK, [2]University College London, UK, [3]National Renewable Energy Laboratory, Golden, Colorado, USA

Quasi-two-dimensional (2D) systems, including surfaces, heterointerfaces and layered materials, have become a rich playground for discovering exotic electronic effects such as high Tc-superconductivity and novel magnetic phases. The formation of polarons and the modification of their properties by reduced dimensionality have been implicated in many of these phenomena, but directly probing their properties experimentally remains extremely challenging.

In this study, we employ fully first principles methods that are free from the usual self interaction problems inherent to density functional theory to investigate the properties of hole polarons in the binary monoclinic oxides HfO_2 and ZrO_2. Although usually considered as 3D materials, our calculations show that they exhibit pronounced 2D polaronic properties. This unexpected effect is due to an asymmetry in the crystal structure of these materials, which induces small polaron formation in only one of its two oxygen sub-lattices, leading to highly anisotropic polaron conductivity. These results demonstrate how a small asymmetry in the lattice structure can determine the qualitative character of polaron localization and significantly broaden the realm of quasi-2D polaron systems.

[1] K. P. McKenna et al, Phys. Rev. Lett. 108, 116404 (2012).

Energy transfer in weakly coupled hybrid nanostructures

S Kawka and G C La Rocca

Scuola Normale Superiore, Italy

Inorganic-organic hybrid materials may allow new possibilities for optoelectronic devices taking advantage of the best of both components. This is of evidence in the strong coupling regime in which novel hybrid quasiparticles are formed, but also, in the weak coupling regime in which Wannier and Frenkel excitons maintain their individuality, an hybrid system offers significant advantages. In the case of OLED, it is a way to overcome the limitations regarding carrier transport in organic materials, using an heterostructure containing an inorganic semiconductor subsystem in which carriers are electrically injected, transported and bound into excitons, coupled to an organic light emitting subsystem via a Förster energy transfer process. This transfer can be efficient enough and has been observed in recent years[1].

Here we consider the non-radiative resonant energy transfer from a two-dimensional Wannier exciton (donor) to a Frenkel exciton of a molecular crystal overlayer (acceptor). As most of the organics are anisotropic, we characterize the effect of the optical anisotropy on this process. Using realistic values of material parameters, we show that it is possible to change the transfer rate within typically a factor of two depending on the orientation of the crystalline overlayer. The resonant matching of donor and acceptor energies is also partly tunable via the organic crystal orientation. We use a macroscopic approach that could be easily extended to different geometries and configurations, from quantum well to quantum dots, to microcavities, possibly including plasmonic effects or vibronic progressions.

[1] Agranovich et al.Chem. Rev. 111, 5179 (2011).

Gap engineering in atomically thin graphitic materials

J P Hague

The Open University, UK

For atomically thin graphitic materials such as graphene to be useful for digital applications, a significant gap of around 1 eV is required. Here, a perturbative theory is presented for the strong enhancement of graphene-on-substrate bandgaps by attractive interactions mediated through phonons in a polarizable superstrate. By constructing a set of self-consistent eqautions, it is demonstrated that gaps of up to 1 eV can be formed for experimentally achievable values of electron-phonon coupling and phonon frequency [1]. Gap enhancements computed using a dynamical mean-field theory range from 1 to 4, indicating possible benefits to graphene electronics through greater bandgap control for digital applications, through the relatively simple application of polarizable materials. I also discuss the effects of substrates on atomically-thin graphitic materials such as boron nitride (BN) and silicene. To cope with more complicated momentum-dependent interactions that may be formed between electrons and phonons within monolayers, I use the dynamical cluster formalism to reintroduce momentum dependence to the perturbation theory. The inclusion of renormalisations to the phonon propagator leads to increased gap enhancement at weak coupling, and a surprising decrease at high coupling.

Additionally, polaron spectral functions are computed for heavily doped graphene-on-substrate systems using the diagrammatic quantum Monte Carlo technique to investigate the effects of interaction on spectral functions when the symmetry between graphene sub-lattices is broken by a substrate [2]. Several polaronic features are visible, including band-flattening and changes in particle lifetimes. The difference between energies on each sub-lattice increases with coupling, indicating an augmented transport gap at the K point, while the spectral gap decreases slightly. In the absence of a gap, additional flattening is found around the K point. Changes in the form of the interaction and phonon dispersion do not strongly modify these results.

[1] J.P.Hague. Tunable graphene band gaps from superstrate-mediated interactions. Phys. Rev. B, 84 (2011) 155438.

[2] J.P.Hague. Polaron effects in heavily doped graphene on substrates. arXiv:1107.2507 (2011).

Divide, reduce and conquer for electronic structure and device simulations

M Iakovidis and G Fagas

Tyndall National Institute – UCC, Ireland

Matrix diagonalisation and inversion are core routines in all fields of computational modelling including materials science and device simulations. Many advanced algorithms exist for both serial and parallel computer architectures. However, a computational bottleneck often arises due to the large number of degrees of freedom that need to be treated in simulators.

Here, we present a divide, reduce and conquer (DRC) parallelisable algorithm that can be used to study the electronic and electrical properties of nanostructures using atomic scale models with tens of thousands of atoms. A performance improvement in computation time of an order of magnitude is demonstrated compared to both serial and parallel conventional implementations of Linear Algebra Package algorithms. This improved performance is achieved by dividing the Hamiltonian matrix into blocks (Divide), reducing the block size through removing unimportant degrees of freedom (Reduce), and finally diagonalising or inverting the new reduced matrix to calculate physical observables (Conquer). In our presentation, we shall introduce the DRC algorithm for matrix diagonalisation as typically encountered in electronic structure problems, and we shall extend our method to treat matrix inversion as required in studies of electron transport using Green's function methods. First, we establish the accuracy of our method and the computational complexity. Then, the DRC performance is benchmarked through efficiency and runtime comparison with established methods.

Defect levels hidden by the Kohn-Sham bands

M Bockstedte

Universitaet Erlangen-Nuernberg, Germany

Defects in semiconductors are decisive for the electronic properties. Furthermore they can implement Q-bits for quantum computing [1]. To access the underlying physics, the accurate theoretical description of defect levels and excited states is highly desirable. Yet, the theoretical work horse, density functional theory (DFT) with (semi-)local XC-functionals, suffers from the well-known Kohn-Sham band-gap error. This not only affects defect states within the gap, but may turn otherwise localized ones into resonances outside the gap. Many-body perturbation theory (MBPT) on top of the DFT electronic structure was shown [2] to yield excellent results for ionization levels and excited states, however, the latter problem of the DFT may easily hamper such calculations. Here we investigate this problem for a experimentally well-identified defect in SiC for the polytypes 3C and 4H with different band gaps using MBPT on top of DFT with LSDA and HSE06 functionals. While in 4H-SiC G0W0 ionization levels for both functionals agree well, the proper defect states in 3C remain resonances within the LSDA. Here simple ad-hoc corrections yield already good results.

[1] Koehl et al, Nature 479, 84 (2011).
[2] Bockstedte et al, Phys. Rev. Lett. 105, 026401 (2010).

Quantum mechanics without wavefunctions: the unfulfilled promise of DFT

P Hasnip and M Probert

The University of York, UK

Density functional theory (DFT) is founded on the Hohenberg-Kohn theorem, which states that the groundstate energy of an interacting system is a unique functional of the particle density. Thus the groundstate energy can be computed without resorting to wavefunctions; yet only by reintroducing the concept of particle wavefunctions were Kohn and Sham able to produce a workable, reliable scheme. Unfortunately the size of these wavefunctions, and the requirement for them to be kept orthonormal, limits the size of system that can be modelled practically. Subsequent attempts to construct "orbital-free" DFT have had mixed success at best, and Kohn-Sham DFT remains the most practical and widely used formulation of DFT.

In this work we will show how an effective "orbital-free" DFT scheme can be constructed dynamically from a Kohn-Sham DFT simulation, and used to accelerate dramatically the performance of Kohn-Sham DFT without sacrificing accuracy.

Oxide and oxide surfaces 5

(invited) Structure and activity of stepped rutile $TiO_2(110)$

B Hammer

Aarhus University, Denmark

The atomic structure and the chemical activity of atomic steps on the rutile TiO_2 surface are discussed in this talk. Using density functional theory (DFT) the atomic structure of a the <1-11> direction on a stoichiometric rutile $TiO_2(110)$ surface is found to involve a reconstruction.[1] The reconstruction places one Ti atom at a half-height position between the upper and lower terrace levels and offers new adsorption sites that are explored with water, methanol, and ethanol. The binding of such adsorbates is weaker at the steps possibly making these sites more active for catalytic reactions than terrace sites[2].

For reduced surfaces, we find with a combined STM and DFT approach that linear strands may evolve from the <1-11> steps.[3] The strands are non-stoichiometric and form since their potential energy is smaller than for the corresponding reference system with scattered point defects in the bulk.

[1] Steps on rutile TiO2(110): Active sites for water and methanol dissociation, U. Martinez, L. B. Vilhelmsen, H. H. Kristoffersen, J. Stausholm-Møller, and B. Hammer, Phys. Rev. B 84, 205434 (2011).

[2] Direct evidence for ethanol dissociation on rutile TiO2(110), J. Ø. Hansen, P. Huo, U. Martinez, E. Lira, Y. Y. Wei, R. Streiber, E. Lægsgaard, B. Hammer, S. Wendt, and F. Besenbacher, Phys. Rev. Lett. 107, 136102 (2011).

[3] Packing defects into ordered structures: Strands on TiO2, R. Bechstein, H. H. Kristoffersen, L. B. Vilhelmsen, F. Rieboldt, J. Stausholm-Møller, S. Wendt, B. Hammer, and F. Besenbacher, Phys. Rev. Lett. 108, 236103 (2012).

Simulated photoemission spectra of hydroxylated MgO(100) at elevated temperatures

L O Paz-Borbón, A Hellman and H Grönbeck

Chalmers University of Technology, Sweden

The understanding of how water adsorbs and dissociates on oxide surfaces is important in several applied fields, where heterogeneous catalysis is only one example [1]. The interaction of water with MgO(100) surface has become in this context, a prototype system thanks to experimental and theoretical advantages.

In this work, we have performed a combination of static density functional theory (DFT) calculations and ab-initio molecular dynamics (AIMD) simulations to investigate the stability of hydroxylated MgO(100) and, in particular, to evaluate the photoemission O1s core level shifts (CLS) as a function of coverage and temperature. From our results, we observe that thermal vibrations and rapid proton-exchange at elevated temperatures yields broad features in the simulated photoemission signal, which is in good agreement with recent experimental observations [2]. Moreover, the results provide further evidence that the stable structure of hydroxylated MgO(100) consists of a partly dissociated water monolayer; a configuration which is also found to be stable even if a second monolayer of water is added. Detailed analysis of the O1s CLS for adsorbed hydroxyl groups at different coverage reveals a pronounced effect on hydrogen bonding to neighboring H_2O molecules.

As the degree of electron localization, in principle could affect stability and CLS, we have compared the results obtained with a standard gradient corrected functional (PBE) with one including exact-exchange (PBE0). For the investigated systems, we find that PBE and PBE0 yield quantitatively similar results [3].

[1] Thiel. P.A.; Madey, T.E.; Surf. Sci. Rep. 7 (1987) 211.
[2] Newberg. J.T.; Starr, D.E.; Yamamoto, S.; Kaya, S.; Kendelewicz, T.; Mysak, E.R.; Porsgaard, S.; Salmeron, M.B.; Brown, G.E.; Nilsson, A.; Bluhm, H.; Surf. Sci. 605 (2011) 89.
[3] Paz-Borbón, L.O., Hellman, A.; Grönbeck, H.; J. Phys. Chem. C 116 (2012) 3545.

Ab-initio study of the $Sr_3Ru_2O_7$ [001] surface

M Hieckel[1], F Mittendorfer[2], J Redinger[2], R Podloucky[4], B Stöger[2], Z Wang[2], M Schmid[2], U Diebold[2], D Fobes[3] and Z Mao[3]

[1]Vienna University of Technology & University of Vienna, Austria, [2]Vienna University of Technology, Austria, [3]Tulane University, USA, [4]University of Vienna, Austria

Oxide perovskite materials have attracted enormous attention because of a variety of intriguing physical properties present not only in the bulk but also at interfaces and surfaces.

Here we present a density functional theory (DFT) study of the Ruddlesden-Popper series compound $Sr_3Ru_2O_7$ employing the Vienna Ab initio Simulation Package (VASP) within the PBE[1] generalized gradient approximation. Structural, electronic and magnetic properties are calculated both for a clean and CO-covered [001] surface. Changes with respect to the corresponding bulk properties will be highlighted. Furthermore, scanning tunneling microscopy (STM) images are simulated within the Tersoff-Hamann approximation and compared to very recent low temperature STM experiments.

[1] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1966).

Atomic scale simulations of oxide surfaces from a tight-binding variable-charge model

R Tétot[1,3], N Salles[1], S Landron[2], E Amzallag[3] and G Sattonnay[3]

[1]CNRS, France, [2]ENSC-Rennes, France, [3]Univ Paris-Sud, France

Realistic atomic scale simulations of oxide surfaces are particularly difficult because of the mixed iono-covalent character of the metal-oxygen bond and accompanying charge transfers. In this work we shall present a new transferable variable-charge model [1] aimed at describe stability, structure and defects at oxide surfaces. In this model, the metal-oxygen covalent bonding energy is calculated thanks to a tight-binding analytical description [2]:, where ξ is the hopping integral between oxygen 2p and outer metal orbitals. Z and Q_0 are the coordination number and the charge of oxygen respectively, and $n_0$is the number of coupled electronic states between oxygen and metal sublattices. The equilibrium charges are determined through a modified form of the QEq formalism [3] which ensures the local electrical neutrality. A number of applications will be then presented concerning TiO_2, SrO, $SrTiO_3$, Al_2O_3 and UO_2 surfaces. In each case, results on energetic, atomic relaxations and oxygen vacancies at most stable surfaces will be presented. These results will be compared with experimental data when available and ab initio calculations performed with the CRYSTAL09 code. Results on Monte Carlo simulations at various temperatures will be also shown.

[1] A. Hallil, E. Amzallag, S. Landron, R. Tétot, Surf. Sci. 605, 738 (2011).
[2] J. Goniakowski, C. Noguera, Surf. Sci. 319, 81 (1994).
[3] A. K. Rappé, W. A. Goddard III, J. Phys. Chem. 95, 3358 (1991).

Oxygen non-stiochiometry in thermoelectric sodium cobalt oxide NaxCoO_2

S Casolo[1], H Fjeld[2], O M Løvvik[2] and T Norby[2]

[1]Università degli Studi di Milano, Italy, [2]University of Oslo, Norway,

Sodium cobaltate Na_xCoO_2 exhibits several interesting electronic properties. These can be asily tuned by changing the Na content, (i.e. the Co oxidation state) exploiting a very rich electronic phase diagram. In particular and at high Na contents, sodium cobaltate is considered as a promising thermoelectric oxide.

The influence of point defects other than Na vacancies on sodium cobaltate is still debated. It has been recently reported that oxygen vacancies could have an interesting two-fold effect on the thermoelectric properties. Firstly, they can affect the cobalt oxidation state reducing the charge carrier concentration and increasing the thermopower. Unfortunately, such defects also lower the phonon scattering so that the overall effect is a reduction of the figure of merit of $Na_xCoO_{2-\delta}$ with increasing the defects concentration (δ). However, experimental data about the concentration of vacancies in sodium cobaltate are very contradictory, especially at $x\sim0.75$. While some groups have identified an oxygen non-stoichiometry up to $\delta= 0.16$, others found no vacancies within the experimental error. In order to clarify this, we have in this work studied the oxygen vacancy formation in Na_xCoO_2 ($x>0.50$) by thermogravimetric analysis and density functional theory calculations, at various temperatures and oxygen partial pressures. We show that the equilibrium concentration of oxygen vacancies in sodium cobaltate is indeed very low at conditions relevant for applications as thermoelectric material. We also suggest other possible sources of the weight loss found in some experiments.

Does the lithium niobate Z cut surface reconstruct?

R Hölscher, S Sanna and W G Schmidt

Universität Paderborn, Germany

$LiNbO_3$(LN) is a frequently used material for optical and acoustic applications due to its strong piezoelectric, pyroelectric, and photorefractive properties. As for other ferroelectric materials, the surface reactivity can be manipulated by polarization reversal. This opens the possibility for the realization of devices like molecular detectors [1].

Unfortunately, there are only few data about the microscopic structure of the surface available. While most existing studies, e.g. Ref. [2], do not find surface periodicities other than the 1x1 bulk-truncated structure, there are very recent indications that at elevated temperatures large surface reconstructions might occur for both the positive and the negative Z cut [3].

Here surface phase diagrams calculated from first principles are presented. Thereby a large number of structures of different morphology and stoichiometry are investigated by means of density functional theory within the generalized gradient approximation (DFT-GGA). In contrast to earlier work [4], the possibility of large surface reconstructions is taken into account. Interestingly, we find that for certain preparation conditions indeed large surface reconstructions may be stable. Their formation is rationalized in terms of surface electrostatic interactions.

[1] D. Li, M.H. Zhao, J. Garra, et al., Nature Materials 7, 473 (2008).
[2] Y. Yun, M. Li, D. Liao, et al., Surf. Sci. 601, 4636 (2007).
[3] A. Kühnle, S. Klassen, S. Rode, Private communication.
[4] S. Sanna, W.G. Schmidt, Phys. Rev. B 81, 214116 (2010).

Poster abstracts

Poster session A and B (CMD/CMMP)
Monday 3 September and Tuesday 4 September

Carbon including nanotubes, graphene, diamonds

P1.001 Graphene islands on Ni(111) surface: a first principle investigation

F Bianchini and M Peressi

University of Trieste, Italy

We investigate by first principles calculations the energetics and the electronic structure of graphene grown on Ni(111), both in case of infinitely extended monolayers and of islands. We use Density Functional Theory in the GGA approximation with semiempirical corrections for the van der Waals interactions, which are essential to study the binding in this system.

We compare different possible configurations which are close in energy in case of the infinite graphene monolayer, focusing in particular on those with carbon atoms in top-fcc hollow, top-hcp hollow or bridge-top adsorption geometries.

We study the relative stabilization of graphene structures limited by edges, i.e. ribbons of different width, considering different possible structures also for edges. We compare our simulations with recent experimental results including scanning tunneling microscopy (TASC Lab, Trieste) [1].

[1] L. Patera, C. Africh, G. Comelli, unpublished.

P1.002 Quantum oscillations due to structural disorder in graphite

B Camargo[1], Y Kopelevich[1], S Hubbard[2], A Usher[2], W Böhlmann[3] and P Esquinazi[3]

[1]Universidade Estadual de Campinas, Brazil, [2]University of Exeter, UK, [3]University of Leipzig, Germany

We studied effects of structural disorder on Shubnikov de Haas (SdH) and de Haas van Alphen (dHvA) quantum oscillations measured in single crystalline and highly oriented pyrolitic graphite samples down to temperature T = 30 mK and magnetic field up to B = 14 T. The measurements were performed on samples with different mosaicity characterized by means of x-ray rocking curves and transmission electron microscopy (TEM). The obtained results revealed a clear correlation between the occurrence of quantum oscillations and the structural disorder. Namely, dHvA and SdH effects are most pronounced in disordered samples that possess a high density of internal interfaces between crystalline regions, and quantum oscillations were essentially suppressed or not detected at all, in most ordered graphite. The lack of quantum oscillations in disorder-free samples can be interpreted as the absence of the Fermi surface on these systems, being at odds with the classical Slonzewski-Weiss-McClure model. Our results strongly suggest that the high enough carrier density leading to the metallic-like behaviour is not intrinsic to the graphite but to a large extent originates from the crystalline defects such as internal interfaces.

P1.003 Molecular rotation and the formation of C_{60} polymers under high pressure

B Sundqvist

Umea University, Sweden

Solid Buckminsterfullerene, C_{60}, is a soft fcc crystal with freely rotating molecules. The molecules are very reactive, and under suitable conditions covalent intermolecular carbon-carbon bonds may form, resulting in a pure carbon polymer. Such polymers can be created by irradiation or by annealing under simultaneous high pressure and high temperature conditions. In the latter case ordered, polymeric, pure carbon structures can be produced. Dimers, linear chains, two types of two-dimensional planes, and even three-dimensional structures have been found. In spite of a large number of investigations, the details of the high pressure reactions and the reaction diagram are still uncertain. A large number of samples have been synthesized using many methods but many results are contradictory, possibly because of the many experimental methods used and the uncertainties in the pressures, temperatures, or times utilized. In this work, several C_{60} samples have been treated for a "long" time at pressures between 0.8 and 2 GPa. A temperature gradient has been applied to provide reaction temperatures over a range of about 200 K in each run. The temperature resolution is better than 0.1 K and the absolute uncertainty about 5 K. The treated samples have been analyzed using Raman spectroscopy, using infra-red excitation to avoid photo-polymerization. The results have been used to redefine polymerization reaction maps given in earlier publications, and the new data are discussed in terms of the orientational and rotational structure of the original material and of the pressure-temperature-time trajectories used.

P1.004 Detailed studies of Si-graphene/SiC(0001)

C Virojanadara[1], C Xia[1], S Watcharinyanon[1], A Zakharov[2], R Yakimova[1], L Hultman[1] and L Johansson[1]

[1]Linkoping University, Sweden, [2]Lund University, Poland

Graphene is one of the most promising candidate materials for future technological applications.Large and homogeneous monolayer graphene is achieved by our epitaxial graphene growth technique on SiC(0001) substrates. However, it is also crucial that bi-layer or even multilayer graphene can be grown homogenously on the SiC surface. So far no one has reported that a large and homogeneous bi- or multilayer graphene can be achieved in a controlled way from the sublimation technique. A solution to this problem may be revealed by investigating the transport behavior of Si atoms through layers of carbon. We have therefore made detailed studies of the transport of Si, specifically the intercalation and de-intercalation mechanism for Si atoms deposited on monolayer and 0 ML graphene samples prepared by ex-situ or in-situ sublimation of SiC substrates. Low energy electron microscope (LEEM) and µ-low energy electron diffraction (µ-LEED) were used to investigate the surface morphology of the graphene grown and the Si intercalation mechanism. Photoemission data were collected utilizing synchrotron radiation, which allowed high-energy resolution core level and valence band studies. The Si deposited on the sample is observed not to be able to penetrate through monolayer graphene when the sample is kept at room temperature. Intercalation is revealed to occur at an elevated temperature of about 800 °C and then the Si atoms are found to migrate through the graphene at domain boundaries and likely other defect areas.More detail findings will be presented and discussed.

P1.005 Improved interfacial bonding of multi-walled carbon nanotubes by plasma treatment

J Du Plessis[1], Z Chen[2], X J Dai[2], P R Lamb[2], D Rubin de Celis Leal[2], B L Fox[2], Y Chen[2], M Field[1] and X Wang[2]

[1]RMIT University, Australia, [2]Deakin University, Australia

It has been shown that amine groups serve as an anchoring point for other functionalities to improve interfacial bonding to carbon nanotubes. In this investigation the amine groups were coated onto the nanotube surface using a combination of continuous and pulsed plasma treatments and a mixture of gases of N2 and H2, which is preferable to using NH3. It is shown that a surface concentration level of primary amines of 2.3% can be achieved, which is higher than previously reported for any nitrogen-containing gas plasma treatment. Even higher surface concentration levels (3.5%) of primary amines can be achieved by coating the MWCNTs with a thin layer of plasma polymerized heptylamine. In both cases, the highest surface concentration levels of primary amines were achieved using a combined continuous plus pulsed plasma mode which was superior to a single mode of either continuous wave or pulsed wave alone. The integrity of the MWCNT structure is maintained by the plasma treatments as observed by HRTEM and XRD measurements. The functionalized surface also improves the dispersion of the MWCNTs. Nanoindentation results show an increase in hardness and modulus as the level of primary amines is increased.

P1.006 Scalable, UHV-based growth of high-quality monolayer graphene

D van Baarle, R van Rijn, G Dong, N Jovanovic, K Uhlirova, M T M Koper and J W M Frenken

Leiden University, The Netherlands

The growth of monolayer graphene by chemical vapor deposition is promising for large-scale production of high-quality graphene. However, at this moment the quality of the graphene synthesized in this way is limited. Improvement can be achieved by a full understanding of the growth process. In our experiments we use a recently constructed UHV setup that allows us to control the graphene growth in a very defined way. Known problems of graphene synthesis in UHV systems are solved, e.g. we control the evaporation of copper during the high temperature processing resulting in full coverage graphene on an extremely flat substrate. The grown graphene is investigated by Raman spectroscopy, scanning electron microscopy and mobility measurements. The initial results show that a low defect density and large grain sizes are achieved. Detailed studies on the growth conditions, such as temperature, partial pressure, geometry and other parameters are underway. The current experimental setup can deliver up to 40 1cm^2 samples per day, each with a full coverage of high-quality monolayer graphene.

P1.007 Sensitive detection of multivalent ions via DNA bridge

T Ignatova and S V Rotkin

Lehigh University, USA

The method is based on the physics of interaction of multivalent ions (Tb^{3+}, Eu^{3+}, Al^{3+}, Ca^{2+}) with SWNTs wrapped with the single strand (ss)DNA, being ionized/negatively charged in the aqueous solution. Using time-resolved photoluminescence (PL) we found positive correlation (attraction) of Tb and Eu to the DNA/SWNT complexes. We speculate that Manning condensation of the multivalent ions on the SWNT/DNA surface happens thereby significantly reducing their spacing. By altering the complexes' geometry one makes the near field energy transfer between the ions and the SWNT possible.

In the case of lanthanide salts we observed a strong dependence of the SWNT near-infrared emission intensity on the lanthanide ion concentration. The lanthanide ion adsorption on the SWNT should lead to an enhanced SWNT emission in NIR range due to the energy transfer from excited ions. At the same time, resonant excitation of the SWNT changes in the presence of lanthanide ions, possibly due to the DNA ordering. The PL dynamics indicates that

the binding of Tb/ Eu ions to the ssDNA/SWNT is followed by two competing processes: (a) a SWNT PL enhancement due to the resonant energy transfer and/or other near-field interactions, and (b) the SWNT agglomeration followed by the PL quenching. In case of Al^{3+} and Ca^{2+} similar processes take place, allowing multivalent ion detection.]

This sensing mechanism is advantageous by showing high sensitivity (0.2mM ion concentration) and capability to trace the kinetics of the ions condensation.

P1.008 Signature of hot electrons in the quantum corrections to the conductivity of graphene

S Hornett, M Heath, A Price, E Hendry and D Horsell

University of Exeter, UK

The potential of graphene for future electronic devices is dictated not only by its conductive but also its thermal properties. Overheating of charge carriers has important implications for devices. In graphene, significant overheating can occur because of the large difference between the heat capacity of the electron system with respect to the phonons [1] combined with a relatively weak electron-phonon coupling [2]. Therefore, it is important to accurately determine the electron temperature and understand how hot electrons influence conduction through the graphene device.

We investigate the effects of hot electrons on carrier conduction through measurements of the quantum corrections to the classical (Drude) conductivity. It has been shown that these corrections [3] can be used as a direct measure of the electron temperature at thermal equilibrium [4]. We investigate how the electron temperature evolves with increasing electric field through detailed measurements of the weak localization (WL) and electron-electron interaction (EEI) corrections, and the universal conductance fluctuations (UCF). We measure the resistance of multi-terminal monolayer graphene devices on silica/silicon substrates at temperatures from 0.02 to 200K with applied AC and DC currents ranging from 0.1 to 20μA . The WL and EEI corrections to the conductivity are determined from the temperature and magnetic field dependence of the resistance, and the UCF are measured as a function of carrier density.

We determine the electron coherence length from the WL and UCF measurements and show that it saturates at low temperatures. The saturation value is found to decrease linearly with increasing current. This is a direct demonstration of overheating [2] and through analysis of the form of the WL [3] and statistics of the UCF [4] we determine the electron temperature far from equilibrium. We show that this temperature can exceed the lattice temperature by several orders of magnitude. The effect of the applied current on the EEI appears to be more complex and cannot be explained by a simple overheating model [5]. Our results indicate the possibility of a direct effect of the field on the interaction.

[1] E.H.Hwang et al. ,Phys. Rev. B 77,115449(2008).
[2] A.S.Price et al. ,Phys. Rev. B 85,161411(2012).
[3] F.V.Tikhonenko et al. ,Phys. Rev. Lett. 100, 056802(2007).
[4] K.Kechedzhi et al. ,Phys Rev Lett. 102, 066801(2009).
[5] V.I.Kozub et al. ,Phys. Rev. B 52,7853(1995).

P1.009 Intercalation of transition metals into stacked benzene rings: A model study of the intercalation of transition metals into bi-layered graphene

I-S Youn and K S Kim

Pohang University of Science and Technology, South Korea

Structures of neutral metal-dibenzene complexes, $M(C_6H_6)_2$ (M = Sc - Zn), are investigated by using Møller-Plesset second order perturbation theory (MP2). The benzene molecules change their conformation and shape upon complexation with the transition metals. We find two types of structures; (i) stacked forms for early transition metal complexes and (ii) distorted forms for late transition metal ones. The benzene molecules and the metal atom are bound together by δ-bonds which originate from the interaction of π-MO's and d orbitals. The binding energy shows a maximum for $Cr(C_6H_6)_2$, which obeys the 18-electron rule. It is noticeable that $Mn(C_6H_6)_2$, a 19-electron complex, manages to have a stacked structure with an excess electron delocalized. For other late transition metal complexes having more than 19 electrons, the benzene molecules are bent or stray away from each other to reduce the electron density around a metal atom. For the early transition metals, the $M(C_6H_6)$ complexes are found to be weakly bound than those of late transition metals. This is because the early transition metal complexes do not have enough electrons to satisfy the 18-electron rule, and so these dibenzene-metal complexes generally tend to have tighter binding with a shorter benzene-metal length than the monobenzene-metal complexes, which is quite unusual. The present results could provide a possible explanation of why on the Ni surface graphene tends to grow in a few layers, while on the Cu surface the weak interaction between the copper surface and graphene allows to form a single layer graphene, in agreement with chemical vapor deposition experiments.

P1.010 Second harmonic generation from vertically aligned CNTs on alumina films

S Okawara[1], M Tanaka[1], S Ohno[1], Y Shimazu[1] and T Suzuki[2]

[1]Yokohama National University, Japan, [2]National Defense Academy, Japan

The enhanced and anisotropic nonlinear optical response is expected for needle-like structures such as carbon nanotubes (CNTs) because of geometrical lightning-rod effect [1] and electronic resonance effect [2]. To distinguish these effects, experiments using highly oriented CNTs are required. In this study, the vertically aligned CNTs were fabricated by alcohol catalyst CVD method on alumina substrate [3]. The orientation and quality of the CNTs were characterized by SEM and Raman spectroscopy, respectively.

We could detect steady signals of second harmonic (SH) wave excited by a nanosecond pulsed laser with the aid of some processing to prevent laser ablation. It is for the first time that SH generation from highly oriented CNTs directly grown on substrates was measured. Polarization dependence is clearly observed ; SH signals are large when the electric field of incident light is parallel to the axial direction of CNTs. On the other hand, the response from the CNTs films of random orientation is isotropic.

To analyze the above experimental data, we approximated the cap of CNT by a spheroidal surface and calculate the intensity of reflected SH wave [4]. The results of the calculation agrees well with the experiment results, which means that the enhanced SH response observed in the CNT films is mainly dominated by purely geometrical effect.

[1] D. L. Mills, Nonlinear Optics: Basic Concepts, Springer (1998).
[2] R. Saito, G. Dresselhaus and M. S. Dresselhaus, Phyisical Properties of Carbon Nanotubes, Imperical College Press (1998).
[3] H. Ohno, D. Takagi, K. Yamada, S. Chiashi, A. Tokura and Y. Homma, Jpn. J. Appl. Phys. 47, 1956 (2008).
[4] G. Berkovic and S. Efrima, Langmuir 9, 355 (1993).

P1.011 The effect of different scattering mechanisms on the 1/f resistance noise in graphene

D Horsell[1], A Kaverzin[1], A Mayorov[2] and A Shytov[1]

[1]University of Exeter, UK, [2]University of Manchester, UK

We experimentally study the effect of different scattering potentials on the 1/f noise observed in graphene devices on silica and silicon nitride substrates. The noise in nominally identical devices is seen to behave in two distinct ways as a function of carrier concentration, changing either monotonically or nonmonotonically. We attribute this to the interplay between long- and short-range scattering mechanisms. Water was found to significantly enhance the noise magnitude and change the type of the noise behaviour. By using a simple model, we show that water is a source of long-range scattering. Its presence on the graphene surface was found to increase the noise by an order of magnitude, yet cause a comparatively insignificant change in the resistance, which demonstrates that low-frequency noise and resistance in graphene can be determined by different scattering mechanisms. We have also shown that the 1/f noise at the Dirac point and at finite concentration originates from different sources of scattering and most likely from different fluctuation mechanisms.

[1] Phys. Rev. B 85, 075435 (2012).

P1.012 Effects of toluene doping on electrical conduction in graphene

D Horsell, A Kaverzin, S Strawbridge and A Price

University of Exeter, UK

The electrical properties of graphene are known to be modified by chemical species that interact with it. As a result, graphene is a promising material for the active element of a chemical or biomolecular sensor. We investigate the effect of chemically reactive species on the graphene surface and show that the reactivity can be detected in the electrical response of a graphene-based field-effect device. We have demonstrated that the doping of graphene by toluene vapour can be understood in terms of an electrochemical reaction mechanism that is mediated by the graphene crystal. We have shown that toluene acts as a donor, but that the transfer of electrons to the graphene can be controlled by changing the magnitude and polarity of an electric field applied between the graphene and a nearby gate electrode. This was demonstrated by a hysteretic dependence of the resistance of a graphene transistor as a function of the applied gate voltage in the presence of toluene vapour. By measuring the point of onset of the doping we were able to determine the magnitude of the redox energy level to be ~0.1 eV for our experimental conditions - an energy much smaller than that expected from simple charge-transfer mechanisms of doping associated with unreactive species. We have also shown that the dipolar nature of the molecule is a factor, the same effect being observed for other dipolar molecules, water and aniline, but not for nonpolar molecules, naphthalene and pyrene (the linker molecule for graphene biosensor receptors). In the case of non-polar molecules, no doping effect was observed.

[1] Carbon 49, 3829 (2011)

P1.013 Spin decoherence by magnetic-like defects in graphene

D Horsell[1], A Kozikov[1], E McCann[2] and V Fal'ko[2]

[1]University of Exeter, UK, [2]Lancaster University, UK

We have measured the weak localisation correction to the conductivity in graphene and found that the dephasing rate at low temperatures is limited by the spin memory. We demonstrate that the spin coherence length, L_s, can be tuned experimentally by showing that it has a direct relation to the mean free path, l_p. By comparing with predictions of the density dependence of L_s and l_p, we suggest that spin decoherence is dominated by spin-flip processes caused by resonant states at the Dirac point. It was shown that these states can be caused by vacancies in the crystal and act like magnetic defects. By varying the level of disorder, we demonstrate that L_s can be varied over an order of magnitude. Our values of L_s of up to ~8 μm clearly show the promise of graphene for future spintronic applications.

[1] arXiv:1108.2067.

Electrochemistry at the atomic molecular scale

P1.014 Peculiarities of obtaining of ZnCdS nanolayers by electochemical deposition for solar cells

M Jafarov and E Nasirov

Baku State University, Azerbaijan

From variety of methods for buffer layers for solar cells based on cadmium sulfide the method of electrochemical bath deposition of films from aqueous solution [ECBD] is well studied. Despite these advantages, it has a lot of technological "niceties" that makes it difficult to produce quality films of zinc cadmium sulfide. Therefore, we deposited layers of zinc cadmium sulfide under different conditions on silicon substrates p-type to study of the photovoltaic characteristics and to study the structure p-Si/n-ZnCdS. Measurement of electrical characteristics of ZnCdS nanolayers and evaluation of the VAC p-Si/n- ZnCdS structure has revealed an optimal composition of electrochemical bath - (1.7 × 10^{-3} M $Zn(CH_3COO)_2$, $Cd(NO_3)_2$, 0.02 M $Na_2S_20_3$, 1.05 M NH4OH. The films are characterized by a high value of transmittance> 70% and a sharp edge of fundamental absorption in the wavelength range of 400-500 nm depending on their thickness. The band gap of ZnCdS films was determined by extrapolating the linear part of the spectral dependence of the square of the absorption coefficient α^2~f(hν) to the axis of the photon energy. Eg increases with decreasing thickness of ZnCdS may be due to the manifestation of quantum-effect. Additional contribution to the shift of the absorption edge can make a change in light scattering and reflection coefficient at the boundaries of nanocrystallites, and the presence of internal stresses in the films. As shown by experimental measurements of grain sizes using atomic force microscopy in films ZnCdS, usually formed crystallites with dimensions ~ 2 - 40 nm.

These results indicate that the ECBD process is best suited for thin film deposition because of simplicity, least expenses to produce uniform, adherent and reproducible large area thin films for solar related applications.

P1.015 In-situ SXRD measurement of PtZn electrochemical alloying

J Drnec[1], D Bizzotto[2], F Carla[1], R Fiala[3], A Sode[4], O Balmes[1], B Deflets[1] and R Felici[1]

[1]European Synchrotron Radiation Faciloty (ESRF), France, [2]University of British Columbia, Canada, [3]Charles University of Prague, Czech Republic, [4]Ruhr-Universität Bochum, Germany

The in-situ Surface X-Ray Diffraction (SXRD) study of formation of PtZn electrode is reported. The PtZn catalyst has been shown to be active for oxygen reduction reaction (ORR) so it is potentially a promising material for fuel cell manufacturing [1].

The catalytic PtZn surface is prepared in electrochemical cell by means of Zn deposition on Pt(111) and Pt(100) surfaces at potentials negative to AgCl reference electrode. The deposition electrolyte is ZnSO4 + MgSO4. The surface rods, reflectivity and powder pattern is measured during the deposition and striping.

We first measure Pt(111) in MgSO4 buffer in order to obtain the reference structural information. As the potential decreases from 125 mV to -850 mV vs Ag/AgCl reference electrode, we observe significant surface roughening and change in reflectivity. All changes are reversible and after the measurement here is no significant difference in surface structure at 125 mV when compared to initial conditions.

The Zn is deposited on the surface at various potentials negative to 125 mV. We found that the Zn is adsorbed as soon as -200 mV and the deposition is followed by immediate diffusion to the bulk (alloy formation). The deposition/alloy formation is a slow process and not immediately visible in cyclic voltammetry (CV). Depositing Zn on the surface inhibits the surface roughening which was observed in $MgSO_4$ buffer. We also found no evidence of ordered Zn UPD layer which precedes the bulk diffusion and for both surface orientations the ZnPt alloy is characteristic by the same diffraction ring pattern. The main difference between Pt(111) and Pt(110) substrate is the kinetics of the alloy formation. The alloy forms significantly faster on more open Pt(110) surface.

[1] A. Sode and D. Bizzotto, Electrochim. Acta 54 (3) (2009) 1095.

Energy conversion: heat dissapation, photovoltaics, etc.

P1.016 Microstructural and optical properties of Cu-Ni deposits for flat solar collector panels

Ł Skowroński, A A Wronkowska and A Wronkowski

University of Technology and Life Sciences, Poland

The solar selective coatings (SSCs) are used as absorbers in the solar collector panels to improve efficiency of converting the solar energy into heat. The SSCs must absorb most of the incident energy and their thermal losses should be at possibly lowermost level [1].

The electrodeposition of Cu-Ni layers was performed using a modified Watt's bath composition [2]. A Cu plate was used as the cathode and stainless steel plate as the anode. Optical properties and microstructure of Cu-Ni deposits were investigated by combining the spectroscopic ellipsometry, reflectometry, confocal microscopy, scanning electron microscopy, X-ray diffraction and energy dispersive X-ray spectroscopy measurements.

The Cu-Ni layers show a granular structure of the surface. In the coatings two types of Cu-Ni alloy microcrystallites have been identified: one type of the Cu-rich alloy structure and the second one being the Ni-rich solid solution. The effective complex dielectric functions of the produced layers, $<\varepsilon(E)>=<\varepsilon_1(E)>+i<\varepsilon_2(E)>$, were determined from ellipsometric quantities Ψ and Δ measured in the broad wavelength range from 300 nm to 20000 nm. The absorption bands parameters were evaluated using the semi-classical Drude-Lorentz model of the effective dielectric function.

The high value of the solar absorptance of the electroplated Cu-Ni coatings (α_s=0.944) is associated with their rough and expanded surface. As an additional advantage, the obtained Cu-Ni deposits demonstrate a low value of the thermal emittance (ε_{IR}=0.02).

[1] J. A. Duffie and W. A. Beckman, Solar Engineering of Thermal Processes, John Wiley & Sons, 2006.
[2] O.P. Watts, Trans. Am. Electrom. Soc. 29 (1916) 395.

P1.017 Nanopillared SnS thin layers for solar cells and secondary batteries

A Khodin[1], J Kee Lee[1], E Outkina[2] and A Vorobyova[2]

[1]Korea Institute of Science and Technology, Korea, [2]Belarussian State University of Informatics and Radioelectronics, Belarus

SnS_x semiconductor is under investigation at present as a prospective material for thin-film solar cells and Li-ion secondary batteries anodes. The nanostructured semiconductors, produced using nanoordered template substrates, are favorable in improving both the photon flux harvesting in solar cells, and charging/discharging performance of the secondary battery elements. It would be reasonable to develop a fully electrochemical low-cost processing technology to fabricate the cells. The developed micromorphology of the cell improves photons absorption efficiency at minimal active layer thickness and reduces losses under photogenerated charge carriers transport to collecting electrodes. The nanopillars-confined space-charge region of p-n junction, as well as built-in charges in alumina could channel the photogenerated carriers transport, reducing recombination losses.

The porous anodic alumina (PAA) technology was used to prepare template substrate for electrochemical deposition of SnS_x. The technology includes electrochemical preparation of template aluminum/alumina substrate and subsequent electrochemical deposition of SnS-based active semiconductor layers in galvanostatic and pulse modes. The composite nanostructured substrate presented a PAA matrix with through pores of 30 to 50 nm diameter, inter-pores distance of 140 to 160 nm, and pores height up to 200 nm. The well-ordered porous structures were fabricated after two-step anodizing processing with etching of the first PAA layer. After the second porous layer partial or complete removal, the template surface was textured as the matrix of semispherical-like grooves. It results in electric field and ionic current redistribution at the pores’ bottoms at the earlier stage of electrochemical deposition to improve the SnS_x microstructure.

P1.018 Experimental QSSPC curves modelling to study the phosphorus diffusion gettering in HEM multicrystalline silicon passivated by iodine-methanol solution

N Khelifati[1], D Bouhafs[1], S-E-H Abaidia[2] and B Palahouane[1]

[1]Silicon Technology Developpement Unit, Algeria, [2]University of M'hamed Bougara, Boumerdes, Algeria

Multicrystalline silicon (mc-Si) wafers are widely used as precursor elements in solar cells manufacturing, and constitute more than half of the overall industrial market. This is due to their low cost of manufacturing as compared to that of monocrystalline silicon (c-Si) [1]. However, the contamination of mc-Si material by metallic impurities (Fe, Cr, Ni, Co, etc...) during its elaboration and also the existence of crystallographic defects those respectively create recombination and trapping centers, are considered as its major disadvantages.

In this present contribution, we have investigated the recombination-trapping activity of minority charge carriers in p-type HEM mc-Si treated by extended phosphorus diffusion gettering (EPDG). The study was made after phosphorus diffusion and according to different extended annealing times t_L. Using quasi-steady state photoconductance (QSSPC) technique and Iodine-Methanol surface passivation method, the bulk apparent lifetime dependent minority carrier density curves have been obtained. The results showed an increment of the bulk minority carrier lifetime for specific annealing times.

The modeling of apparent lifetime curves using Hornbeck-Haynes model [8], leads to estimate and follow the variation of the surface-bulk recombination and trapping parameters according to t_L. Indeed, the modeling results showed a significant decrease of recombination centers density between t_L=60 min and 180 min, and a quasi-constancy of the symmetry parameter ($k=\sigma_n/\sigma_p$) around the values associated to interstitials Co, W atoms and CrB, FeB pairs. On the other hand, the trapping centers concentration increased slightly according to T_L with stability of their localised energy levels (E_C-E_T) in the band gap.

[1] A. Cuevas, in: Materials 2003 Conference, The Institute of Materials Engineering Australasia, Sydney, 1-3 October 2003.
[2] J. A. Hornbeck and J. R. Haynes, Physical Review 97, 311-321 (1955).

Liquids

P1.019 Crystallization and glass transition in a supercooled ionic liquid

M Ribeiro, L Faria and J Matos

Universidade de São Paulo, Brazil

The ionic liquid butyltrimethylammonium bis(trifluoromethylsulfonyl)imide, $[C_4C_1C_1C_1N][Tf_2N]$, is a glass-forming liquid that exhibits partial crystallization depending on the cooling rate. Partial crystallization along a fast cooling protocol is followed by cold crystallization as the glass is reheated to the supercooled liquid phase. Differential scanning calorimetry (DSC) indicates crystallization at $T_c = 227$ K, melting at $T_m = 258$ K, glass transition at $T_g \sim 193$ K, and cold crystallization at $T_{cc} \sim 219$ K. Crystallization is only partial either by slow or fast cooling, since Raman spectra in the low frequency range exhibit superposition of a broad bands characteristic of amorphous phase and sharp peaks characteristic of lattice vibrations of crystalline phase. Raman spectroscopy shows that local structures that are optimized during slow cooling select a preferred configuration for $[Tf_2N]^-$, namely the cisoid conformer. No preferred conformation of the butyl chain of the $[C_4C_1C_1C_1N]^+$ cation is favored by slow or fast cooling of $[C_4C_1C_1C_1N][Tf_2N]$. The conformational change of $[Tf_2N]^-$ must imply collective rearrangements, so that faster cooling rates produce crystalline structures with ions in conformation similar to already existent in the supercooled liquid, i.e. $[Tf_2N]^-$ in transoid conformation. The finding of transoid conformation during cold crystallization indicates that crystal nuclei that have been formed during fast cooling of the supercooled liquid grow while reheating the glass, but this is not the structure that should be found in a better formed crystal during slow cooling of $[C_4C_1C_1C_1N][Tf_2N]$. The glass-forming ability of $[C_4C_1C_1C_1N][Tf_2N]$ is reasonable in this scenario, since the slow collective dynamics hinders crystallization.

P1.020 Magneto-structural properties of lithium-phosphate glasses doped with iron ions

C Andronache

Technical Univeristy of Cluj-Napoca, Romania

The temperature dependence of the magnetic susceptibility and IR investigations of $xFe_2O_3 \cdot (100-x)[P_2O_5 \cdot Li_2O]$ glasses with $0 < x < 50$ mol % have been performed. The valence and the distribution of iron ions in the glass matrix depend on the Fe_2O_3 content. For the glasses with $x \leq 3$ mol % only Fe^{3+} ions are evidenced. In the case of the glasses with $5 \leq x < 20$ mol % both Fe^{3+} and Fe^{2+} ions co-exist in the $P_2O_5 \cdot Li_2O$ glass matrix, the Fe^{2+} ions content is higher than that of Fe^{3+} ions for glasses with $x \geq 20$ mol %. The results indicate that the iron ions are isolated or participate in dipole-dipole interactions for glasses with $x < 20$ mol % and are antiferromagnetically coupled for higher contents of Fe_2O_3. IR spectra of the studied glasses pointed out the depolymerization process induced by the addition of Fe_2O_3 content because for $x > 20$mol % the significant reduction of the bonding force between P and O atoms lead to the appearance of more non-bridging oxygen ions that are involved in new Fe-O bonds.

P1.021 Dynamic scaling for supercooled liquids

F Akira

University of Tokyo, Japan

We construct a dynamic scaling theory for anomalous mesoscopic transport of supercooled liquids. First, using three-dimensional molecular dynamics simulation, we show that the dynamic correlation length, ξ, can be identified as a crossover length between the microscopic and macroscopic transport.

We also find the dynamic scaling behavior; in highly supercooled states, where a clear stress plateau is observed in the stress-autocorrelation, cooperative transport, in both the (longitudinal) density diffusion and the (transverse) viscous relaxation, can be characterized by a single length scale, ξ.

The present identification of the dynamic correlation length has an advantage over other characterization methods in that it directly interprets the anomalous hydrodynamic transport in terms of the growing length scale. Especially, in the context of the present study, we can provide a phenomenological explanation for the long-standing problem of the breakdown of the Stokes-Einstein relation.

We then derive a scaling law for the structural relaxation time τ_α (or the macroscopic shear viscosity η) vs ξ. The underlying assumption in the present work is that a transiently correlated structure with the characteristic size ξ and time τ_α, which is comparable to those of dynamic heterogeneity, sustains the long-lived stress and dynamically couples with hydrodynamic transport.

P1.022 How liquid is a liquid metal?

F Demmel

The Science and Technology Facilities Council (STFC), UK

Does a unique temperature range exist where a liquid metal starts to feel more solid? From neutron scattering experiments on liquid metals we derive generalized viscosities, structural relaxation times and elastic moduli. All findings point to a more solid-like behaviour, beginning distinctly above the melting point, which evidences a universal temperature range when solidification sets in on an atomistic level for metals.

P1.023 Osmosis in a minimal model system: a molecular dynamics simulation study

T Lion and R Allen

The University of Edinburgh, UK

We present a minimal model system which allows the microscopic dynamical processes underlying osmotic pressure and concentration gradients to be investigated. In our model, solute and solvent are represented by repulsive particles with identical interactions; the solute particles are confined to the solution by an external potential. Using molecular dynamics simulations, we show that the osmotic pressure difference can be predicted using a simple virial-like relation, and that the solute interactions with the solvent play a key role. We present a simple and intuitive picture to explain the underlying basis of osmosis in this system.

P1.024 Observation of crossover from ballistic to diffusion regime for excimer molecules in superfluid ^{4}He

D Zmeev[1], F Pakpour[2], P Walmsley[2], A Golov[2], W Guo[3], D McKinsey[3], G Ihas[4], W Vinen[5], S Fisher[1] and P McClintock[1]

[1]Lancaster University, UK, [2]The University of Manchester, UK, [3]Yale University, USA, [4]University of Florida, USA, [5]University of Birmingham, UK

Einstein's model for Brownian motion suggests that the particle moves ballistically between collisions with the molecules of the surrounding medium. As the medium gets more rarefied, the free path of the particle increases until the particle becomes ballistic on a macroscopic scale. Superfluid helium at low temperatures poses as a convenient reservoir for the gas of phonons with its density changing with temperature as T^4. If one uses a Brownian particle, whose size is much smaller than the wavelength of phonons $2\pi/k$, the particle will experience Rayleigh scattering with the cross-section $\sigma \sim k^{-4} \sim T^4$. Overall, the free path λ of such a Brownian particle would scale as T^8, and its behaviour can be scanned through many orders of magnitude of λ in a narrow temperature range. This would allow the regime between ballistic motion and diffusion to be studied. One such probing particle is the helium excimer molecule, which in liquid helium forms a bubble of 1.3 nm in diameter. We report the measurement of the temperature dependence of the time of flight of helium excimer molecules He_2* in superfluid ^{4}He and find that the molecules behave ballistically below ~ 100 mK and exhibit Brownian motion above ~ 200 mK. In the intermediate temperature range the transport cannot be described by either model.

P1.025 Computation of the structural properties of liquid metals

R A Raheem and M Osiele

Federal University of Technology, Nigeria

Using the soft-core mean spherical approximations, the dynamical structure factor and pair correlation function of liquid metals were computed. The effects of density and temperature on peak heights and peak position of the dynamical structure factor of liquid metals were studied. The results obtained revealed that the computed dynamical structure factor and pair correlation function of liquid metals were in good agreement with experimental values. The peak heights and peak positions were also in agreement with experimental values. Increase in particle density and temperature causes an increase in peak heights but does not affect the peak position.

P1.026 Capillary rise in rectangular microchannels with patterned walls

H Javed[1], M Newton[1], G McHale[2], F Ouali[1] and N Shirtcliffe[3]

[1]Nottingham Trent University, UK, [2]Northumbria University, UK, [3]Hochschule Rhein-Waal, Germany

In this work, we study the dynamics of capillary rise of polydimethylsiloxane oils in vertically mounted, open rectangular microchannels, which were lithographically structured with in-phase and out-of-phase triangular and saw-toothed periodic patterning, transverse to the direction of flow. The texture of microchannel is characterised by a roughness parameter, r, defined as the fractional increase in the wall solid/liquid area as compared to its projected area and varies experimentally from r=1(smooth channels) to r=3. The width of channel is increased with roughness in such a way as to keep its average value constant (600µm), thus allowing a direct comparison with smooth microchannels. Measurements on smooth channels show very prominent fingers spreading ahead the main meniscus of the liquid along the corners of the channel walls, consistent with previous observations, and are accounted for by the wetting effects of the corner edges. We investigate how roughness and patterning configuration modifies the flow of the main meniscus and that of the fingers, both in single and parallel microchannels, and whether pinning of the liquid contact line occurs at high values of r. Preliminary measurements on parallel microchannels with symmetric triangular patterning show a reduction in the prominence of the fingers with increased roughness and a corresponding increase in equilibrium height. The data are fitted and compared to an analytical viscous-gravitational model modified to take into account of the increase in the capillary force with roughness, resulting from the increase in wall surface area, but which assumes that roughness does not alter viscous dissipation.

P1.027 The superfluid helium-3 AB interface probed by quartz tuning forks

R Haley, I Bradley, M Fear, S Fisher, A Guenault, C Lawson, G Pickett, R Schanen and V Tsepelin

Lancaster University, UK

We are studying the AB phase boundary in superfluid helium-3 at low temperatures in the pure condensate ballistic limit. The phase change between A and B is an exemplar first order transition, and the interface between the two is arguably the most highly ordered to which there is experimental access. The A phase order parameter transforms coherently through the interface to that of the B phase over a distance of the order of a few coherence lengths. However, no direct measurements of the boundary region have yet been undertaken. Our experimental cell consists of a vertical cylinder of superfluid, 5.7 cm long and 1.2 cm in diameter. We create and stabilize the AB interface across the cylinder using a controllable magnetic field gradient. At zero pressure the transition from B to A occurs at a field on the order of 0.3 T. Ramping the field gradient moves the AB interface up and down the cylinder, converting B phase to A phase and vice versa. The motion and properties of the interface are inferred from the behaviour of quartz tuning fork resonators that project into the superfluid from the sidewalls of the cylinder. These resonators are sensitive to the density of broken Cooper pair quasiparticle excitations, and are thus used to detect any changes as the interface is moved through the cell. Such changes are due to several effects, for example simple heating, the presence of defects, or the underlying order parameter texture of the surrounding superfluid phase. Here we present measurements of the interaction of quartz tuning forks with the AB interface itself, and their response when immersed in B phase whose energy gap structure has been severely distorted by the large magnetic field.

P1.028 Anomalous damping of a low frequency vibrating wire in superfluid helium-3-B due to vortex shielding

R Schanen, I Bradley, M Fear, S Fisher, A Guenault, R Haley, C Lawson, G Pickett and T Viktor

Lancaster University, UK

We have investigated the behaviour of a low frequency vibrating wire in the B phase of superfluid helium-3 at zero pressure and temperatures around 0.15 T_c . The vibrating wire has a goalpost shape with a 25 mm leg length and 8 mm crossbar. It has a low resonant frequency around 60 Hz. Placed in a vertical magnetic field of ~100 mT, it is forced into oscillatory motion by passing an ac current through the wire. Its velocity can be inferred from the ac Faraday voltage generated as the crossbar sweeps through the magnetic field. At low velocities the motion of the wire is impeded by its intrinsic (vacuum) damping and by the scattering of thermal quasiparticles. At higher velocities we would normally expect the motion to be further damped by the creation of quantized vortices and broken Cooper pair excitations. However, for a range of temperatures, as we increase the driving force we observe a sudden decrease in the damping of the wire. This indicates that the wire is shielded from thermal quasiparticles by quantized vortex lines created by the wire itself.

Low temperature/superconductivity

P1.029 Integrated superconducting NbSi nanowire devices for a quantum phase-slip current standard

J Fenton[1], C Webster[2], N Constantino[1], C Nash[1] and P Warburton[1]

[1]University College London, UK, [2]National Physical Laboratory, UK

There is increasing interest in coherent quantum phase-slip devices for a new range of electronic devices. A superconducting nanowire exhibiting quantum phase-slips placed in a voltage-biased circuit with inductive and resistive elements is predicted to exhibit Shapiro steps in current under microwave irradiation. Such a device is a candidate for a new quantum current standard, dual to the Josephson voltage standard. We describe our fabrication of such devices and report our latest progress in experiments where the devices are irradiated with microwaves.

P1.030 Device to measure current-voltage curves in thin-films superconductors down to microsecond range: First applications to $Y_1Ba_2Cu_3O_{7-d}$ microbridges

F Vidal[1], G Ferro[2], J Doval[1], D Vidal[1], J Maza[1] and J Antonio Veira[1]

[1]Universidade de Santiago de Compostela, Spain, [2]Asociación de Investigación Metalúrgica del Noroeste (IMEN), Spain

A device based on short (microseconds) pulsed electrical currents to measure the current-voltage characteristic (CVC) in thin-film superconductors is described, together with its first applications to study CVC in $Y_1Ba_2Cu_3O_{7-d}$ microbridges. The device allows us to extend our previous CVC measurements in the millisecond range (1) to the microsecond range. The results will probe the different scenarios that are being proposed to explain the quenching to the normal state induced by high current densities in thin-film of high-temperature cuprate superconductors (2, 3, 4).

[1] See, e. g., M. Ruibal, G. Ferro, M. R. Osorio, J. Maza, J. A. Veira and F. Vidal, Phys. Rev. B 75, 012504 (2007), and references therein.
[2] J. Maza, G. Ferro, J. A. Veira and F. Vidal, Phys. Rev. B 78, 094512 (2008).
[3] P. Bernstein, J. Mosqueira, J. Siejka, G. Ferro, Y. Thimond, C. McLoughlin, and F. Vidal, J. Appl. Phys. 107, 123901 (2010).
[4] J. Maza, G. Ferro, M. R. Osorio, J. A. Veira, and F. Vidal, Phys. Rev. B 84, 214530 (2011).

P1.031 Phase diffusion in intrinsic Josephson junctions

P Warburton, J Fenton, S Saleem, T Wootton, L Ward and I Rizvi

University College London, UK

When an overdamped (non-hysteretic) Josephson junction is biased at a current below its critical current, the phase advances diffusively, leading to a small thermally-activated voltage. Since the activation energy of this phase-diffusion process decreases with increasing current, the diffusivity increases exponentially with current, leading to a current-voltage characteristic (IVC) with negative curvature. Phase diffusion can also be observed in hysteretic Josephson junctions (i.e. when the low-frequency dynamics are underdamped) provided that the viscosity is frequency-dependent and the damping is high at the plasma frequency. Furthermore Josephson junctions irradiated at microwave frequencies display a strong enhancement of the phase diffusion voltage [1], which at strong irradiation leads to a non-linear regime with *positive curvature* in the IVC.

While the experiments are well understood for single Josephson junctions, it is less well-characterized in the case of arrays of junctions, including the so-called intrinsic junctions formed by adjacent cuprate planes in anisotropic high-temperature superconductors. Classical phase diffusion with IVC's with negative curvature was observed by both us and the Erlangen group [2, 3]. We further showed [4] that the damping depends upon the number of junctions which are in the voltage state. In the presence of microwave radiation, Koval et al. [1] showed that the dissipative branch with positive curvature which had formerly been attributed to microwave-induced vortex-flow, was due to microwave-enhanced phase diffusion.

Here we will survey the phase diffusion phenomena which can be observed in intrinsic Josephson junctions. We will additionally show that, by integrating passive components in close proximity to the junction stack, we can control the dissipation at the plasma frequency. This has enabled us to observe a new phase-diffusion phenomenon: namely a branch with positive curvature in the absence of external microwave radiation. We propose that this branch arises from mutual coupling of thermally-activated phase-slips between the junctions in the stack – or, in other words, self-induced “microwave”-enhancement of the phase diffusion voltage.

[1] Koval *et al.* Phys. Rev. Lett. 93 087004 (2004).
[2] Warburton *et al.* Phys. Rev. B 67 184513 (2003).
[3] Franz *et al.* Phys. Rev. B 69 014506 (2004).
[4] Warburton *et al.* Phys. Rev. Lett. 103 217002 (2009).

P1.032 Stencil lithography for top-down fabrication of sub-20nm superconducting nanowires

N G N Constantino[1], J C Fenton[1, 2], C R Nash[1] and P A Warburton[1]

[1]University College London, UK, [2] National Physical Laboratory, UK

Quantum phase slip phenomena occur in nanowires with cross-sectional dimensions near the superconducting coherence length. It has been shown [1] that such a wire could be used to yield a new current standard. These nanowires have been made using a variety of different techniques; here we describe a new process we have developed: stencil masks defined using e-beam lithography and Ar milling. We have demonstrated that this technique can produce measurable NbSi nanostructured devices with controlled dimensions. This could be used in the repeatable, top-down fabrication of sub-20nm nanowires. We discuss the benefits and challenges in using the stencil technique and describe our latest progress in the fabrication and characterisation of QPS nanowire devices.

[1] J. E. Mooij and Y. V. Nazarov, “Superconducting nanowires as quantum phase-slip junctions,” Nature Physics, vol. 2, 2006, page 169.

P1.033 Fabrication of chromium oxide resistors and their use in a quantum phase-slip circuit

C R Nash[1], J C Fenton[1,2], N G N Constantino[1] and P A Warburton[1]

[1]University College London, UK, [2] National Physical Laboratory, UK

On-chip thin-film resistors have numerous applications in nanoscale circuit fabrication, where delicate components need to be electrically isolated from their surroundings. We report on fabrication of chromium oxide resistors with a tuneable resistivity, by sputter deposition. Their low-temperature sheet resistance was tuned between 450 Ω per square and 500 kΩ per square by adjusting oxygen concentration during deposition.

An application for the resistors is as part of quantum phase-slip circuit which could provide a new current standard, analogous to the Josephson voltage standard [1]. We report on the fabrication of such a circuit, consisting of a NbSi nanowire, inductor and CrO thin-film resistors with a combined resistance above 60 kΩ and describe how we have optimised the contact resistance of the inter-connects between these circuit elements.

[1] J E Mooij, Y V Nazarov, Nature Physics 2 169 (2006).

P1.034 Simultaneous measurements of the thermal conductivity and response to torsional oscillation of solid ^{4}He

M Brazhnikov[1], D Zmeev[2] and A Golov[1]

[1]The University of Manchester, UK, [2]Lancaster University, UK

In our experiments the anomalous response to the torsional oscillation of solid ^{4}He is examined along with its thermal conductivity. Polycrystalline samples of ^{4}He grown in annular cell by blocked capillary method have been studied before and after annealing. In previous experiments with either isotopically pure ^{4}He or ^{4}He with about 0.3ppm of ^{3}He no correlation has been found between the low-temperature shift of the resonant frequency of oscillator and phonon mean free path. Investigations of samples with a higher concentration of ^{3}He impurities are ongoing; results will be presented at the conference.

P1.035 Study of excimer molecules in superfluid ^{4}He at T

D Zmeev[1], F Pakpour[2], P Walmsley[2], A Golov[2], W Guo[3], D McKinsey[3], G Ihas[4], W Vinen[5], S Fisher[1] and P McClintock[1]

[1]Lancaster University, UK, [2]The University of Manchester, UK, [3]Yale University, USA, [4]University of Florida, USA, [5]University of Birmingham, UK

Excimer molecules He_2 are good candidates for tracer particles in the studies of vortex dynamics in superfluid ^{4}He: they are small, long-lived, and they can be visualised using laser-induced fluorescence. In this work we studied dynamics of the molecules in the stationary superfluid as well as in the presence of quantized vortices. The molecules, created by electrons field-emitted from a tungsten tip, travelled several centimetres to gridded detector electrodes with electric field 10^4–10^5 Vcm^{-1}. We were able to measure the time of flight of the molecules and interpret the results in terms of interaction with phonons. We were also able to measure the attenuation of the detected signal in the presence of vortex lines and deduce the trapping cross-section of the molecules on vortices. These results indicate that the decoration of vortices with the molecules is possible at low temperatures.

P1.036 A new compact rotating dilution refrigerator

M Fear[1], P Walmsley[1], D Chorlton[1], M Sellers[1], S Gillott[1], D Zmeev[2], A Golov[1], H Agrawal[3] and G Batey[3]

[1]The University of Manchester, UK, [2]Lancaster University, UK, [3]Oxford Instruments Nano Science, UK

Rotating a superfluid is the analogue of applying a magnetic field to a superconductor and has thus proved to be a vital tool for investigating quantized vortices in superfluid helium. These can take the form of a rectilinear array of vortex lines during steady rotation, but in addition turbulent vortex tangles (quantum turbulence) can be created following rapid changes in angular velocity. We are constructing a new rotating dilution refrigerator that will complement the existing rotating microkelvin cryostat already present in Manchester. The design of the new instrument is based upon two coaxial rotating carousels that are driven synchronously. The pumps, gas handling system and other noisy electrical equipment are mounted on the upper carousel. Housing all equipment necessary for the running of the refrigerator and equipment required for experiments in the rotating frame means that the only two simple connections to the laboratory frame are required for helium gas recovery and a single phase mains electrical supply. The lower carousel supports a bespoke axially-symmetric wet dilution refrigerator (cooling power 300 microwatts at 100 mK, base temperature 12 mK) built by Oxford Instruments. A Joule-Thompson stage is used instead of a 1K pot to simplify the gas handling system. When it is fully operational, this cryostat will be used for a series of experiments that aim to understand the dynamics of quantum turbulence in the zero-temperature limit. It can also be used to search for superfluid flow through solid helium.

P1.037 Detectors of quantum turbulence with the use of charged vortex rings

F Pakpour[1], D E Zmeev[2], P M Walmsley[1] and A I Golov[1]

[1]The University of Manchester, UK, [2]Lancaster University, UK

To measure the density of quantized vortex lines forming Quantum Turbulence in the zero temperature limit, we designed detectors that rely on scattering charged vortex rings (CVRs) of well-known radius off vortex lines. The aim was to have compact and portable injector-collector pairs suitable for using with various techniques of generating turbulence such as by a towed grid or current of injected ions. An experimental cell was built that contains removable encapsulated injector and detector that are positioned across a sample region of a square cross-section suitable for pulling a grid through. A sharp tungsten tip serves as an injector of electrons with two grids in front of it for growing CVRs to a suitable radius. The collector is a metal plate covered by a Frisch grid. The experimental region between the injector and collector grids is field-free to keep the radius of CVRs constant. We expect to report preliminary experimental results of measuring the density of vortex lines generated in superfluid ^{4}He by injected currents.

P1.038 Observation of vortex ring emission within vortex tangles in superfluid ^{4}He at low temperatures

P Walmsley, M Fear and A Golov

The University of Manchester, UK

Turbulence in a superfluid (quantum turbulence) in the zero-temperature limit, where there is no classical viscous fluid component, is fully described by a dynamic tangle of quantized vortex filaments. At length scales greater than the inter-vortex spacing, locally polarized tangles of vortex lines can mimic classical eddies and produce large scale flow. However, at length scales comparable to the inter-vortex spacing the classical model must break down due to the quantized nature of vorticity and thus new mechanisms for transferring energy down to short dissipative length scales are expected. Hence, new experimental techniques that are capable of probing vortex dynamics at small scales are required. We report the use of injected charge to probe the internal dynamics of vortex tangles. We injected electron bubbles into a cubic container with sides of length 4.5 cm filled with superfluid 4He at temperatures below 1 K. When there is no turbulent tangle present, charged vortex rings travel across the container. However, when the container is filled with a dense vortex tangle and seeded with charge in the vicinity of the injector, we find that for $T<0.5$ K, a fraction of the charge travels across the container quickly. Such fast transport of charge does not occur at the slightly higher temperature of 0.7 K. These observations can be explained if, at $T<0.5$ K, vortex reconnections within the tangle lead to the emission of very small charged rings. These rings are initially emitted isotropically, but when an electric field is applied they are rapidly redirected towards the collector electrode. One potential explanation for why this does not happen at $T>0.7$ K is that the damping provided by mutual friction prevents the fractalization of vortex lines at the small length scales where self-reconnections can lead to the emission of small rings. Instead, the trapped charge drifts slowly with the vortex tangle. This appears to be a useful technique that is now enabling us to gain some insight into the dynamics of vortex lines on small length scales in the zero-temperature limit.

P1.039 Diamond like carbon (DLC) thin film for industrial application

M Khalid[1], M Waqar[1], M Maqsood[1] and M Arif[2]

[1]National Institute of Vacuum Science and Technology, (NINVAST), Pakistan [2]University of Engineering and Technology (UET), Lahore

Thin film of amorphous carbon (DLC) was deposited on 316 steel using Nd:YAG laser having energy 300mJ. Pure graphite was used as a target. The vacuum in the deposition chamber was generated in the range of 10-6 mbar by turbo molecular pump. Ratio of sp3 to sp2 content shows amorphous nature of the film. This was confirmed by Raman spectra having two peaks around 1300 cm-1 i.e. D-band to 1700 cm-1 i.e. G-band. If sp3 bonding ratio is high, the films behave like diamond-like whereas, with high sp2, films are graphite-like. The ratio of sp3 and sp2 contents in the film depends upon the deposition method, hydrogen contents and system parameters. The structural study of the film was carried out by XRD. The hardness of the films as measured by Vicker hardness tester and was found to be 28 GPa. The EDX result shows the presence of carbon contents on the surface in high rate and optical microscopy result shows the smoothness of the film on substrate. The film posses good adhesion and can be used for industrial purpose.

P1.040 2D Fermi liquid collective excitations at high energy and wave-vector: neutron measurements on a liquid ^{3}He monolayer

A Sultan[1], H Godfrin[1], H-J Lauter[2,3], M Panholzer[4] and H Schober[2]

[1]CNRS et Université Joseph Fourier, France, [2]Institut Laue-Langevin, France, [3]Oak Ridge National Laboratory, USA, [4]Johannes Kepler University, Austria

We present the results of inelastic neutron scattering experiments performed on the IN6 time-of-flight spectrometer ILL on a two-dimensional liquid ^{3}He film of atomic thickness. The measurements, performed at a wavelength of 0.41nm, extend our previous results (Nature 483, 576–579, 2012) to higher energy and wave-vector. We observe that at high energies the zero-sound collective mode remains close to the low-energy limit of the incoherent particle-hole band.

P1.041 Spin lattice relaxation at very low temperatures

J Owers-Bradley[1], D Peat[1], K Goh[1], A Horsewill[1] and D Gadian[2]

[1]University of Nottingham, UK, [2]University College London, UK

Nuclear spin-lattice relaxation times T1 for species such as protons or ^{13}C in solids tend to become very long as the ratio of magnetic field to temperature is increased. This is a nusiance when trying to exploit the 'brute force' method of polarisation with a view to generating hyperpolarised materials for magnetic resonance imaging. The long relaxation times may also contribute to long lasting heat leaks in ultra-low temperature experiments. We report measurements of T1 in materials at high B/T>1 T/mK and we describe various attempts to shorten T1. As an example, we have investigated the effect of doping with lanthanide compounds, e.g dysprosium and holmium. One general feature is that proton T1s are much shorter than other spins such as ^{13}C but that by field-cycling to zero magnetic field we are able to polarise the slower relaxing components.

P1.042 Angle-dependent measurements at low temperature and high magnetic fields with in-situ double rotator

F Otto, D Andres, G Coustou and T Lindenberg

Attocube Systems, Germany

Many interesting quantum phenomena require the relative rotation of a strong magnetic field at low (or even ultra-low) temperature with respect to a mesoscopic sample, be it semiconductors / nanomagnets with magnetic anistropies or superconductors with anisotropic gap structures. While readily available, commercial vector magnets (2D/3D) are usually significantly more expensive than single solenoids, despite delivering much smaller fields due to the limitations set by split coil magnets. Instead of rotating the field vector, the atto3DR - attocube's 3-dimensional rotator module - provides access to the full magnetic field (e.g. 9 T) in all directions relative to the sample surface, by rotating the sample *in-situ*. We discuss the key features of the setup, and show first measurement results at both 4 K and mK temperatures.

P1.043 Studies of dielectric loss and noise in superconducting resonators

J Burnett [1,2], T Lindström [1], M Oxborrow[1], G Ithier[2], Y Harada[3], Y Sekine[3], P Meeson[2] and A Y Tzalenchuk[1]

[1]National Physical Laboratory, UK, [2]Royal Holloway University of London, UK, [3]NTT Basic Research Laboratories, Japan

The current interest in superconducting resonators is motivated by their applications in quantum information processing (QIP) and photon detection. Detectors are typically operated at applied microwave powers of around -90dBm, whereas powers as low as -150dBm are common in QIP experiments. This power range spans complete saturation to desaturation of the resonant two level fluctuators (TLFs) which are a dominant source of loss.

TLFs have been extensively studied in recent years and methods of producing resonators with a low loss tangent have been developed. Yet the effects of dielectric loss remain problematic.

We present an uncertainty analysis for the measurement of dielectric loss tangents using a so-called Pound-loop. The goal of our measurements is to investigate the link between dielectric loss and frequency noise.

[1] J. Burnett, T. Lindström, M. Oxborrow, G. Ithier, Y. Harada, Y. Sekine, P Meeson and A .Ya. Tzalenchuk. In preparation

[1] T. Lindström, J. Burnett, M. Oxborrow and A. Ya. Tzalenchuk Rev. Sci. Instr. vol 82, issue 10, 2011.

[2] T. Lindström, J. E. Healey, M. S. Colclough, C.M. Muirhead and A. Ya. Tzalenchuk Phys. Rev. B , vol 80, 132501, 2009.

P1.044 Mobile small bipolarons on a three-dimensional cubic lattice

A Davenport[1], J Hague[1] and P Kornilovitch[2]

[1]The Open University, UK, [2]Hewlett-Packard Company, USA

We present analytical calculations and quantum Monte Carlo simulations describing the formation of bipolarons on a three-dimensional cubic lattice. Dramatic changes to the bipolaron properties found when inter-site interactions are turned on, producing minima in the effective mass and small bipolarons sizes in the intermediate regime where preoperative methods fail.

The results obtained are precursors to to possible Bose Einstein condensation (BEC). Calculating the critical BEC temperature we see that maxima are produced where the bipolarons are small and mobile with a low effective mass. Possible BEC temperatures for our system have maxima appearing where small light bipolarons appear, reaching values of 20K-30K where bipolarons are 10 sites apart. A Tc of 50K can be reached by decreasing the bipolaron spacing to 8 sites.

P1.045 Nanoscale Superconducting Quantum Interference Devices for Millikelvin Magnetometry

L Hao[1], A Blois[2], S Rozhko[2], J Gallop[1] and E Romans[2]

[1]National Physical Laboratory (NPL), UK, [2]University College London, UK

Nanoscale Superconducting Quantum Interference Devices (SQUIDs) potentially have spin sensitivities approaching that required to detect the flip of a single spin in samples coupled in close proximity. Certain magnetic systems undergo phase changes at sub-kelvin temperatures, and to study these requires the development of nanoscale SQUIDs that can operate at such low temperatures. The difficulty is that most nanoscale SQUIDs are based on nanobridges as the Josephson elements, and at temperatures well below their transition temperatures these can have non-sinusoidal current-phase relations and hysteretic IV characteristics due to hot spot formation.

To extend downwards the possible operating range we have developed a range of nanoscale SQUIDs from superconductor-normal metal proximity effect bilayers with lower transition temperatures. These are patterned using lift-off and e-beam lithography (EBL). We report on their IV characteristics, noise performance and behaviour in magnetic fields at temperatures down to 60 mK.

P1.046 Superconducting microbolometer for the measurement of energy deposited by proton and ion beams

L Hao[1], S Galer[1], J Gallop[1], H Palmans[1], K Kirkby[2] and A Nisbet[3]

[1]National Physical Laboratory (NPL), UK, [2]University of Surrey, UK, [3]Royal Surrey County Hospital, UK

We have developed a form of bolometer based on the principle of the Inductive Superconducting Transition Edge Detector (ISTED). This detector consists of a passive superconducting absorber which is read out using a D.C. SQUID. The SQUID is made from a loop of thin film niobium interrupted by two nanobridge Josephson junctions which have been milled using a focussed ion beam (FIB).

The purpose of this detector is to measure the energy deposited by single protons and ions used in radiotherapy treatments in order to better understand the relative biological effectiveness of different treatments. These detectors bring together low-temperature ISTED detectors and FIB deposited tissue equivalent materials to create devices with similar dimensions and physical composition to cells.

We present here measurements of the current-voltage and current-applied magnetic field characteristics of the detectors, carried out using a two-stage pulse-tube cooler as well as results from irradiations carried out using a proton beam.

This work builds on the current worldwide emphasis on hadron-based radiotherapies including the UK's current proton beam centre at Clatterbridge and the new proposed centres under development. At present there are 39 centres worldwide treating patients and another 22 centres planned for the next 5 years.

P1.047 Design and measurements of quartz tuning fork arrays for quantum turbulence studies in superfluid Helium-3

E Guise, M Clovecko, S Fisher, V Tsepelin, R Haley, G Pickett, I Bradley, T Guenault, M Poole, S Ahlstrom and A Woods

Lancaster University, UK

Vibrating wire resonators have been widely used to study properties of superfluid Helium-3 at ultra-low temperatures. Our goal is to create a 2D detector to probe quantum turbulence and investigate quasiparticle beam propagation. We have found that to manufacture multiple wires sufficiently close together is extremely challenging. However, miniature quartz tuning forks might become an excellent detector for this purpose. Quartz Tuning Forks have proved to be good tools for performing measurements in quantum fluids.

We have designed 1D arrays (of thickness either 50 or 75μm) consisting of five tuning forks on a single quartz wafer. All forks have the same tine width (90μm), but are of a different lengths (ranging from 1400μm to 1900μm) giving each a unique resonant frequency (ranging from approximately 20-40kHz). We plan to mount five such arrays in a copper holder resulting in a grid of twenty-five forks, to be placed into the experimental cell with their tines pointing towards the quasiparticle beam source.

By observing the resonant properties of each fork we hope to be able to produce a spatial image of a quasiparticle beam as well as measuring the propagation of Quantum Turbulence; it's spatial and time correlation and its effects on the beam. To date, quartz tuning fork arrays have been manufactured and tested at room temperature, in vacuum conditions down to 4.2K and in superfluid Helium-4. We will present results of these measurements and compare them with our design considerations.

P1.048 Thermal conductivity measurements of $Dy_2Ti_2O_7$(Spin Ice) and $Y_2Ti_2O_7$ in the temperature ranges 15mK to 20K

S L Ahlstrom, D I Bradley, M Človečko, S N Fisher, D Garg, A M Guenault, E Guise, G R Pickett, R P Haley, M Poole, R Schanen, V Tsepelin and A Woods

Lancaster University, UK

Spin Ice is an interesting material which is able to support magnetic monopoles at low temperatures. We have studied the thermal conductivity of two samples prepared as single crystals. The two compounds have very similar structures but the Yttrium compound is non-magnetic and therefore cannot support monopoles.

We can therefore investigate the influence of magnetic monopoles on the thermal conductivity by comparing these two compounds. The current results show a T^2 dependence of the thermal conductivity of the $Dy_2Ti_2O_7$ sample at low temperatures. The measurements of the thermal conductivity of the $Y_2Ti_2O_7$ sample are still in progress.

Three Ruthenium Oxide resistors are mounted on our sample. One of these resistors is used as a heater to create a temperature gradient in the sample and the other two resistors which are used as thermometers to measure the temperature either side of the sample. This samples are mounted on the mixing chamber of a homemade dilution refrigerator. The temperature was varied from 15mK to 20K in magnetic fields of 0 and 3.3 Tesla.

P1.049 Hydrodynamic properties of a low frequency resonator in normal and superfluid Helium 4

A Woods, S Ahlstrom, M Človečko, S N Fisher, E Guise, M Poole, V Tsepelin, R P Haley, G R Pickett, D I Bradley and A M Guenault

Lancaster University, UK

Mechanical resonators such as vibrating wires and tuning forks are widely used for the study of the properties of quantum fluids. In this we focused on the properties of a type of low frequency (approximately 50Hz) large goal-post shaped vibrating wire called a ‘floppy wire’. The wire was mounted in a cell containing two pressure sensors and an array of quartz tuning forks of various frequencies (between 6 and 160kHz). We investigated the AC response of this wire at low temperatures in pure helium 4. It is also possible to perform DC measurements on this wire to effectively form a zero frequency resonator.

We have investigated the crossover from classical to quantum turbulence on this wire by measuring it’s response on cooling to temperatures of the order of a few mK. The response of the wire was characterised by measuring the dissipative and inertial drag coefficients and comparing this behaviour to the high frequency tuning forks.

We aim to use this wire to investigate the frequency dependence of quantum turbulence by either operating it in a DC mode or as an arbitrary frequency resonator and to use the pressure sensors to detect pressure fluctuations due to the formation of quantum turbulence.

P1.050 Double-oscillator observation of 'Supersolid' effects in solid Helium

B Cowan, G Nichols and J Saunders

Royal Holloway University of London, UK

We present experimental results exploring the 'supersolid' anomaly in ^{4}He below 100mK. A rigid two-mode compound torsional oscillator is used with resonant modes at 400Hz and 2kHz. By studying these two widely spaced frequencies we are able to distinguish between resonant period shifts arising from 'NCRI' effects and variation in shear modulus. An in situ pressure gauge allows careful characterization of annealed crystals to study the effect of disorder on these phenomena.

P1.051 A scalable architecture for solid-state quantum metamaterials

R Wilson, M Everitt, S Savel'ev and A Zagoskin

Loughborough University, UK

Quantum metamaterials provide a promising potential test bed for probing the quantum-classical transition. We propose a feasible and scalable architecture for a solid-state quantum metamaterial. This consists of an ensemble of superconducting flux qubits inductively coupled to a superconducting transmission line. We make use of a quasi-classical model to study the transmission properties of the proposed architecture and we also discuss the possibilities for experimentation with this type of extended quantum system.

Magnetism/spintronics/inter-metalic phases

P1.052 Synthesis and magnetic properties of bulk ferrites spinels $Ni_{0.5}Zn_{0.5}Fe_2O_4$: experimental an ab-initio study

H El Moussaoui[1,2] , E Salmani[2] , O Mounkachi[1], R Masrour[3], H Ez-Zahraouy[2], M Hamedoun[1,4*], E K Hlil[5] and A Benyoussef[1,2,3]

[1] Institute of Nanomaterials and Nanotechnologies, Morocco, [2]Laboratoire of Magnetism and the Physics of the High Energies, Morocco, [3]Cady Ayyed University, Morocco, [4] Hassan II Academy of Science and Technology, Morocco, [5]Institut Néel, France

Polycrystalline $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrites have been prepared using solid-state reaction technique. The structure of ferrite was measured using X-ray diffractometer (XRD). It is shown that the structure of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ ferrites is a single spinel structure. The magnetic properties of the samples were tested at room temperature by a superconducting quantum interference device (SQUID) to determine magnetic properties versus temperature and applied magnetic field. Based on first-principles spin-density functional calculations, using the Korringa-Kohn-Rostoker method (KKR) combined with the coherent potential approximation (CPA), the ferromagnetic and half metallic behaviors was observed when LDA (local density approximation) and LDA-SIC (local density approximation-self-interaction correction) approximation.

P1.053 Structure and magnetism of FePt nanoparticles generated with a gas aggregation source and embedded in a solid matrix

S D'Addato, V Grillo, A di Bona, P Luches, S Frabboni, S Valeri, P Lupo, F Casoli, P Ranzieri and F Albertini

Università di Modena e Reggio Emilia, Italy

Fabrication of nanoparticles (NP) with desired shape, structure and size is an important research area, as it presents different and fascinating possibilities, like for instance, shell-driven magnetisation stability, and realisation of high density memory units. In this work it is reported a detailed investigation of the structure, morphology and magnetic properties on FePt NP with linear size in the range between 3 and 10 nm. An experimental set-up was realised for the preparation and the study of pre-formed NP films [1]. The experimental system allows assembly of NP with a gas aggregation source, that can be mass selected with a gas-aggregation source, and co-deposition with other metals, in order to embed them in solid matrix. We could produce in this way FePt NP films in MgO and Ni matrix, to prevent them from NP coalescence during successive thermal treatment and to investigate soft/hard ferromagnetic coupling. The samples were investigated with XPS, SEM, AFM and HR-TEM to study the chemical state of the different atomic species and to determine their morphology and structure. The HR-TEM analysis was performed by making use of exit wave reconstruction method [2], and of STEM-CELL advanced simulation package [3]. Magnetic properties were studied with AGFM and MFM. It was found that the as-deposited NP, have an icosahedral structure, determined by multitwinning during their assembly in the source, a situation similar to the results from Ni [3] and other metals NP obtained previously. The films showed a soft ferromagnetic behaviour characteristic of FePt A1 phase. Annealing to T=550 °C in vacuum gives rise to hardening of the hysteresis cycles for FePt NP embedded in MgO, while HR-TEM on "naked" NP presented dramatic changes in their structure, revealing a transition to the hard $L1_0$ phase, albeit with residual presence of some crystal twinning. Recent results on of FePt NP embedded in Ni matrix will also be presented.

[1] S. D'Addato et al. J. Phys.: Condens. Matter 23 (2011) 175003.
[2] http://www.hremresearch.com
[3] V. Grillo,   http://tem-s3.nano.cnr.it/stemcell.htm
[3] S. D'Addato et al. J. Phys. Chem. C 115 (2011) 14044.

P1.054 Electronic, optical and magnetic properties of Mn doped BN semiconductor

B Abdelaziz and F Mohamed

University of Mostaganem, Algeria

We have performed first-principles calculations using the full-potential linearised augmented plane-wave (FP-LAPW) method and the generalized gradient approximation (GGA) to investigate the structural, electronic and magnetic properties of $B_{1-x}Mn_xN$ semiconductor in zinc-blende ferromagnetic phase. The calculations are spin-polarized and the alloys are simulated using 8, 16 and 32 atoms unit cells, containing one substitutional Mn atom for a B atom. Our results show that for x =0.625, $B_{1-x}Mn_xN$ exhibit a half-metallic characteristic, the majority-spin band has a rather sharp peak, characteristic of a narrow band, while the minority-spin has a gap. We found a total magnetic moment of 2 μB per supercell, the local moment at Mn is 1.24 μB, and the B and N atoms are polarized with a magnetic moment of 0.03 μB and -0.01 μB respectively. The band gap reduction of Mn doped BN for the minority spins increases with increasing Mn concentration and follows the simple fitted formula, $\Delta E_g = 0.3\ x^{0.55}$.

P1.055 Crystal structure and magnetic ordering in ultrathin manganese pnictides films: an ab initio study

M Otrokov[1], A Ryabishchenkova[1], M Otrokov[1], I Rusinov[1] and E Chulkov[2]

[1]Tomsk State University, Russia, [2]Donostia International Physics Center (DIPC), Spain

We present an *ab initio* study of the crystal structure and magnetic ordering in free-standing ultrathin MnX (X = Sb, Bi) films with thickness ranging from one to four bilayers. The calculations are carried out in the framework of the density-functional theory using the projector augemented-wave method and PBE exchange-correlation functional, as implemented in the VASP code. The Hamiltonian contained the scalar relativistic corrections and the spin-orbit coupling has been taken into account by the second variation method.

Since ultrathin films might be expected to have different crystal structure from that of the bulk material, special attention was paid to accurate structure determination. To this end, the (0001)-oriented NiAs-type and wurtzite-type structures as well as zinc-blende-type structure with (111) and (001) orientations were calculated to reveal the most energetically favorable one. We found, that all MnX films under consideration strongly prefer the hexagonal structure but its morphology varies with the film thickness. The magnetic ordering and the electronic structure of the MnX films are discussed for the most stable crystal structures.

P1.056 Study of microstructure and magnetic of electrodeposited CoFeCu in self-assembled mesoporous silicon

G Fortas[1], N M Dempsey[2], S Sam[1], N Haine[3], H Menari[1] and N Gabouze[1]

[1]Silicon Technology Developpement Unit, Algeria, [2]Néel Institute, France, [3]University of Sciences and Technology Houari Boumediene-Algiers, Algeria

The development of novel magnetic material has been subject of wide scientific research which has led to reduce physical dimensions. The fabricated arrays of high aspect ratio has a great interest for use as sensors and ultra high density information storage. Self assembled mesoporous silicon open new opportunities to prepare novel composite nanostructured materials exhibiting an ordering arrangement.

This paper reports the preparation and the characterisation of CoFeCu nanostructured inside self assembled mesoporous silicon.CoFeCu thin films were electrodeposited from sulphate baths. Self–organized quazi-2D regular pore arrangements, with a diameter about 80nm and a depth 3 μm have been fabricated by electrochemical anodization process. The effect of current density on the morphology, microstructure and magnetic properties of CoFeCu were studied by SEM, EDS, DRX and VSM. The images show the growth of CoFeCu wires on surface of mesoporous silicon. From hysteresis loops, the CoFeCu nanowires exhibit soft magnetic proprieties and parallel magnetic anisotropy.

P1.057 A Hall junction element for memory and logic applications

S Zhang[1], Y Liu[2], S Wang[3], T Hesjedal[1] and G Yu[2]

[1]University of Oxford, UK, [2]University of Science and Technology Beijing, China, [3]Chinese Academy of Sciences, China

Spintronics-based information technology involves encoding and reading information in materials by utilizing the spin degree of freedom of the electron together with its charge. Magnetic tunnel junctions (MTJs), e.g, are the promising spintronic element for future memory and logic schemes. Due to their remarkable features, i.e, no volatility, low power consumption, high speed, and high density; MTJs-based devices have the potential to defeat traditional transistor-based circuits. However, MTJs may expose its weakness when it comes to reading the state compared with transistors. Reading out the tunneling magnetoresistance, MTJs have low ON/OFF ratio compared with transistors. This presents challenge for conventional binary circuits. So the MTJs have to be combined with complementary metal oxide semiconductors (CMOs) for applications. Further research is focused on improving the magnetoresistance of the MTJs. Here, we demonstrate the use of the spin degree of freedom to store information, meanwhile utilizing the electronic charge to read information in a ‘Hall Junction’ (HJ) element. The ON/OFF ratio, inferred from the Anomalous Hall Resistance (AHR), between the two states was found to reach about 30,000%, thereby realizing an instant ON/OFF operation which has solved the main difficulty of MTJs. Further, the multivalued output of the HJ pushes its functionality far beyond a simple switch. We show that a single HJ is able to perform ternary and quaternary logic. As a consequence, binary full addition and Boolean operations are performed more efficiently.

P1.058 Field dependence of microwave frequency absorption in antiferromagnet/ferromagnet exchange coupled multilayers

F Trindade[1], S O'Reilly[2], R Bowman[2], T Drysdale[1], D Schmool[3] and R Stamps[1]

[1]University of Glasgow, UK, [2]Queen's University of Belfast, UK, [3]Universidade do Porto, Portugal

Control of ferromagnetic resonance frequencies can be achieved through exchange coupling anisotropies across a ferromagnet/antiferromagnet interface. The magnitude of the shifts depends upon film thickness, quality of the interface, magnitude of the coupling, and the type of anisotropy. [1] An advantage of exchange coupled multilayers for microwave applications is the high saturation magnetisation, large filling factor, and soft coercivity of the ferromagnet component. [2,3] We report magnetisation and broadband VNA ferromagnetic resonance studies of FeNi/FeMn multilayers. Analysis of fine structure in the resonance spectra allow us to determine the magnitude of variations in the exchange anisotropy field at interfaces buried in the structure. In some cases, it is possible to associate exchange field values with specific layers in the stack by correlating soft modes with structure observed in magnetisation loops.

[1] R. L. Stamps, R. E. Camley, R. J. Hicken, Phys. Rev. B 54, 4159 (1996).
[2] Y. Lamy, B. Viala, IEEE Trans. Magn. 42, 3332 (2006).
[3] N. N. Phuoc, F. Xu, C. K. Ong, Appl. Phys. Lett. 94, 092505 (2009).

P1.059 Low frequency spin dynamics in unsaturated YIG films: correlation of spin dynamics with magnetic domain structures

F Trindade[4], D Schmool[1], R Magaraggia[2], J Teixeira[1], A Rodríguez[3], L Prado[3], J Martín[3], and R Stamps[4]

[1]Universidade do Porto, Portugal, [2]University of Western Australia, Australia, [3]Universidad de Oviedo, Spain, [4]University of Glasgow, UK

Yttrium iron garnet (YIG) is a well-known and studied magnetic material, having a number of high frequency applications. In this work we describe low frequency spin dynamics in YIG. We have studied thick films of single crystal YIG. The room temperature low frequency (0 - 4 GHz) spin dynamics were studied systematically using a vector network analyzer (VNA) at low applied magnetic fields. In order to better analyze the VNA data, we have performed Kerr microscopy and SQUID magnetometry on the samples in the same field configurations as the VNA measurements. In the saturated state we observe the expected uniform mode ferromagnetic resonance (FMR) line. However, for fields below saturation we register a strong deviation from uniform FMR behaviour, where various additional features are present. In particular, we note two specific field regimes below saturation, which correlate with the domain patterns (as observed using Kerr microscopy). For very low fields this corresponds to zig-zag domains, while for intermediate field strengths we observe a stripe domain structure. In the former, there is a strong absorption feature, which appears to be virtually frequency independent, persisting up to about 1 mT. An abrupt transition between the zig-zag and stripe domain patterns corresponds perfectly with the sharp changes observed in the frequency - field characteristics noted from the VNA measurements. In the region between 1 and 3.5 mT, the field at which saturation is almost complete, the frequency - field characteristics show several lines, which appear to be related to domain wall motion and resonance conditions in the different aligned domains. SQUID hysteresis loops support these findings.

P1.060 Critical Properties of a two-dimensional site-diluted Ising model

U Fulco, E Albuquerque and L da Silva

Universidade Federal do Rio Grande do Norte (UFRN), Brazil

Although a large effort has been dedicated to the investigation of disordered magnetic systems, a lot of controversial aspects remain with no definitive answer. From the theoretical point of view there exist only a few exact results, in such a way that approximation methods ought to be employed. Among them, disordered ferromagnets [1] have faced the attention of many researchers, and a proper understanding of their behavior represents a great challenge in the physics of disordered systems. As a consequence, disordered Ising ferromagnets in two dimensions have been the object of a lot of controversy, with different scenarios emerging.

In the present work we investigate the ferromagnetic Ising model on a square lattice with dilution of sites (probability p for active sites and $(1-p)$ for diluted ones), in the short-time regime. Several values of site concentrations p are considered in the range $0.65 \leq p \leq 1.00$. The scaling of quantities, like the magnetization and some of its moments, as well as simple correlation functions, are considered within the short-time-dynamics procedure. For the dynamical critical exponents, a clear breakdown of universality is found, with exponents varying typically by a factor of two in the range of the site concentrations considered. Contrary to that, the static critical exponents β and g follow universality within the error bars.

[1] L.R. da Silva, U.L. Fulco and F.D. Nobre, J. Phys.: Condens. Matter, 21 (2009) 346005.

P1.061 Transmission band gaps in generalized Fibonacci magnonic crystals

P W Mauriz[1], M S Vasconcelos[2] and C H O Costa[2]

[1]Instituto Federal de Educação Ciência e Tecnologia, Brazil, [2]Universidade Federal do Rio Grande do Norte (UFRN), Brazil

In recent years, many interesting properties and effects have been observed in magnetic materials, like spin Seebeck effect, spintronics, and topological insulators, among others [1]. In this context, the investigation of a new kind of material, the so-called magnonic crystals (MCs) [2], has attracted the attention of many theoretical and experimental works. This new magnetic system is made up by a stacking of magnetic materials, in which the magnetic properties change periodically in space, in such a way that the spin waves (SWs) propagation can be modulated and controlled. Therefore, MCs may be defined as the magnetic analogous of the photonic crystals (PCs), which are dielectric microstructures with modulated periodicity that control the electromagnetic wave propagation. Similar to PCs, magnonic structures can also display frequency regions in which magnons, with a given wavevector, do not propagate, the so-called magnonic band gaps (MBGs).

The magnetic multilayer arrangement can be done following a non-periodic deterministic quasiperiodic structure, the most popular of them being the Fibonacci, Thue-Morse, Rudin-Shapiro, and double-period sequences [3]. Such systems do not have translation symmetry, being a suitable theoretical model to describe the conceptual transition from a perfect periodic structure to a randomic one.

In this work, we make use of a transfer-matrix approach to investigate the SWs propagation in quasiperiodic MCs. The calculations are carried out for the exchange dominated regime within the framework of the Heisenberg model, together with the equation of motion of the spin operators, taking into account the random-phase approximation (RPA). We generalize previous results concerning MBGs [2], by investigating the correspondence between the magnon dispersion relation and the transmission spectra in generalized Fibonacci structures.

[1] K. S. K. Uchida, et. al, Nature Materials 10, 737 (2011).
[2] V. Kruglyak and R. Hicken, J. Magn. Magn. Mater. 306, 191 (2006).
[3] E. L. Albuquerque and M. G. Cottam, Polaritons in Periodic and Quasiperiodic Structures (Elsevier, Amsterdam, 2004).

P1.062 Ab-initio and tight-binding calculations of magnetic anisotropy phenomena in CoPt

J Zemen[1], J Mašek[2] and T Jungwirth[2]

[1]The University of Nottingham, UK, [2]Institute of Physics at the Academy of Sciences, Czech Republic

Ordered CoPt alloys hold potential for applications in high density magnetic recording due to the combination of exchange and spin-orbit interactions giving rise to large magnetic anisotropies. Tunneling Magnetoresistance [1] and Tunnelin Anisotropic Magnetoresistance [2] have been demonstrated in tunneling devices with CoPt electrodes. Controlling the spin-orbit coupling (SOC) phenomena is essential as the same anisotropy that ensures thermal stability of a memory element makes the writing by external magnetic fields or electric currents challenging. An alternative to the spin transfer torque (STT) effect in multi-domain systems is based on current induced polarization of the conduction electron spins in structures possessing SOC and lacking inversion symmetry. Switching of a ferromagnetic layer induced by in-plane current has been shown recently in a Co-Pt bilayer [3]. Another promising way of controlling the magnetic anisotropy via SOC utilizes lattice strains induced by piezo stressors. We study SOC effects in strained CoPt multilayer structures using a relativistic full-potential linearized augmented plane-wave method. We compare the variations of anisotropies of magnetic total energies (MAE) and density of states (ADOS) also to our tight-binding calculations using a realistic Slater-Koster parametrisation which provide more practical basis for further research of magnetotransport anisotropies in CoPt based nanostructures.

[1] Gukcheon Kim, Yuya Sakuraba, Mikihiko Oogane, Yasuo Ando, and Terunobu Miyazaki, Appl. Phys. Lett. 92, 172502 (2008); doi:10.1063/1.2913163.

[2] B. G. Park, J. Wunderlich, D. A. Williams, S. J. Joo, K.Y. Jung, K. H. Shin, K. Olejník, A. B. Shick, and T. Jungwirth PRL 100, 087204 (2008).

[3] Ioan Mihai Miron, Kevin Garello, Gilles Gaudin, Pierre-Jean Zermatten, Marius V. Costache, Stéphane Auffret, Sébastien Bandiera, Bernard Rodmacq, Alain Schuhl & Pietro Gambardella, Nature 476, 189-193 (11 August 2011), doi:10.1038/nature10309.

P1.063 Quantitative estimation of the contribution of the metallic Co nanoparticles magnetization to the total magnetization in In_2O_3

M Alshammari[1], M Alqahtani[2], Q Feng[2], A Hakimi[3], S Heald[4], M Fox[2], H Blythe[2] and G Gehring[2]

[1]King Abdulaziz City for Scince and Technology, Saudi Arabia, [2]University of Sheffield, UK, [3]University of Cambridge, UK, [4]Argonne National Laboratory, UK

This study shows that the combination of magnetic measurements and magnetic circular dichroism (MCD) is a powerful tool to detect the contribution of metallic Co nanoparticles to the overall magnetism, and the result that the formation of nanoparticles is inhibited by the inclusion of tin. Thin films of cobalt-doped indium oxide, $(In_{1-0.95}Co_{0.05})_2O_3$ were deposited using pulsed laser deposition (PLD) on sapphire substrates. Extended X-ray Absorption Fine Structure (EXAFS) measurements shows that, the quantity of metallic Co nanoparticles increased with the oxygen deficiency in the PLD chamber and also after annealing in vacuum, resulting in an increase of the magnetization. The MCD spectra show two features one at 2.3eV and the other below the band edge of In_2O_3 at 3.5eV. The MCD spectrum is well fitted by a combination of the spectrum from the nanoparticles in the In_2O_3 matrix as calculated using Maxwell-Garnett theory and a contribution from polarized carriers as seen for substitutional cobalt [1]. The changes in the saturation magnetization and the two components of the MCD are used to get a quantitative estimate of the contribution of the nanoparticles magnetization to the total magnetization in each sample. The MCD signal due to Co nanoparticles was completely suppressed by adding 5% of Sn, and that from polarized carriers enhanced strongly. This indicates that, the magnetization of the carriers in Sn and Co co doped In_2O_3 is particularly high.

[1] A. M. H. R. Hakimi, M. G. Blamire, S. M. Heald, M. S. Alshammari, M. S. Alqahtani, D. S. Score, H. J. Blythe, A. M. Fox and G. A. Gehring, Physical Review B 84, 085201 (2011).

Magnetism at the atomic and molecular scale

P1.064 Domain walls nucleation of super paramagnetic Cobalt nano-wire on Pt(111) by Magnetic Molecular Dynamics simulations

D Beaujouan, P Thibaudeau and C Barreteau

Combustion Engineering Association (CEA), UK

The understanding of the magnetization dynamics at an atomic level becomes essential with the miniaturization of magnetic materials devices. For example in the super-paramagnetic regime, magnetization reversal is intrinsically a dynamical phenomenon with spin-waves excitations [1]. However, micromagnetic simulations are no longer suitable for nano-objects smaller than the typical wall length. Atomic Spin Dynamics (ASD) simulations are performed to describe properly their magnetization dynamics [2,3].

Molecular Dynamics (MD) and ASD timescales suggest a connection to take into account the temperature and pressure effects [4]. A Magnetic Molecular Dynamics model is developed in which positions, impulsions and spins are allowed to evolve simultaneously in time. The energy of the system is a sum of a mechanical part and magnetic terms combining Heisenberg isotropic exchange, pseudo-dipolar and pseudo-quadrupolar anisotropy. A radial dependence of exchange and anisotropy functions, leading to the existence of atomic magnetic forces, is introduced to describe the internal magneto-elastic couplings. An enhanced spin-pair model is presented to reproduce the four magnetostrictive constants of an hcp Cobalt. This model is verified on ab-initio calculations of anisotropy performed on an isolated wire of Cobalt.

An investigation of thermally induced spin and lattice dynamics of varying sizes nanowires of Cobalt on (111)Pt substrate is presented and exhibits a crossover in the activation energy between a single domain regime and many domain walls nucleation.

[1] L. Néel, Ann. Geophys. 5, 99 (1949), W.F. Brown, Phys. Rev, 130, 1677 (1963).
[2] D. Hinzke and U. Nowak, Phys Rev B, 61, 6734 (2000) .
[3] D. Beaujouan, P. Thibaudeau and C. Barreteau, J. Appl. Phys. 111, 07D126 (2012).
[4] Pui-Wai Ma, C.H. Woo and S.L. Dudarev, Phys. Rev B, 78, 024434 (2008).

P1.065 Magnetic stability of rare earth atoms and clusters on metallic surfaces

T Miyamachi[1], T Schuh[1], S Gerstl[1], A Ernst[2] and W Wulfhekel[1]

[1]Karlsruher Institut für Technologie (KIT), Germany, [2]Max-Planck-Institut für Mikrostrukturphysik, Germany

Magnetic stability of bits in information storage relies on the magnetic anisotropy energy (MAE) and the details of the magnetization dynamics. Recent inelastic tunneling spectroscopy (ITS)studies have revealed that a strong hybridization of 3d transition metal atoms and clusters with metallic surfaces induces giant MAEs of the range of several meV, but extremely short lifetimes of spin states [1]. To achieve higher magnetic stability, i.e., larger MAEs and longer lifetimes, we investigated the magnetic stability of 4f rare-earth Gd atoms and clusters on metallic Pt(111) and Cu(111) surfaces with ITS. Since the relativistic spin orbit interaction plays a crucial role for the MAE, rare-earth metal atoms with larger spin and orbital momenta could show larger MAEs than transition metal atoms [2]. In addition, as the 4f states are inner orbitals, less hybridization with the substrate is expected, leading to longer lifetimes. The ITS spectra of Gd reveal a giant MAE of the order of 10 meV/atom and longer lifetimes than transition metal small clusters nearly independent of the supporting surface and cluster size. ITS also gives information on the exchange between Gd atoms, showing much smaller exchange constant than that of 3d transition metals. All the obtained results are in line with the strongly localized character of 4f electrons of Gd.

[1] T. Balashov et al., Phys. Rev. Lett. 102, 257203 (2009).
[2] T. Schuh et al., Phys. Rev. B. 84, 104401 (2011).

P1.066 Local magnetism control with surface states confinement and electric fields

O Brovko, P Ignatiev and V Stepanyuk

Max Planck Institute of Microstructure Physics, Germany

We show that quantum confinement of surface state electrons combined with band-structure manipulation by an electric field can be used to locally tailor the spin-polarization of electrons and such associated values as the TMR ratio of a tunnelling junction. We use *ab initio* calculations [1] to illustrate the concept by the example of spin-polarized surface states confinement on Co islands on Cu(111) surface [2]. In that particular system the sign of the surface states spin-polarization can be locally reversed by changing the confinement geometry or exposing the system to an external electric field.

[1] P. A. Ignatiev, V. S. Stepanyuk, Phys. Rev. B 84, 075421 (2011).
[2] H. Oka *et al.*, Science 327, 843 (2010).

P1.067 AC magnetic susceptibility measurements at high pressure in uranium intermetallics

M Kepa, C O'Neill and A Huxley

The University of Edinburgh, UK

Physics in the uranium compounds, UGe_2 and UNi_2, is governed by 5f electrons. The p-T phase diagram of UGe_2 [1], a ferromagnetic superconductor, is relatively well known but the mechanism for the spin-triplet pairing and the superconducting state are not fully understood and require more experimental investigations [2]. Furthermore, the so-called wing structure of the p-T-H is yet to be studied.

On the other hand, the phase diagram of UNi_2 is not yet explored. However, it is known the magnetic properties of UNi_2 are very susceptible to changes in pressure since the 5f uranium atoms overlap is very sensitive to interatomic distances. Knowing the rich physics of UGe_2, UNi_2 is therefore an interesting material for further investigation.

Finally, it might be expected that the Quantum Critical Points (QCP) play an important role in the formation of the superconducting state in UGe_2 and possibly UNi_2.

The project makes use of the diamond anvil cells (DAC) to apply static pressures. The standard two coaxial coils set-up of an AC-susceptometer and also the so-called designer diamond (which encapsulates a thin-film micro-coil) are used for magnetic susceptibility measurements. Application of the DAC allows achieving regions on the phase diagram with the predicted location of the QCPs.

[1] S.S. Saxena et al. Superconductivity on the border of itinerant-electron ferromagnetism in UGe_2. Nature, 406 (2000).
[2] J. Flouquet et al. Trends in Heavy Fermion Matter. Journal of Physics: Conference Series, 273 (2011).

Nanostructures

P1.068 Strain in free standing core-shell nanocrystals

F Rajadell, J Planelles, C Segarra and J-L Movilla

Universitat Jaume I, Spain

Semiconductor quantum systems are greatly impacted by the effects of strain arising in heterojunctions, in both the solid state phase and also in the colloidal state. In solid state phase, lattice strain is the reason of Stranski-Krastanov self-assembled growth. In colloidal semiconductor core-shell materials, strong strain fields can severely influencing optical and electronic properties. [1]

A main technical difference arises between QDs embedded in an infinite matrix and free-standing core-shell nanocrystals: in the first case, boundary condition of null deformation field far away of the QD border, while in the last one, zero normal stress for the free nanocrystal surface, must be imposed. [2] A second difference is the fact that most commonly synthesized QDs buried in a matrix are made of III-V cubic (zinc-blende) semiconductors, while free nancrystals are mostly made of II-IV semiconductors and have hexagonal (wurtzite) crystalline structure.

Here we address the main characteristic trends of strain and its relation to QD aspect ratio and shell thickness in the case of core-shell systems. We study the relevance of either boundary condition and of the internal crystalline structure. Hexagonal symmetry compared to cubic and also to the isotropic approximation reveals that, with the appropriate parameters, isotropic strain mimics very well to cubic and hexagonal strain distribution, thus confirming and extending previous work in this direction. [3]

[1] A. M. Smith et. al, Nat. Nanotechnol. 4 (2009) 56.
[2] F. Rajadell et a., J. Appl. Phys. 111 (2012) 014303.
[3] M. Tadic et al. J. Appl. Phys. 92 (2002) 5819; Phys. Rev. B 65 (2002) 165333.

P1.069 Tunable generation of correlated vortices in open superconductor micro- and nanotubes

V M Fomin[1], R O Rezaev[2] and O G Schmidt[3]

[1]Institute for Integrative Nanosciences, Germany, [2]Tomsk Polytechnic University, Russia, [3]Chemnitz University of Technology, Germany

Advancements in fabrication of rolled-up micro- and nanotubes including superconductor layers (e.g., InGaAs/GaAs/Nb [1]) open new possibilities for investigation of the vortex matter in superconductors with curved geometries. We investigated theoretically the dynamics of superconducting vortices in the presence of transport currents in open superconductor micro- and nanotubes subject to a magnetic field orthogonal to the axis [2]. In low magnetic fields, vortices nucleate periodically at one edge of the tube, subsequently move along the tube under the action of the Lorentz force and denucleate at the opposite edge of the tube. In high magnetic fields, vortices pass along rows closest to the slit. Characteristic times of nonequilibrium vortex dynamics in an open tube are efficiently controlled by the tube radius. They are significantly different from the characteristic times in a planar film under the same magnetic field. This difference is caused not only by a spatial dependence of the magnetic field component normal to the cylindrical surface but also by correlations between the states of the superconducting order parameter in the opposite areas of the cylindrical surface. The experimentally achievable superconductor tubes of ∼1 μm radiusact as a periodic generator of correlated vortex pairs in the tunable frequency range to 10 GHz. The frequency is tuned by changing the magnetic field. Our results demonstrate perspectives of tailoring non-equilibrium properties of vortices in curved superconductor nanomembranes and of their application as tunable superconducting flux generators for fluxon-based information technologies.

[1] D. J. Thurmer, C. C. Bof Bufon, C. Deneke and O. G. Schmidt, Nano Letters 10, 3704–3709 (2010).
[2] V. M. Fomin, R. O. Rezaev and O. G. Schmidt, Nano Letters, DOI: http://dx.doi.org/10.1021/nl203765f (2012).

P1.070 Noise rectifier based on two-dimensional electron gas

M Cheremisin

A.F. Ioffe Physical-Technical Institute, Russia

Under zero-current conditions and without noticeable external excitation a nonzero dc voltage is observed [1,2] in 2D electron sample at liquid-helium temperatures. The magnitude(∼ mkV) and the sign of the dc potential depend on a actual contact pair. In strong magnetic fields the nonzero dc voltage demonstrates the so-called "zero" oscillations(∼ mV), which exhibit the 1/B-periodicity and the temperature dependence of the amplitude similar to that known for Shubnikov-de Haas oscillations. In contrast to Shubnikov-de Haas oscillations, the "zero" oscillations are alternating. The amplitude and the phase shift of the zero oscillations depend on a chosen contact pair. These effects are observed in various 2DEG systems and for arbitrary sample geometry.

In [3] we demonstrate that the observed nonzero dc voltage is caused by the noise rectification by the Schottky diodes formed at the sample contacts. At low noise strength the rectified voltage as a function of the noise amplitude follows the trivial quadratic law. Unexpectedly, at higher noise magnitudes the rectified voltage exhibits a nearly linear behavior, and, finally saturates. The rectified voltage is shown to depend on the Schottky contact pair asymmetry. We suggest the shunting of the sample contacts by a capacitance could be useful regarding the suppression of the spurious nonzero dc voltage.

[1] I.I. Saidashev et al, JETP Lett. vol.45, 120, 1987.
[2] V.G. Veselago et al,JETP Lett. vol.44, 490, 1986.
[3] M.V. Cheremisin, arXiv:1007.4020, Sov.Phys.JETP, in press, 2012.

P1.071 The spectral properties of the Doppler's effect in dispersive metamaterials

G Burlak

Universidad Autónoma del Estado de Morelos, México

Recently in various publications were reported on the experimental observation of the inverse Doppler's effect at the optical frequencies in photonic-crystals with a negative-index material (NIM). However such effect was observed only at a fixed frequency source f_0. In this Report a numerical study of the properties of optical field radiated by the moving source (v is velocity of source) for a large frequency range in dispersive metamaterials in various geometries is presented. It is shown that a material dispersion leads to that the Doppler's formula becomes a self-consistent equation for a shifted frequency f (with a control parameter f_0) even in a simple 1D geometry. It brings that the Doppler's effect acquires new properties in dispersive metamaterials with negative refraction index $n(f) < 0$ depending on the frequency f_0. The group velocity v_g also becomes the frequency function, so the retardation time τ will be different in the different frequency range. Our simulations have shown that both shifted frequency $f=f(f_0)$ and time dependencies $\tau=\tau(f_0)$ acquire well pronounced nonlinear shape that is strictly defined by a dispersive spectrum of metamaterial. In the Report we consider both 1D and 2D geometries with details.

P1.072 Changes in nanoparticle's spectroscopic signal mediated by the local environment

A Corbani Ferraz[1], F Diniz Kiss[1] and R Miotto[2]

[1]Universidade de São Paulo, Brazil, [2]Universidade Federal do ABC, Brazil

Using a first principles theoretical model the adsorption of methyl radical on different sized silver nanoparticles are compared to the adsorption of the same radical on model surfaces. Our structural, dynamical and electronic properties calculations indicated that small changes in the local environment will lead to small changes in infrared (IR) wave numbers, but in dramatic changes in the IR signal. Methyl radicals are found to preferentially adsorb on lower coordinated sites, in agreement with experimental observations. Changes in the Ag-Ag and Ag-C bond lengths, for example, found to be smaller than 0.01 Angstroms, leads to changes in the wave numbers for the adsorbate groups smaller than 0.03%. Changes in the IR signals, on the other hand, are found to be two or three orthers of magnitude higher. Our calculations also indicate that the smaller the nanoparticle, the higher the signal strength. In a similar manner, the lower the adsorption site coordination, the higher is the signal strength. We explain these differences in terms of changes in the local distribution of the charge density, which is directly related to the polarizability of the material. In this sense, small changes in the electronic charge distribution will result in bigger changes in the polarizability for smaller nanoparticles. This effect explains, among others, the signal magnification observed for nanoparticles in Surface Enhanced Raman Spectroscopic (SERS) experiments.

P1.073 High-magnetic-field thermopower in layered electron systems

S Figarova[1], A Bahram[1], M Mehdi[1] and F Vagif[2]

[1]Baku State University, Azerbajan, [2]Institute of Physics, Azerbajan

The electron diffusion contribution to the thermoelectric power is calculated for layered electron systems in a high magnetic field B. Effects of temperature, the spin splitting, magnetic-field magnitude and the degree of band filling are discussed. The energy spectrum of the system is assumed to be cosinusoidal. Generate and nongenerate electron gases are considered.

For a generate electron gas the thermopower is proportional to the density of states $g_F(\zeta)$ at the Fermi level and is given by

$$\alpha_{2D}(B)=-(\pi^2 k^2 T/3en)\, g_F(\zeta)\ , \qquad (1)$$

where n is the charge carrier concentration. The density of states has a peculiarity each time as ε_z=2 ε_0 , here ε_z is the energy of an electron in k_z -direction, ε_0 is the mini-band half-width [1]. It was found that the thermopower oscillates in a high magnetic field and is non monotonously dependent on the degree of band filling. The influence of the spin splitting on the thermopower of a quasi-two-dimensional electron gas in layered crystals is theoretically investigated.

For a nongenerate electron gas the thermopower has the appearance

$$\alpha_{2D}= \alpha_{3D} -(k/2e)\ ln(m/m_{||})\ , \qquad (2)$$

where m and $m_{||}$ are electron effective masses along and across the layer, respectively.

In this work we study dependence on temperature and magnetic field.

The thermopower of a nongenerate quasi- two-dimensional electron gas increases with the magnetic field and temperature. The additive contribution to thermopower of a nongenerate three-dimensional electron gas is determined by the ratio of electron effective masses along and across the layer.

[1] S.R.Figarova, Physica Status Solidi (b), 2006, v.243, p. R41–R43.

P1.074 Achieving broadband transparency with multishelled spherical metamaterial coatings

K W Yu and L Sun

Chinese University of Hong Kong, China

The possibility of using metamaterial coatings to reduce the total scattering cross section of spherical and cylindrical objects has been extensively discussed in the literature. Guided by the scattering cancellation scheme, Alu and Engheta proposed an initial design of a metal-dielectric coating near the plasma resonance and showed that there is a substantial drop in the scattering cross section, making the enclosing objects nearly invisible or transparent to an outside observer. However, their design was limited to a narrow frequency band near the plasma resonance. In practical applications, broadband electromagnetic transparency is needed. Moreover, it is not obvious the effect of loss can be addressed properly in their design. In this work, we propose a new strategy of designing metamaterial coatings to reduce the scattering cross section of a spherical dielectric object of moderate permittivity in a broad frequency range. The design starts with a core of a given permittivity. Then we enclose the core by several metal-dielectric shells each of proper radius and volume fraction of metal nanoparticles. The dipole moment of the resulting multishelled sphere is calculated by Maxwell-

Garnett embedding formula. The volume fraction of each shell is chosen so as to achieve nearly equal measured frequencies within the operating frequency range, and the radius is determined so as to null the dipole moment of the multishell sphere at the measured frequencies. In this way, we achieve nearly vanishing scattering cross section over a broad frequency range. The drastic reduction of the scattering cross section offers potential applications for broadband electromagnetic transparency. The physical mechanism and some numerical results are provided to confirm the design.

P1.075 Electronic transport in InAs nanowires

M Sourribes, I Isakov, M Panfilova and P Warburton

University College London, UK

Nanowires are attracting a growing interest in the semiconductor industry due to their numerous potential applications including field-effect transistors, elementary logic gates and light-emitting diodes. It has also been demonstrated that nanowires with superconducting electrodes could be used as Josephson devices. Indium arsenide (InAs) nanowires are of special interest as InAs can form ohmic contacts with metals. However a native oxide layer is known to develop easily on InAs nanowires and this must be removed prior to metallization to achieve highly transparent contacts.

Here we report our experiments on minimising the contact resistance to InAs nanowires. The nanowires are grown via molecular beam epitaxy on Si (111) substrates without the use of metal catalysts. The metallic contacts are attached to the nanowires by using an electron-beam lithography process. We have made a quantitative comparison between two techniques used to treat the nanowires before deposition of the contacts: (a) a wet etching process in an ammonium polysulfide solution and (b) a sputter-cleaning process by argon-ion milling with a current density of 1.4 C/cm^2. Nanowires treated by either of these two processes exhibit lower contact resistances by several orders of magnitude compared with untreated nanowires. From field-effect measurements, we have established that the InAs nanowires are n-type and that their mobility at room temperature lies between 100 cm/V/s and 600 cm/V/s. We will also report ongoing electrical transport measurements performed on nanowires with superconducting contacts both at room-temperature and at low temperature.

P1.076 Profile of the potential step in semiconductors and the example of Galium Nitride

B Santic

Ruder Boskovic Institute, Croatia

It is generally assumed that the quantum step (QS), quantum well (QW) and quantum barrier have the rectangular potential profiles.

We show that the potential profiles are not rectangular. A quantum step is a smooth, gradual change of potential over a distance larger than one monolayer. We demonstrate this by calculating the electrostatic contribution to the total potential. For this purpose we examine the dipole layers formed by the ions.

Although similar to those of the Density Functional Theory, our results are obtained in a much simpler way. Furthermore, our approach provides an intuitive insight into the relation between the potential profile and the positions of the ions in the crystal planes. Remarkably, the minimal thickness of the QS is not determined by the distance between the charged planes, but by the lateral spacing between ions of the same polarity.

For a narrow QW, instead of the quantum well, a more appropriate term is the quantum valley. Due to the smooth potential profiles of the narrow QWs, the energy level positions will be different in comparison to the rectangular

QWs.

In the example of GaN, we show that the QS cannot be thinner than about 3 A.

P1.077 SnO_2 nanobelts: back-to-back Schottcky diodes theory in analysis and extraction of electrical parameters

L Araujo, C Amorim, O Berengue, E Bernardo, E Leite and A Chiquito

Universidade Federal de São Carlos, Brazil

In this work we explored the characteristics of SnO2 device based on a dispersion of nanobelts. For the experiment, different metal electrodes were used in order to investigate the characteristics of the metal/SnO2/metal interface. The electrical characterization (current-voltage curves) of these different electrical contacts on nanobelts was performed providing data on the current injection trough the interface. The analysis of non linear current-voltage characteristics exhibited by a set of blocking metal/SnO2/metal allowed the extraction and analyses of the Schottky barrier heights in both interfaces independently and their dependence on the metal work function. The disorder-induced interface states effectively pinned the Fermi level at the SnO2 surface, leading to the observed Schottky barriers. The model presented is useful for any two terminal device which cannot be described by a conventional diode configuration.

P1.078 Electron temperature in isolated quantum dot structures

P Chapman, A Rossi and D Williams

Hitachi Cambridge Laboratory, UK

Electron confinement in silicon double quantum dots (DQD) [1] has attracted wide interest, as it can be exploited to implement solid-state quantum computation. One key requirement to perform quantum logic operations is a long-coherence time for the qubit-embodying state. In order to suppress efficiently the decoherence introduced by the interaction with the environment, exchange processes between the connected electrons and the reservoirs have to be significantly inhibited [2]. To this end, we fabricated and investigated fully trench-isolated DQDs realised in phosphorus-doped silicon on insulator in close proximity of a single electron tunnelling device (SET) that we use to detect charge transitions in our system. Since the DQD structure is completely disconnected from the room temperature electronics, a quantitative estimate of the advantage of this design choice is needed. By means of time-resolved detection measurements, we probe the crossover from localised to delocalised charge states as the control gate is swept across a degeneracy point for different cryostat base temperatures. This allows us to indirectly estimate the electron temperature in the DQD as well as its lever arm [3]. This latter is a crucial parameter to determine the energy scale but its determination is not straightforward as direct transport measurements are not possible with such an arrangement. As for the temperature, we observe that the electrons in the lead-less DQD are significantly colder than those in the SET reservoirs, as expected from design considerations. This highlights the benefit of using isolated architectures and sets promises to make these systems a suitable platform for long-coherence quantum computation.

[1] J. Gorman et al., Phys. Rev. Lett. 95, 090502 (2005).
[2] I. V. Yurkevich et al., Phys Rev. B 81, 121305 (2010).
[3] A. Rossi et al., Appl. Phys. Lett. 100, 13, 133503 (2012).

P1.079 Microwave manipulation of electrons in silicon quantum dots

P Chapman[1], A Rossi[1], T Kodera[2], T Kambara[2], W Lin[2], S Oda[2] and D Williams[1]

[1]Hitachi Cambridge Laboratory, UK, [2]Tokyo Institute of Technology, Japan

In quantum computation, either electro-magnetic pulses or photons are used to control the qubits [1, 2, 3]. However, for Kane-related proposals, electrical pulses are generally privileged. By the use of isolated double quantum dot structures (IDQD), the number of connected leads can be minimized, the noise reduced and scalability increased. In this system, two possible charge qubits states could be implemented: a molecular state where electrons of each dot are coupled and formed a bonding/anti bonding state or localized states where an excess of charge in one of the dot determines the state of the qubit. In both cases the energy necessary to do a swap operation is of the order of few meV so that, only THz photons are expected to be able to operate the qubit. To this end, most previous investigations have been carried out using electrical pulses on the gates [4]. However, recent results have indicated the possibility of inducing spatial Rabi oscillation with microwave photons [5]. Here we present the results of an investigation on microwave-induced effects that we have observed in silicon devices, including phosphorous-doped and Metal-Oxide-Semiconductor Single Electron Transistors (SET)[6]. Continuous pulsed microwave and single shot measurements are used to demonstrate that GHz photons can control electron tunnelling in doped SETs, despite the high value for the charging energy and in a regime where photon assisted tunnelling is not observable. The method is applied to a device made of a SET with a capacitively coupled IDQD. Partial control of the qubit is obtained and results in the possibility of manipulating charge states in an isolated structure with GHz photons.

[1] S. Furuta et al, Phys. Rev. B 70, 205320 (2004).
[2] C. H. W. Barnes et al, Phys. Rev. B 62, 8410 (2000).
[3] P. T. Greenland et al, Nature 465, 1057 (2010).
[4] J. Gorman et al, Phys. Rev. Lett. 95, 090502 (2005).
[5] A. Rossi et al, J. Appl. Phys. 108, 034509 (2010).
[6] T. Ferrus et al, New J. Phys. 13, 103012 (2011).

P1.080 Structure and evolution of a gold nanowires at the room temperature: a kinetic monte carlo investigation

K Andrey, S Kolesnikov and A Saletsky

Lomonosov Moscow State University, Russia

Gold nanowires have been the object of intense theoretical and experimental investigations in the last years [1-3]. One of the mostly used ways to prepare stable nanowares is electron-beam irradiation on a gold thin film in an ultrahigh vacuum transmission electron microscope [2]. In this methodology, the microscope electron beam is focused to generate holes in a self-supported thin metal film until neck is formed between them. The nanocontacts spontaneously become thinner due to displacements of the apexes, reach the size of a few atoms and finally break. This process usually took 5-30 min at the room temperature.

We present the detailed theoretical investigation of the gold nanocontacts formation in gold thin film between two holes at the room temperature. For simulation of long-time evolution we used the following MD-kMC scheme. All relevant atomic events were calculated by means of the molecular dynamics (MD) method with ab initio based interatomic potentials. The evolution of the gold atoms system was simulated using the kinetic Monte Carlo (kMC) method. We explained why wires along the [110] direction show a rod-like morphology while [100] and [111] nanowires show a bi-pyramidal shape [3].

[1] N. Agraït, A.L. Yeyati and J.M. van Ruitenbeek, Physics Reports, 377, 81 (2003).
[2] Y. Kondo and K. Takayanagi, Phys. Rev. Lett., 79, 3455 (1997).

[3] M.J. Lagos, F. Sato, P.A.S. Autreto, D.S. Galvao, V. Rodrigues and D. Ugarte, Nanotechnology, 21, 485702, (2010).

P1.081 The study of electron scattering mechanisms in single crystal oxide nanowires

O Berengue[1], R Simon[2], E Leite[1] and A Chiquito[1]

[1]Universidade Federal de São Carlos, Brazil, [2]Universidade Federal Tecnológica do Paraná, Brazil

In this work we report on transport measurements of individual Sn doped In_2O_3 nanowires. From these measurements we pointed that spin-orbit and boundary scattering mechanisms seems to give a negligible contribution to the transport of electrons in these nanowires. In fact, these results can be extended to another oxide systems: the presence of a weak disorder arising from the random potential at the boundaries screen electrons away from the surface into the nanowire. Electrons traveling through the nanowire in inner conducting channels are not directly influenced by the surfaces and the boundary scattering is decreased. These findings were also supported by calculations of the electron distribution in the cross section of the nanowires when some disorder is accounted.

P1.082 HRTEM and XPS study of highly dispersed palladium on the surface of Pd/CeO_2 catalysts

O Stonkus, V Zaikovskii, R Gulyaev and A Boronin

Institute of Catalysis, Russia

The main objective of the presented work is a detailed investigation of the palladium interaction with the support surface and determination of its electronic and structural state in the 1%Pd/CeO_2 catalysts for low-temperature CO oxidation. In the case of large particles of CeO_2 (40-50 nm) we observe small metallic palladium particles 1-2 nm in diameter. The particles have flattened shape due to epitaxy between (111) or (100) facets of Pd and CeO_2. This result is in agree with XPS data showing the presence of doublet in Pd3d spectrum with the E_b = 336.3 eV attributed to small oxide clusters PdO_x. Pd3d spectra also contain doublet with $E_b(Pd3d_{5/2})$ = 338.0 eV, which is explained by the formation of surface interaction phase Pd_xCeO_{2-d}. According to XPS data the initial state of palladium is oxidized, and the presence of metallic clusters in HRTEM-images is accounted for the effect of electron beam which leads to partial reduction of the catalysts surface. In this work different types of structural relations between contacting facets were investigated using computer modeling of HRTEM-images.

Decreasing the size of the CeO_2 particles to 30 nm or less leads to higher palladium dispersion, thus no three-dimensional palladium particles can be found in HRTEM-images, while palladium is present in EDX-spectra of support. Using computer modeling of HRTEM-images the presence of highly-dispersed palladium clusters less than 1 nm in diameter was established by analyzing the periodic crystal lattice of the support. The XPS data is in a good agreement with HRTEM results.

P1.083 Interactions of nano and micro objects with MEMS and NEMS devices

V Afonina[1], V Koledov[1], V Kalashnikov[1], A Irzhak[2] and D Zakharov[2]

[1]Kotelnikov, Russia, [2]National University of Science and Technology (MISIS), Russia

One of the most actual problems nowadays is an investigation of interaction of nano and micro objects with NEMS and MEMS devices to obtain the breakthrough results in different fields of modern technology. Recently was proposed an original scheme of bimorph composite based on a layer of alloy possessed SME and a layer of elastic metal which provides giant reversible deformations without the training of alloy [1]. On the base of the new scheme was produced the record small nanopincer – 15 mkm long. The composite nanopincer, attached to the needle of

Omniprobe, is controlled by heating of semi-conductor laser in the vacuum chamber of Ion Scanning Microscope. It is capable to grip and carry objects with the size from 1 mkm to 10 nm such as CNT, graphene, etc. In the present work was analyzed the behavior of interaction of various objects with the microgripper. In particular, was examined electrostatical aspect of interaction of whiskers and micropincer in the vacuum chamber of FIB. Moreover, were carried out experiments on studying of particularities of biological objects gripping.

Obtained results show that on the base of new amorphous and nanocrystalline composites might be developed a new technology of usage of nano and micro objects which will ensure progress in such areas as MEMS and NEMS technologies, nanoelectronics, microbiotechnology, etc.

[1] Zakharov, D, Koledov, V Irzhak, A., Afonina, V., Shavrov, V. etc. An enhanced composite scheme of shape memory actuator for smart systems. Physics Procedia 10, pp. 58-64 (2010).

P1.084 Functional properties of NI-TI shape memory alloy processed by ECAP for medical applications

V Kalashnikov[1], V Koledov[1], R Gizatullin[2], A Petrov[3] and P Mazaev[3]

[1]Kotelnikov, Russia, [2]ISC "Nano-dent" Ltd., Russia, [3]Bauman Moscow State Technical University, Russia

Shape memory alloy (SMA) tools and implants with high mechanical and functional properties, capable of working under extreme conditions, are in high demand for the treatment of severe diseases in dental and surgical practice. One example is the small dental or surgical implant for thin and/or weak bones [1]. Nanostructured Ni-Ti alloy, processed by equal channel angular pressing (ECAP), demonstrates optimal functional properties, essential for these implants [2]. The goal of the present work was to compare the performance of Ni-Ti SMA samples processed by ECAP to those processed by quenching.

Ni49,8Ti50,2 SMA was chosen for this study. The alloys were processed by quenching (S1) and ECAP (S2) as described elsewhere [2]. The structure of the S2 revealed by TEM appears to be in the submicron scale with an average grain size 250 nm. The stress-temperature-strain dependencies were obtained by a three-point bending method.

It was demonstrated, that the martensitic phase transformation (MPT) has two stages in the both samples. The comparative study of the two processes was done based on “energy capacity” (Wmax) and “functional inflexibility” (Ef). Ef of SMA is the ability of the SMA element to overcome external stress during reverse MPT and to deform. Wmax is the measure of the maximal work produced by SMA after reverse MPT under the stress. The experiments show that Wmax and Ef for S2 are more than twice higher than for S1 in agreement with previous results [3]. The ECAP processed sample demonstrated high recoverable strain (~ 6-7 % at stresses of resistance to deformation about 1200 MPa), suitable temperatures of MPT (lower than 36.6 ℃ at stresses of up to 1500 MPa), high Ef (22 GPa) and Wmax (88 MJ/m3). In summary, the ECAP processed sample (S2) was found to be favorable for producing tools and implants in dental and surgical practice.

[1] V. Gunther, Nickelide titanium. Medical Supplies of the new generation, Moscow-MIC, Tomsk, Russia, 2006, 296
[2] Pushin V.G., et. al. Nanostructures and phase transformations in TiNi shape memory alloys subjected to severe plastic deformation . Ultrafine grained materials III TMS, Charlotte: NC, USA. 2004. p. 481-486.
[3] R.Gizatullin, et. al. Study of nanostructured NiTi shape memory alloy’s structure and functional properties. ESOMAT 2009. Program and Abstract Book. Sept. 7-11, 2009, Prague, Czech Republic, p.153.

P1.085 Atom-sized contacts of HCP metals and their conductance at room temperature

A Sakai, A Takahashi, T Horiuchi and S Kurokawa

Kyoto University, Japan

A large number theoretical and experimental studies have been made on the atom-sized contacts of archetypal FCC metals such as Au, Ag, Cu, and Al, and their electronic and mechanical properties are now well documented. On the other hand, little has been understood on the atom-sized contacts of HCP metals, in particular their conductance at room temperature (RT). In this work, we present the results of our conductance measurements made on Co, Hf, Ti, Cd, and Mg alloys at RT in ultrahigh vacuum. We employed a break-junction method (both STM-type and MCBJ) for producing atom-sized contacts and analyzed their conductance by constructing the conductance histogram. It is found that the histogram becomes featureless for Co and Hf but shows a couple of low-conductance peaks for Cd and Mg alloys. These observations suggest that atom-sized contacts are rarely formed at RT in break junctions of Co and Hf but relatively abundant for Cd and Mg alloys. Results on Ti contacts are yet inconclusive due to their possible reaction with residual hydrogen. We, however, note that junctions of Ti and Cd are frequently found to form a single-atom contact during their junction closure. The jump-into-contact thus appears more effective for producing single-atom contacts of Cd and Ti than the usual junction breakup. Molecular dynamics simulations are currently under way on the necking deformation of some HCP nanocontacts, and our experimental observations will be discussed in reference with simulated contact configurations and their theoretical conductance.

P1.086 Silver-doped CeO_2 thin film catalysts prepared by magnetron sputtering on carbon substrates

M Chundak, K Veltruská, I Matolínová, I Khalakhan, M Vorokhta, M Vaclavu and V Matolín

Charles University, Czech Republic

Hard X-ray photoelectron spectroscopy and scanning electron microscopy (SEM) have been used to study interaction of Ag doped ceria on different substrates. 20 thin films were prepared by rf-magnetron sputtering on Si(001), graphite foil, multiwall carbon nanotubes deposited on gas diffusion layer, chemical vapour deposited carbon nanotubes on gas diffusion layer (CNT(CVD)/GDL). Research showed that substrate has high influence on morphology and chemical composition of $AgCeO_x$ sputtered layers. Fuel cell measurements of sputtered $AgCeO_x$ on CNT(CVD)/GDL have been investigated for the development of proton exchange membrane fuel cells.

P1.087 Light emission from single-walled carbon nanotube on Au(111) induced by scanning tunneling microscope

S Katano and Y Uehara

Tohoku University, Japan

Optical properties of single-walled carbon nanotubes (SWCNTs) are currently the focus of intense study in relation to the nanoscale electronics, and their optical spectra have been attributed to transitions between free-particle bands. In this paper, we will present the defect creation of SWCNT using scanning tunneling microscope (STM) tip and discuss the STM tip-induced light emission spectra obtained from intact and defect sites of SWCNT.

All experiments were carried out in an ultrahigh vacuum (UHV) chamber with the base pressure of 7.0×10^{-11} Torr. The photons emitted from the STM tip-sample junction were collected by a liquid N_2-cooled charge-coupled device (CCD) camera through a grating spectrometer. STM imaging and spectroscopy were performed at 298 K using W tip.

SWCNTs were deposited on Au(111) by the dry contact method in a UHV environment, which resulted in the isolation of individual SWCNTs. We have created the defect on SWCNT by positioning the STM tip above the SWCNT followed by applying the sample bias of 3.0 V and the tunneling current of 5.0 nA. It was found that the light emitted from the SWCNT and the defect is relatively weak compared with that from Au. Moreover, the peak observed at 1.5 eV for SWCNT is shifted to higher energy (1.7 eV) when the STM tip was fixed at the defect. This would be responsible for the change in the electronic states of SWCNT induced by the STM tip.

P1.088 First principles study on the oxygen-vacancy migration in $LaGaO_3$

T Wungu[1], S Aspera[1], M Alaydrus[1], T Thuy[1], M Sakaue[1], S Kunikata[1], H Nakanishi[1], W Dino[1], H Kasai[1] and T Ishihara[2]

[1]Osaka University, Japan, [2]Kyushu University, Japan

Investigation towards alternative energy is recently conducted to solve problems being faced in replacing fossil fuels with sustainable and clean energy to meet the increasing global demand. Solid oxide fuel cells (SOFCs) are promising power storage devices for supporting future power supplies. The long lasting performance and their safety mechanism of SOFCs make them highly desirable for a number of electronic devices. To realize the performance of SOFCs at low temperature, it is important to design materials acting as fast oxygen ionic conductors. Recently, perovskite-like materials such as lanthanum gallate ($LaGaO_3$)and lanthanum germanate (La_2GeO_5)have been found to exhibit high ionic conduction, replacing yttria-stabilized zirconia (YSZ) and ceria-based ceramics. The ionic conduction in both $LaGaO_3$ and La_2GeO_5 takes place via lattice defect which is considered from oxygen vacancy migration [1]. However, atomic-scale studies on the conduction mechanism in these materials are still lacking; such mechanism is important for developing and improving the performance of SOFCs. Through first principles calculations based on the density functional theory, we report the structural and the electronic properties of orthorhombic $LaGaO_3$ as well as the oxygen-vacancy formation for understanding the mechanism of oxygen conduction in $LaGaO_3$. We confirmed the barrier energy of oxygen vacancy migration of about 0.79 eV which is similar to the experimental value [2]. The density of states analysis shows that the presence of oxygen vacancy in the $LaGaO_3$ creates a state below the Fermi level.

[1] M. Sakaue, W. T. Cahyanto, W. T. D. Kencana, S. M. Aspera, K. Miwa, H. Kishi, S. Kunikata, H. Nakanishi, W. A. Diño, H. Kasai and T. Ishihara, J. Phys.: Conf. Ser., accepted.

[2] T. Ishihara, J. A. Kilner, M. Honda, and Y. Takkita, J. Am. Chem. Soc. 1997, 119, 2747 – 2748.

P1.089 Photodesorption and thermal desorption of water from nanostructured carbon surfaces

A Clemens, L Hellberg and D Chakarov

Chalmers University of Technology, Sweden

Dynamics and kinetics of water interaction with interstellar grains are expected to be strongly dependent on their surface morphology. However, most model laboratory studies are performed without paying attention to the surface structure. Here we present a comparative study pointing out the role of carbon nanostructures on thermal desorption and photodesorption of water in comparison to the processes on flat, pristine graphite surfaces [1]. The model substrate consists of truncated cone structures of highly oriented pyrolytic graphite (HOPG), with an upper diameter of 190 nm and a height of 100 nm that cover approximately 30% of the sample surface. The structures are prepared by colloidal lithography and oxygen plasma etching. Because of an enhanced (resonant) optical absorption in nanostructured samples (described before by us in [2]), the photodesorption rate is strongly affected. Similarly, the thermal desorption spectra show additional peaks, compared to pristine HOPG surfaces. These are assigned to defect-bound water as well as water diffusion and intercalation.

[1] D. Chakarov, L. Österlund and B. Kasemo, Langmuir 11, 1201-1214 (1995).

[2] H. Fredriksson, T. Pakizeh, M. Käll, B. Kasemo and D. Chakarov, J. Opt. A 11, 114022 (2009).

P1.090 In-situ measurement of Piezo-driven nanomechanical resonators in a Scanning-Electron-Microscope

H Wang, O Chiatti, F Jon and P Warburton

London Centre for Nanotechnology, UK

Nanoscale mechanical resonators exhibit excellent sensitivity and therefore potential advantages for application as sensitive mass balances by comparison with micromachined cantilevers. The measurement of nanoscale displacements of such resonators remains a challenge, however, since an optical signal reflected from a cantilever whose dimensions are sub-wavelength is at best very weak. Here we describe an electron-microscopy technique for characterising nanomechanical resonators. The resonators are mounted on a piezo-actuator inside a field-emission scanning-electron microscope (SEM). With the piezo-actuator being driven at frequency f, the secondary electron signal is recorded as the electron beam is scanned linearly across the resonator. From this signal, the amplitude of the mechanical vibrations can be determined with a noise floor of around 5 nm (comparable to the electron beam width of 1.5 nm) by numerical deconvolution using the response measured when the piezo-actuator is stationary.

We have characterised our technique by using tungsten nanowires grown by focused ion beam (FIB)-assisted deposition. The nanowires had lengths 10-30 µm, radius 50-80 nm and resonant frequencies in the range 50-200 kHz, scaling with r/L^2, in accordance with standard cantilever theory. We also discuss the variation of amplitude along the resonator length and the influence of the scan-speed of the electron beam on these measurements.

P1.091 Fractal morphology of water on chromium oxide ultra-thin films

K Esat[1], Ö Birer[2] and O Gürlü[1]

[1]Istanbul Technical University, Turkey, [2]Koc University, Turkey

Chromium is a routinely used element in thin film studies. Strong oxidation tendency of the Cr is the reason for the adhesive behavior of this element between glass substrates and Au films. The thin-Cr film surface oxidizes immediately under ambient conditions, after preparation by thermal evaporation of Cr, on to glass substrates, in vacuum. Besides oxidization of the film, the diffusion of the Cr into the glass matrix is known. We prepared various films with different thicknesses by thermal evaporation of Cr on to glass substrates. Heat treatment of these samples altered the surface morphology entirely. Distinguishable island formations were observed on surfaces. With the help of a thickness gradient along the surface, differences in the size and the distribution of these islands could be observed. Due to the ambient humidity, water droplets on the surfaces formed. Following this observation, we contaminated pristine Chromium-Oxide ultra-thin films with water in a controlled fashion and by increasing the humidity near the sample surface, we observed fractal formations of water, such as fingering and aggregation. The effects of these chromium oxide structures on the formation of water fractals and the structure of water on these surfaces will be discussed.

P1.092 Combining selected plastic materials with diamond-like carbon coatings

C B Fischer[1], M Rohrbeck[1], S Wehner[1], M Richter[2] and D Schmeißer[2]

[1]University Koblenz-Landau, Germany, [2]Brandenburg University of Technology Cottbus, Germany

The engineering of plastic materials and their popular application is accompanied by essential requirements. Besides the basic performance such as flexibility or fracture strength, further determinants are durability or biocompatibility. Concerning materials features especially the surface is in charge of intensive interaction touching the environment. To avoid incompatibilities in surface characteristics of the optimal parent plastic these materials can be customized for their intended use by coating.

Protective coatings of selected plastic materials have been realized by a few layers of diamond-like carbon (DLC). The assembly of soft plastic material and robust carbon layers is important for the resulting material characteristics. Several ways of interaction for plasma generated DLC-coatings with basic plastic material are presented and discussed. The detailed understanding of the interphasing between these unequal materials and the connection of carbon centers in a chemically different neighborhood is the perspective of the presented work.

Depending on the content of sp^2- and sp^3-carbon centers the material exhibits different properties ranging from medium-hard to stiff. Increasing layer thickness has been examined by the use of synchrotron radiation and multiscale microscopic analysis. Results will help to provide an enhanced understanding of layer formation at the interface of the coating and will help to optimize parameters for the surface coating to achieve improved product characteristics. Collected information will be transferable to other plastic materials with diverse needs, e.g. energy storage devices, water treatments and coatings for everyday commodities or industrial parts.

P1.093 Fabrication and characterization of CdTe nanocrystals thin films embedded in a polystyrene matrix

B Fahima, N Fatima, B Asma, B Boubaker, H Ouahiba and S Miloud

University Mentouri, Algeria

Recently, nanocrystalline large band gap semiconductors, embedded in various materials, arise a special interest. This research effort is stimulated by the interesting properties that appear as size decreases. Indeed, confinement of excitations to a narrow space is then observed [1, 2]. Intensive research is conducted in order to fabricate nanocrystals having a desired size and shape [3], and to understand the influence of the fabrication conditions [4] and the host matrix on the properties of the nanocrystals.

The present work consists on the fabrication and the characterization of PS/CdTe composite thin filmsin order to improve structural and optical properties .The Fabrication of the samples was carried out with soft chemistry. The spin coating methods was used for deposing the thin films of PS/CdTe composite on the glass substrate. The incorporation of the nanocrystals of the semiconductor CdTe was affected at liquid state. X-rays diffraction characterization and micro-Raman spectrometry of PS/CdTe composite revealed the inclusion of CdTe hexagonal structure inpolystyrene with nanocrystalline size. The characterizationby optical density measurements in the UV-Visible range of the CdTe nanocrystals embedded in the polystyrene show a presence of excitonic peaks and a shift of the absorption threshold to the low waves lengths (a shift of the gap to the height energy).This shift is due to theconfinement caused by the nanometric size of CdTe semiconductor. The Photoluminescence spectrum has showedthat the fabricated samples have luminescence bands in the visible range. This result finding should lead to potential application in optoelectronics.

[1] A. Ekimov Journal of Luminescence 70, I (1996).
[2] B. Pejova, I.Grozdanov Materials Chemistry and Physics 90, 35 (2005).
[3] J.Mazher, S.Badwe, R.Sengar, D.Grupta, R.K.Pandey Physica E 16, 209 (2003).
[4] N.Murase, M.Gao Materials Letters 58, 3898 (2004).

P1.094 Synthesis and characterisation of PbS nanoparticle thin films for use in solar photovoltaics

D Cant, K Syres, J Thomas and W Flavell

University of Manchester, UK

Due to their unique properties, nanoparticles have been a focus of significant research interest for use in various opto-electronic applications, particularly in the field of solar energy generation. In order to realize a nanoparticle based solar cell, it is important to be able to create thin films of organised nanoparticles and to be able to control their surface properties. Colloidal synthetic methods often result in nanoparticles which are prone to surface oxidation, which can affect their electronic properties.[1]

Here we explore a novel method for the direct chemical synthesis of nanoparticle thin films at the interface between two immiscible liquids without the use of stabilising ligands.[2] X-ray diffraction of lead sulfide films produced by this method have shown the presence of crystallites with a range of sizes and morphologies. In particular, Scherrer-formula calculations have estimated crystallites sizes of <10 nm diameter for crystallites with strong (220) and (311) reflections, as well as larger crystallites with strong (200) and (111) reflections. X-ray diffraction has also shown a strong dependance of morphology on the volume of solvent used in synthesis. Scanning electron microscopy and transmission electron microscopy of these films have shown agglomerates of particles of ~10 nm diameter. X-ray photoelectron spectroscopy performed at beamline I311, MAX-lab synchrotron, Sweden and beamline BACH, ELETTRA synchrotron, Italy has shown a variation in film stoichiometry dependant on the precursors used. The level of oxidation present in films produced by this method has been studied, and appears lower than has been observed in colloidally produced nanoparticles[3].

[1] J. Akhtar, M. Azad Malik, P. O ′Brien, K. G. U. Wijayantha, R. Dharmadasa, S. J. O. Hardman, D. M. Graham, B. F. Spencer, S. K. Stubbs, W. R. Flavell, D. J. Binks, F. Sirotti, M. El Kazzi, and M. Silly, Journal of Materials Chemistry, 2010, 20, 2336.

[2] D. Fan, P. J. Thomas, and P. O ′Brien, Journal of the American Chemical Society, 2008, 130, 10892-4.

[3] Hardman, S. J. O., Graham, D. M., Stubbs, S. K., Spencer, B. F., Seddon, E. A., Fung, H.-T., Gardonio, S., et al. Physical Chemistry Chemical Physics, 2011,13(45), 20275-83.

P1.095 Towards the transparent and flexible field emission displays using ion-induced conical nanocarbon structures

M Tanemura, P Ghosh, T Noda, M Zamri Yusop, S Sato, T Tsuchiya, G Kalita and Y Hayashi

Nagoya Institute of Technology, Japan

Transparency and flexibility are key words required for the devices of next generation. Nanocarbon, such as carbon nanotubes (CNTs) and graphene, based transparent and flexible devices have been demonstrated in various fields such as electrode, organic light-emitting diodes and thin film transistors. In this talk, a new approach to the transparent and flexible field electron emission displays (FEDs) based on ion-induced nanostructures will be dealt with.

FEDs offer promising advantages such as high brightness, low power consumption, wider viewing angle, etc. Recently some groups have demonstrated the fabrication of nanocarbon based flexible (opaque) FEDs [1, 2]. The next step is the realization of transparency [3-5]. To achieve this, direct fabrication of fully transparent conical nanocarbon structures (CNCSs) on a controlled nanoscopic dimension on flexible nafion substrates were employed for a field electron source by a simple room temperature ion irradiation technique [6]. By optimizing the sizes of CNCSs in the range smaller than the wavelength of the visible light, the transparency of the substrate can be tailored satisfactorily. The transparency of the CNCSs was observed to be around 90% in the visible regime depend on the ion irradiation parameters. This result suggest that direct fabrication of well controlled fully transparent CNCSs on any transparent and flexible substrates at room temperature could open a novel route for potential application in future highly transparent, flexible (bendable), low weight and portable FEDs. In this talk, in addition, in situ transmission electron microscope (TEM) observation of structural change of nanocarbon induced by electron current flow (control in crystalline structure of nanocarbon) will be also demonstrated [7].

[1] H. S. Sim, et al., Appl. Phys. Lett., 90 (2007) 143103-143105.

[2] B-J. Yoon, et al., J. Am. Chem. Soc., 127 (2005) 8234-8235.

[3] P. Ghosh, et al., J. Am. Chem. Soc., 132 (2010) 4034-4035.

[4] D. Ghosh, et al., Chem. Commun., 47 (2011) 4980-4982.
[5] M. Tanemura and S. P. Lau: "Flexible Field Emitters: Carbon Nanofibers" in "Carbon Nanotube and Related Field Emitters: Fundamentals and Applications" Edited by Y. Saitoh, Wiley-VCH (Weinheim) (2010), Ch. 15.
[6] P. Ghosh, et al., Phys. Status Solidi RRL, 6(2012) 184.
[7] M. Tanemura and M. Kitazawa: "Fabrication of Ion-Induced Carbon Nanocomposite Fibres and their Application to Magnetic Force Microscope Probes" in "Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications" Edited by Boreddy Reddy (InTech Publisher) (2011), Ch. 35.

P1.096 Thermocouple of a single metal

S Xu, H Liu and W Sun

Peking University, China

A conventional thermocouple is made of two arms of different conductors (metal, alloy or semiconductor) that have remarkable difference in their Seebeck coefficients. A thermocouple has its merits of passive function, high sensitivity, high reliability and excellent versatility, therefore has been extensively applied. We have developed a novel type of thermocouple made of only one metallic thin film, and demonstrated that this kind of single-metal thermocouple can be embedded in a device as build-in arrays for precise mapping of local temperatures. Having extremely simple configuration, free of interface, and a variety of choices for the potential building materials, these sensors may be further developed into a family of long-lifetime, versatile thermometry device that finds its unique role in both science research and industry applications. Therefore, we believe this work will attract extensive attention.

P1.097 Synthesis and properties of antihistamine-layered double hydroxide nanocomposites based on cetirizine

M Z Hussein, S Hasan H A Ali and Z Zainal

Universiti Putra Malaysia, Malaysia

The intercalation of cetirizine into two types of layered double hydroxides, Zn/Al and Mg/Al has been investigated by the ion exchange method to form CTZAN and CTMAN nanocomposites, respectively. The basal spacing of the nanocomposites were expanded to 31.9 Å for CTZAN and 31.2 Å for CTMAN, suggesting that cetirizine anion was intercalated into LDHs and arranged in tilted bilayer fashion. FTIR study supported the formation of both nanocomposites and the intercalated cetirizine is thermally more stable than its counterpart. The loading of cetirizine in the nanocomposite was estimated to be about 57.2 % for CTZAN and 60.7 % CTMAN. The release of cetirizine from their respective nanocomposites show controlled release manner with the release rate of cetirizine from CTZAN and CTMAN nanocomposites at pH 7.4 is remarkably lower than that at pH 4.8. This presumably due to different release mechanism. The inhibition of histamine release from RBL2H3 cells by the free cetirizine is higher than the intercalated cetirizine both in CTZAN and CTMAN nanocomposites.

P1.098 Hole transport properties in modulation doped germanium heterostructure

A Hassan and A Dobbie

University of Warwick, UK

Germanium channel devices are a promising alternative to Si MOS devices owing to their higher hole mobility. Introducing strain leads to a reduction to the hole effective mass and results in mobility enhancement. However, high hole mobility devices require good hole confinement in the Ge layer. Ideally the Ge layer should be grown directly on Si, but would then only be thermally stable below a thickness of 1nm which is not suitable for device application. Instead, introducing a SiGe virtual substrate layer (VS) on Si provides a platform of adjustable lattice constant allowing the thickness of the strained Ge layer to be increased and improve the hole confinement.

This work aims to study the hole transport properties in modulation doped germanium on a SiGe virtual substrate grown by reduced pressure chemical vapour deposition (RP-CVD). Resistivity and hall mobility has been performed for structures with differing channel thickness and doping either above or under the channel. An extremely high mobility has been observed at low temperature for samples with doping above the channel (normal structure). For the inverted structure, the behaviour of the mobility with different channel thickness is found to be higher than previous reports in the literature.

P1.099 Structure transition of annealing Zn nanoparticles

J-H Lin and Y-R Ma

National Dong Hwa University, Taiwan

In this article, the critical temperature of phase transformation of Zn to Zn oxide in high vacuum was found. According to previous studies, all of the Zn nanoparticles are stable. When increasing the temperature of chamber, the Zn nanoparticles will inflate as a balloon and explode finally. X-Ray diffractometry (XRD) studies revealed the crystalline of Zn nanoparticles and shows that the Zn nanoparticles will transform to Zn oxides above 300˚C. The high magnification image and select area electron diffraction (SAED) pattern of tunneling electron microscope (TEM) technique mutually proof the results of XRD. Finally, photoluminescence (PL) spectra show visible–near infrared broadband emission for polycrystalline Zn and Zn oxides prepared at various annealing temperature. This result indicates that polycrystalline Zn and Zn oxides can be a promising candidate for broadband optical device.

P1.100 Effect of annealing on the structural, optical and electrical properties of sol-gel derived zinc oxide thin films

V Luthra[1], A Gautam[1], Ritu Shrivastva[2], M Arora[2], M N Kamalasanan[2]

[1]Gargi College, India, [2]National Physical Laboratory, UK

The ZnO has attained much attention in recent years due to its excellent basic properties on one hand and wide range of technological applications on the other. Good quality thin and transparent films of zinc oxide have multiple applications. In the present work, thin films of ZnO have been fabricated using simple and inexpensive sol-gel route. Zinc acetate dehydrate, 2-methoxyethanol and ethanolamine (EA) were used as starting material, solvent and stabilizer respectively. Two and Six-layered coatings of these films were deposited on various substrates such as glass, indium-tin oxide coated glass and quartz.The films have been characterized using various analytical techniques such as X-Ray diffraction (XRD) , UV-Visible (UV-Vis) spectroscopy, Atomic Force Microscopy (AFM) and electrical characterization. The effect of post deposition annealing temperature (350°C- 550°C) on the structural, optical and electrical properties on ZnO thin films has been investigated. The XRD pattern of these films show characteristic hexagonal wurtzite structure with dominant c-axis orientation as the annealing temperature is increased. The band gap has been calculated by UV-Vis absorbance data which has been monitored as a function of annealing temperature. The band gap approaches the theoretical value as the annealing temperature is increased from 350º C to 550º C. The films show transmission above 85 % up to 800 nm wavelength. The AFM shows that these nanostructures gain densification as the annealing temperature is increased. The room temperature Current-Voltage (I-V) measurements have been done on ZnO thin films which show an increase in conductivity with increasing annealing temperature. The developed films could be well exploited for various optoelectronic applications.

P1.101 In situ X-ray scattering investigations of semiconductor nanowires during their growth by UHV-CVD

G Renaud[1], V Cantelli[1], T Zhou[1], O Ulrich[1], N Blanc[1] and O Geaymond[2]

[1]Combustion Engineering Association (CEA), France, [2]Centre National de la Recherche Scientifique (CNRS), France

Controlling the growth of semiconductor nanowires (NWs) is fundamental for their applications in nanoscale electronic/photonic/sensor devices. Experimental methods that follow growth dynamics and extract quantitative parameters remain a challenge. Si NWs are grown by Chemical Vapour Deposition (CVD) via the Vapour – Liquid – Solid (VLS) mechanism, in which NWs spring up from catalyst-substrate eutectic droplets (AuSi) under a flux of silicon fuelled by the decomposition of precursor gases.

X-ray scattering is a unique tool that can probe, qualitatively and quantitatively, the structural properties during the growth of NWs and their evolution non-destructively, independent of the gas-pressure or the sample temperature. These motivated the development of a reactor adding the possibility of CVD growth to the already unique characteristics (MBE, RHEED, Residual gas analyser) of the In Situ growth of Nanostructures on Surfaces (INS) set-up of the IF-BM32 beamline at the ESRF. This CVD/MBE reactor allows to investigate in situ the role of different growth parameters on the Si and Ge NW morphology and crystallographic structure by use of GIXD and GISAXS.

We report on the first grazing incidence x-ray scattering study of Si nanowires (NWs) during their growth, performed in situ by UHV-CVD. In situ grazing Incidence X-ray scattering observation at wide angle (GIXD) during growth reveals perfect accordance of lattice parameters between the NWs and the substrate, unlike what has been previously reported, and shows well-dewetted sawtooth faceting, while in situ Grazing Incidence Small Angle X-Ray Scattering (GISAXS) observationd grants us insight to some mysterious change of faceting behaviour in the very first phase (0s - 300s) of growth, the origin of which is yet to be fully understood. We confirm that NWs grown under UHV condition behave differently from those grown in conventional atmospheric environment. Our results fit well with other in-situ UHV-TEM experiments while providing more generalized results as the X-ray averages over the entire illuminated area.

P1.102 Two-qubit parametric amplifier and stochastic resonance in qubits: large amplification of weak signals

Z Washington[1], S Savel'ev[1], A Zagoskin[1], A Rakhmanov[2], A Omelyanchouk[3] and F Nori[4]

[1]Loughborough University, UK, [2]Russian Academy of Sciences, Russia, [3]Academy of Sciences of Ukraine, Ukraine, [4]Advanced Science Institute, Japan

Using numerical simulations, we show [1] that two coupled qubits can amplify a weak signal about a hundredfold. This can be achieved if the two qubits are biased simultaneously by this weak signal and a strong pump signal, both having frequencies close to the interlevel transitions in the system. The weak signal strongly affects the spectrum generated by the strong pumping drive by producing and controlling mixed harmonics with amplitudes of the order of the main harmonic of the strong drive. We show that the amplification is robust with respect to noise, with an intensity of the order of the weak signal. When deviating from the optimal regime (corresponding to strong qubit coupling and a weak signal frequency equal to the interlevel transition frequency), the proposed amplifier becomes less efficient, but it can still considerably enhance a weak signal (by several tens). We therefore propose to use coupled qubits as a combined parametric amplifier and frequency shifter. We also predict theoretically the enhancement [2] of quantum coherence in a superconducting flux qubit by a classical external noise. The coherence-enhancing effects of the classical noise can be considered as a manifestation of quantum stochastic resonance and are relevant to experimental techniques, such as Rabi spectroscopy.

[1] S. Savel'ev, A. M. Zagoskin, A. L. Rakhmanov, A. N. Omelyanchouk, Z. Washington, and F. Nori, Phys. Rev. A 85, 013811 (2012).

[2] A. N. Omelyanchouk, S. Savel'ev, A. M. Zagoskin, E. Il'ichev, and F. Nori, Phys. Rev. B 80, 212503 (2009); S. Savel'ev, A. M. Zagoskin, A. N. Omelyanchouk, and F. Nori, Chem. Phys. 375, 180 (2010).

Non-covalent interactions

P1.103 Benzene strongly adsorbed on metal surfaces: chemisorption, physisorption, or both?

W Liu[1], J Carrasco[2], B Santra[1], A Michaelides[2], M Scheffler[1] and A Tkatchenko[1]

[1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, [2]University College London, UK

The adsorption of aromatic molecules on metal surfaces is of key importance in the fields of biochemicals, petrol industry, molecular electronics, and gas sensors. Depending on the interaction strength between the adsorbed molecule and the surface, the adsorption process is typically categorized into physisorption or chemisorption. Van der Waals (vdW) energy contributes significantly to the molecule-surface interaction in the physisorption case, but the role of vdW energy remains unclear for strongly adsorbed systems. We find that vdW interactions are larger in a typical strongly adsorbed system benzene@Pt(111) than in a typical physisorbed system benzene@Au(111). This finding arises from the fact that benzene adsorbs closer to Pt than to the Au surface, leading to a much stronger vdW energy contribution than expected in the case of strong adsorption. This behavior is observed consistently from two different dispersion-inclusive density functional methods [1-2]. The calculated adsorption distances and binding energies are in excellent agreement with the experiments [3-5], confirming the validity of our findings. The observed trend of larger vdW energies in strongly bound systems is generalized to a wide variety of adsorption systems (examples include benzene, naphthalene, and anthracene on Pd, Pt, Rh, and Ir surfaces), blurring boundaries between our notion of physisorption and chemisorpiton.

[1] V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, Phys. Rev. Lett. (2012).
[2] J. Klimeš, D. R. Bowler, and A. Michaelides, J. Phys. Condens. Matter 22, 022201 (2010).
[3] A. Wander, G. Held, R. Hwang, G. Blackman, M. Xu, P. de Andres, M. Van Hove, and G. Somorjai, Surf. Sci. 249, 21 (1991).
[4] H. Ihm, H. Ajo, J. Gottfried, P. Bera, and C. Campbell, J. Phys. Chem. B 108, 14627 (2004).
[5] D. Syomin, J. Kim, B. E. Koel, and G. B. Ellison, J. Phys. Chem. B 105, 8387 (2001).

Polymer surfaces and interfaces

P1.104 Dielectric and electro-optic behavior of Liquid Crystal dispersions exhibiting planar or homeotropic anchoring at the Liquid Crystal/polymer interface

M Boussoualem, F Roussel, M Ismaili and J-M Buisine

University of Science and Technology Lille (USTL), France

The dielectric and electro-optic properties of liquid crystal (LC) dispersions are investigated. In particular, the role of surface anchoring conditions at the polymer/LC interface are studied by changing the side chains of the polymeric matrix. The ability to impose a given surface anchoring (planar or homeotropic) to LC molecules leads to either bipolar or radial LC droplets. For both systems, the dielectric spectrum exhibits in the low frequency region a broad absorption domain which is strength and frequency dependent on the geometry of the confined LC phase. This absorption domain has been assigned to a depolarization field effect also known as the Maxwell-Wagner-Sillars (MWS) mechanism. It is also shown that the MWS effect associated with the anchoring conditions strongly influence the electro-optic response of the as-prepared LC dispersions-based displays. The best electro-optical performances were obtained for polymer/LC interfaces leading to a planar anchoring, i.e. bipolar droplets, which exhibit faster reorientation dynamics.

P1.105 Nanocomposites based on porous silicon for ammonia gas sensing

N Chiboub[1], M Ayat[1], A Cultrera[2], N Gabouze[1], L Boarino[2] and S Sam[3]

[1]University of Science and Technology Lille (USTL), France, [2]L'Istituto Nazionale di Ricerca Metrologica (INRIM), Italy, [3] Unité de Développement de la Technologie du silicium (UDTS), Algeria

The very large specific area of porous silicon (PSi) have motivated the scientists to introduce different material into the pores forming composite structures devoted to different applications such as (bio)sensors. On the other hand, the polyaniline (PANi) is an intrinsically conducting ammonia vapor sensitive polymer. The responsive nature of PANi is highly dependent on the processing techniques employed. We report herein on the preparation of thin film of conducting polyaniline via electrochemical methods on porous silicon substrate. The composite structures have been characterized by Scanning Electron Microscopy (SEM), and Fourier transformed infrared spectroscopy (FTIR). The conductivity measurements were also performed. Different dopants are used. The SEM analysis showed that the morphology of PANi nanostructures changed with dopant used. The current-voltage curves were measured for ammonia gases and showed rectifying behavior due to a diode structure between the PSi substrate and the polymer. The sensors have a high sensitivity for ammonia gas and a good response and recovery time. in addition, it can operate at low voltages. .

P1.106 The molecular order in P(NDI2OD-T2) and PBTTT thin films

L Thomsen[1], C McNeill[2] and T Schuettfort[3]

[1]The Australian Synchrotron, Australia, [2]Monash University, Australia, [3]University of Cambridge, UK

The Soft X-Ray beamline at the Australian Synchrotron currently allow for measuring techniques such as X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. The latter technique is a very powerful tool for probing the degree of order and measuring the orientation of molecular films in organic electronic samples. In this presentation we use zone-casting as well as spin coating techniques to produce highly aligned poly(N,N-bis 2-octyldodecyl-naphthalene-1,4,5,8-bis dicarboximide-2,6-diylalt-5,5-2,2-bithiophene) (P(NDI2OD-T2)) and poly(2,5-bis(3-tetradecylthio- phen-2-yl)thieno[3,2]thiophene) (PBTTT) thin films. Both molecules produce films that exhibit strong optical and NEXAFS dichroism. This large degree of dichroism does allow us to determine the molecular tilt angle of the back bone by changing the x-ray angle of incidence with respect to the surface. Furthermore Grazing Incidence X-ray Diffraction (GIXD) data collected on the above mentioned samples at the SAXS/WAXS beamline at the Australian Synchrotron and device performance data will also be presented for these systems.

Polymers/biology

P1.107 Modelling the cell cytoskeleton and understanding how eukaryotic cells move

E Tjhung, D Marenduzzo and M Cates

The University of Edinburgh, UK

The cell cytoskeleton comprising protein filaments (actin) cross-linked by motor proteins (myosin) forms the bulk of eukaryotic cells and plays an important role in cell motility. In particular, cell extracts (mostly made up of actins and myosins) have been observed to be able to crawl on a 2D substrate. Such ability to move is due to two mechanisms known to exist in the cytoskeleton: i) Polymerization of the actin filaments at the leading edge and ii) Actin-myosin contraction at the rear. Actin polymerization at the leading edge, helped by friction against a 2D substrate, pushes the membrane forwards. Consequently, the cell/cell extracts will move in the direction of actin polymerization. Towards the centre of the cell, actin-myosin pair can also generate contractile stress due to the activity of the motor protein pulling the actins. However, the role of actomyosin contraction on cell motility is much less clear. Only recently, experiments on cell migration in 3D environments show that actin polymerization plays little or no role in 3D motility. This suggests that cell motility in 3D is dominated by actomyosin contraction alone. Using a simple hydrodynamic model to approximate the cell cytoskeleton, we show that actomyosin contraction alone (without the presence of polymerization) can indeed give rise to a unidirectional motion in both 2D and 3D environments. We also report that such motions occur spontaneously at large enough motors' activity through the breakdown of a discrete global symmetry. This is analogous to second order phase transition in equilibrium thermodynamics.

P1.108 Solution-phase visible laser processing of Pi-conjugated polymers: optical detection of transition between different molecular states

A Tomioka, K Takada and Y Kondo

Osaka Electro-Communication University, Japan

Starting from the liquid phase laser processing (LLP), where a solid target immersed in water to avoid material deterioration is irradiated by UV pulse laser, we step further utilizing a molecularly dispersed solution (SLP), free from molecular binding energy, as a laser irradiated target, so as to attain a phase transition of the polymer electronic state: microdroplets of MEHPPV solution suspended in insoluble water were photoexcited resonantly by visible pulse laser, leading to the polymer vibrational motion due to an electron-phonon coupling of the π-conjugated system.

MEHPPV solution in chloroform and its spin-coat film had a similar type A photoluminescence (PL), whereas the SLP processed precipitates showed blue-shifted type B PL consistently. The difference of PL indicates that the type A and type B reflect different electronic states of MEHPPV π electrons. Activation potential between the type A and type B ground states should be higher than $kT = 50$ meV, judging from the annealing experiments. Only with the laser processing, type A state is converted to type B, and not vice versa, which suggests that type B ground state has lower energy than type A.

To be noted is that dichloromethane solution and its spin-coat film showed type B PL and annealing did not alter the PL: this solvent dependence indicates that the lower energy type B state is attainable by the dichloromethane solvation. This is not a solvatochromism because the PL remained in type B even after the solvent removal by thermal annealing. Also the electron-phonon coupling is similar between the spin-coat film and SLP processed particles made from the same solvent solution, but dissimilar among different solvents. These two observations imply a "memory effect" of the MEHPPV induced by the solvation: the "memory" may be recorded as the MEHPPV polymer conformation.

P1.109 Identification of mitochondrial proteins of malaria parasite using Chou's pseudo amino acid composition

C Yi[1] and Q Li[2]

Inner Mongolia University, China

The rate of human death and morbidity due to malaria is increasing in many parts of the developing countries. Thus, there is a great need to understand the critical pathways in malaria parasite in order to develop effective drugs and vaccines. In this work, based on the measure of diversity definition, we introduce the increment of diversity fusion (IDF), an improved hybrid method to predict mitochondrial proteins of malaria parasite. We conduct our experiment on an expanded protein dataset where we require the pairwise identity between two proteins is less than 25%. In this study, using the n-peptide composition of reduced amino acid alphabet obtained from structural alphabet named Protein Blocks as feature parameter. By choosing amino acids composition as the only input vector, we are able to achieve 65.4% accuracy with 0.32 Mathew's correlation coefficient (MCC)for the jackknife test. Further, incorporting the compositions of the N-terminal and C-terminal regions into the input vector,we show that the prediction results are improved to 82.0% accuracy with 0.64 MCC in the jackknife test. In addition, by combining with the Chou's pseudo amino acid composition and the hydropathy distribution along protein sequence, we achieve maximum 83.4% accuracy with 0.67 MCC in the jackknife test. The results indicate that the IDF is a simple and efficient prediction method for mitochondrial proteins of malaria parasite.

P1.110 The thermomechanical properties and morphological characteristics of agar gel

S Kouider Akil[1] and M Lounis[2]

[1]Centre Universitaire de Khemis Miliana, Algeria, [2]LAAR Laboratory, Algeria

Agar gels have the interest of both isotropic scattering homogeneous and linear in first approximation. this type of gel properties close to that of biological tissues. The aim of this study is to highlight the links between the conditions of formation, structure and physicochemical properties, more particularly their properties by thermal techniques (DSC, TGA) and mechanical.

Semiconductors

P1.111 Thermoelectric properties of uniaxial strained Bi wires

E Condrea[1], A Gilewski[2] and A Nicorici[1]

[1]Academy of Science of Moldova, Romania [2]International Laboratory of High Magnetic Fields and Low Temperatures, Poland

We report the results of the effect of uniaxial strain on the thermopower and electric resistance of glass-coated individual Bi wires with diameters of 0.1 – 2.0 μm. By combining thermal annealing, uniaxial deformation, and magnetic field, we have succeeded in conducting with thermoelectric parameters. A fairly high value of thermoelectric power factor was found in a temperature range of 77 – 150 K at a strain value of 2.5 %.

At low temperatures, the thermopower dependences on strain S(ε) exhibit a non-monotonous behavior inherent in thinner wires, where S is dominated by diffusion transport mechanism of holes. Hole-dominated transport can be transformed into electron-dominated transport through a smooth manipulation with the phonon spectrum and Fermi surface by applying a uniaxial strain. The transport properties of Bi wires are examined in the light of a strain-induced Electronic Topological Transition.

P1.112 Anisotopic magnetoresistance and magnetometry studies of GaSb based dilute magnetic semiconductors

B Howells, K Edmonds, B Gallagher, M Wang, R Campion and A Rushforth

Nottingham University, UK

Mn-doped III-V semiconductors are model systems for understanding the fundamental physics of carrier-mediated ferromagnetism, with potential applications in spintronics. Here we report on two different Sb-based dilute magnetic semiconductors (DMS), which we anticipate to have a shallower acceptor level, higher mobility, and larger valence band spin-orbit splitting compared to (Ga,Mn)As. We present the magnetotransport and magnetic properties of the DMS (Ga$_{0.94}$,Mn$_{0.06}$)As$_{0.9}$Sb$_{0.1}$ with an emphasis on its anisotropic magentoresistance (AMR), as well as the magnetic properties of the DMS (Ga$_{0.94}$,Mn$_{0.06}$)Sb for both as-grown and annealed samples for both DMS.

It was observed that incorporating 10% Sb into the (Ga,Mn)As host lattice resulted in a DMS with a reduced Curie temperature (55K), reduced moment per Mn atom, higher resistivity, and increased strain in comparison to similar (Ga,Mn)As samples.

In-depth investigation of the AMR in the annealed (Ga$_{0.94}$,Mn$_{0.06}$)As$_{0.9}$Sb$_{0.1}$ sample revealed a huge difference in both the magnitude and shape of the AMR for current flowing along the [110] direction compared with the [1-10], [100], and [010] directions. The differences in the AMRs are explained by consideration of the relative sizes and interplay of non-crystalline and crystalline AMR contributions.

Magnetometry measurements of the (Ga$_{0.94}$,Mn$_{0.06}$)Sb sample reveal a Curie temperature of 34K, and that the sample is strongly uni-axial with its easy axis lying along the [1-10] plane which contrasts with other (Ga,Mn)Sb samples previously investigated whose easy axes lie along the [001] plane. Interestingly the sample's magnetization does not increase upon annealing, unlike the (Ga$_{0.94}$,Mn0.06)As$_{0.9}$Sb$_{0.1}$ sample and (Ga,Mn)As in general.

P1.113 Electrical and structural properties of thermally grown GeO$_2$ on epitaxial Ge on Si(001) substrate

C Antunes Casteleiro, M Myronov, J Halpin, V Ajit Shah and D Leadley

University of Warwick, UK

The Ge-channel MOSFET has recently been identified as a promising candidate for future device structures beyond the scaling limit of Si CMOS technology. However, the realization of a superior metal-insulator-semiconductor (MIS) interface remains one of the most critical issues for establishing Ge MOS technology. Low interface state density, which is a key parameter responsible for degradation of carrier mobility in the Ge channel and the gate leakage current, has recently been reported for the GeO$_2$ /Ge interface. Although, all previous results were demonstrated for GeO$_2$ grown on Ge substrates, for the technology to be introduced into mainstream production, the GeO$_2$ has to be on Ge that is epitaxially grown on a Si(001) substrate.

For the first time, we demonstrate electrical and structural properties of GeO$_2$ thermally grown on relaxed Ge epilayers on a Si(001) substrate in an industrial type Reduced Pressure CVD (RP-CVD) reactor. Both p- and n- type doped Ge epilayers were produced and used for GeO$_2$ growth and subsequent characterization. High quality GeO$_2$/Ge interfaces were obtained for GeO$_2$ growth at temperatures below 550°C.

P1.114 Electronic properties of site-controlled (111)-oriented zinc-blende quantum dots

E O'Reilly, S Schulz and O Marquardt

Tyndall National Institute, Ireland

We present and evaluate a (111)-rotated eight-band k ・ p Hamiltonian for the zincblende crystal lattice to investigate the electronic properties of site-controlled InGaAs/GaAs quantum dots grown along the [111]-direction. We derive the rotated Hamiltonian including strain and piezoelectric potentials. In combination with our previously formulated (111)-oriented continuum elasticity model, we employ this approach to investigate the electronic properties of a realistic site-controlled (111)-grown InGaAs quantum dot. We combine these studies with an evaluation of single-band effective mass and six-band k・p models, to investigate the capabilities of all these models to describe the electronic properties of (111)-grown zinc-blende quantum dots. Moreover, the influence of second-order piezoelectric contributions on the polarization potential in such systems is studied. We show that typical dots have highly asymmetric electronic properties, with few confined electron and many closely spaced confined hole states. The description of the electronic structure of these systems can now be achieved with significantly reduced computational costs in comparison to calculations performed using the conventional (001)-oriented models.

P1.115 Theory of the electronic structure of dilute bismide and bismide-nitride alloys of GaAs

E O'Reilly, M Usman and C Broderick

Tyndall National Institute, Ireland

The highly mismatched semiconductor alloy GaBiAs, comprised of dilute concentrations of bismuth (Bi) incorporated in GaAs, is an attractive candidate for the design of highly efficient mid- and far-infrared optical and spintronic devices. It has been shown both experimentally and theoretically that isovalent substitution of a small fraction of Bi atoms in GaAs drastically reduces the band gap (E_g) by ~90 meV/% Bi replacing As. A giant bowing of the spin-orbit-splitting energy (E_SO) has also been observed in GaBiAs, leading to the onset of an E_g < E_SO regime. This characteristic is of technological importance as it opens up the possibility to suppress the dominant CHSH Auger recombination losses suffered by conventional III-V optical devices operating at high temperatures. We have developed a nearest neighbor tight binding (TB) Hamiltonian to investigate the electronic structure of dilute bismide alloys of InAs and GaAs. By applying our model to large supercells, we demonstrate that isovalent Bi substitution introduces Bi-related defect states which interact with the host Ga(In)As matrix valence band edge via a Bi composition dependent band anti-crossing (BAC) interaction. Our calculations show that the observed strong variations in E_g and E_SO can be well explained in terms of a BAC model, with the change in E_g also having a significant contribution from a conventional alloy reduction in the conduction band edge energy. Our calculated E_g and E_SO are in good agreement with experimental measurements throughout the investigated composition range (x ≤ 13%), in particular reproducing the E_g < E_SO crossover at x~10.5% in free-standing GaBiAs. We further extend our TB model to the dilute bismide-nitride alloy (GaBiNAs)and derive k.p Hamiltonians both for GaBiAsand GaBiNAs. We demonstrate that the impacts of Bi and N incorporation on the GaAs electronic structure are largely independent of each other, with N-related defect states mainly perturbing the conduction band edge according to the well understood BAC model. Since N weakly perturbs the GaAs valence band structure, the bowing of E_SO in GaBiNAs is similar to that in GaBiAs. Co-alloying of Bi and N in GaAs also allows the possibility of precise strain control in GaBiNAs thereby opening up a large and flexible parameter space for band engineering. This is of significant importance for the design of highly efficient optoelectronic devices operating with reduced temperature sensitivity at telecommunication and longer wavelengths, a key requirement for future 'green' commercial telecommunication networks and sensors.

P1.116 Effect of heat treatment on physical properties of ZnO thin films deposited by DC reactive sputtering

A Boughelout, L Chabane, M Kechouane and N Zebbar

USTHB, Algeria

The material zinc oxide (ZnO) thin films with c-oriented were grown on corning glass and crystalline silicon substrates at room temperature and 100°C using DC reactive sputtering with an argon/oxygen plasma mixture at constant working total pressure of 100 Pa. Optical emission spectroscopy (OES) is used in order to provide information on the species present in the plasma The ZnO thin films were investigated by optical transmission, X-ray diffraction (XRD), scanning electron microscopy (SEM), Rutherford backscattering spectrometry (RBS), photoluminescence (PL), Raman spectroscopy and electrical conductivity measurements. OES show the presence of several reactive oxygen species with a dominant emission peak at 777.6nm corresponding to the transition O

($3p^5P$-$3s^5S^0$)).The crystalline structure of ZnO thin films indexed by XRD reveals hexagonal ZnO phase with cell parameters a=3.2499 Å and c=5.2066 Å. Post-deposition annealing influences the structure of ZnO films. XRD results reveal that the thermal annealing have the effects of narrowing the diffraction peak, indicating that grain growth has occurred, and shifting the (002) peaks to higher 2q angles. From the scanning electron microscopy images a uniform and compact surface with a presence of crystallites distributed over the surface is revealed. Significant changes are observed after vacuum-annealing at 300°C for one hour, resulting in the appearance of sticks distributed over the surface. A very large increase in electrical conductivity, up to ten orders of magnitude, was observed in as-grown ZnO films upon vacuum-annealing at 300°C for one hour. A Raman spectrum obtained by orientation of ZnO thin film deposited on oriented silicon is normalized and compared with a pure Si wafer. We can clearly distinguish the ZnO mode at 585cm^{-1}. The mode at 437cm^{-1} is close to the shoulder (2LA, Brillouin zone-corner) of silicon at 433cm^{-1}, but nevertheless, the shape is clearly different.

P1.117 Ion beam analysis for Hall Scattering Factor measurements in antimony-implanted silicon

T Alzanki[1], B Sealy[2] and R Gwilliam[2]

[1]Public Authority for Applied Education and Training (PAAET), Kuwait, [2]University of Surrey, UK

A viable way to produce ultra-shallow n^+-p junctions for the next generation of Complementary Metal Oxide Semiconductor (CMOS) devices (10-20nm node or logic technology) will be presented. The study of the electrical characteristics of the antimony implanted at energy level of 2 keV into silicon layer as a function of annealing conditions lover the range 600°C to 1100°C for various periods. Doping profiles will be investigated at a depth resolution of 2nm with junction depths of about 20nm. A comparison between Differential Hall Effect (DHE) measurements of carrier concentration and mobility profiles and Secondary Ion Mass Spectroscopy (SIMS) measurements will be presented. The atomic profiles for different annealing temperatures will be done using Rutherford Back Scattering (RBS) method to calculate the retained dose of the samples both as implanted and after thermal treatment. Information relating to atomic distribution of the dopant inside the layer, in terms of its lattice location, and of the damage induced by the injection will be studied.

P1.118 InGaN light-emitting diodes with a reduced barrier thickness

C-L Tsai, W-J Huang, C-T Yen, C-C Lin, C-Y Chou and Z-F Xu

Chang Gung University, Taiwan

In this study, we have demonstrated that the improvement in light output power of InGaN light-emitting diodes (LEDs) can be achieved by modifying GaN barrier thicknesses. In comparison with normal LED ("sample A") with five pairs of $In_{0.135}Ga_{0.865}N$ (2 nm)/GaN (10 nm) multiple-quantum-well (MQW), a modified MQW with three thinner barriers (~5 nm) near the n-GaN layers were used to facilitate the uniformity of carrier distribution in InGaN wells. High-resolution transmission electron microscopy analysis shows that the modified MQWs have a reasonable crystalline quality even though two kinds of quantum wells with different periods are combined together to form the active regions of sample B. It was also found that the thermal activation energy of samples A and B extracted from the high-temperature section (> 200 K) of the Arrhenius plots is evaluated as 67.6 and 67.1 meV, respectively. Such results suggest that the probability of nonradiative recombination associated with the photogenerated carriers escape out of the potential minima caused by the fluctuation of indium composition in InGaN and being captured by the material defects should be similar for both LEDs. In addition to a 16.1% increase in light output power at an injection current of 150 mA, the quantum efficiency of the proposed LEDs drops to 50% of its peak value occurred at higher injection currents as compared to that of their counterparts, i.e., 129 mA versus 88 mA. The reason for that could be attributed to more uniform carrier distribution among quantum wells as the thickness of GaN barriers near the n-GaN layers was reduced.

P1.119 Electronic and optical properties of amorphous semiconductors: a-SiO_2 and a-TiO_2 bulk, solid solution, and interface

M Landmann[1], T Köhler[2], E Rauls[1], T Frauenheim[2] and W G Schmidt[1]

[1]Universität Paderborn, Germany, [2]Bremen Center for Computational Materials Science, Germany

Both titania (TiO_2) and silica (SiO_2) are oxides whose extraordinary physical and chemical properties are demonstrated by manifold traditional fields of application. For gaining a basic estimation of the technological potential of SiO_2/TiO_2 hybrid materials a detailed understanding of the electronic and optical properties of such materials is required. Here, we have calculated the electronic structure and optical response of the SiO_2 and TiO_2 crystalline and amorphous bulk [1,2], solid solution, and interface. The calculations have been done by standard (PBE) and hybrid (HSE06) exchange-correlation functional density-functional theory (DFT). The HSE06 hybrid functional's suitability to correct for a large part of the DFT intrinsic band gap underestimation and to give a reliable approximation of quasiparticle properties is demonstrated. The optical spectra are calculated in independent particle approximation (IPA) from the DFT band structure and compared to existing experimental data.

[1] M. Landmann et al., submitted to J. Phys.: Cond. Mat. (2012).
[2] M. Landmann et al., to be published.

P1.120 Surface states influence in Al Schottky barrier of Ge nanowires

H Kamimura, R Simon, O Berengue, E Leite and A Chiquito

Universidade Federal de São Carlos, Brazil

The back-to-back model for Schottky barrier was used to extract the barrier height for germanium nanowires with aluminum contacts. Germanium nanowires were grown on Si/SiO_2 substrates by VLS method using gold seeds as catalysts. Devices were fabricated by evaporation of metallic electrodes directly on the substrate used in the synthesis over the layer formed by nanowires. We conducted temperature dependent resistance measurements to study the transport process in these structures; the results exhibited a semiconductor behaviour dominated by the variable-range-hopping transport mechanism, typical of disordered systems. Current-voltage curves were adjusted using a back-to-back Schottky barrier model and the barrier energies were found to be different (~0,53 eV) from the usual values for bulk-Ge/Al interface (0,58 eV). This difference was explained by the presence of a disordered Ge-GeO_2 interface, naturally and unavoidably formed during the growth process. Disorder leads to localized states which can act as charge traps at the interface: in fact, these states act as interface traps pinning the Fermi level at the semiconductor surface and determining the value of barrier height. In order to confirm the experimental data, we conducted numerical calculations for an estimate of the density of surface states and we found 10^{13}cm^{-2}, corresponding to a theoretical barrier height of 0,52 eV.

P1.121 Interface-induced cation ordering in InGaAs/InP(100) heteroepitaxial structures observed by reflectance difference spectroscopy

R Kanemura[1], S-Y Ohno[1], M Tanaka[1], A Ohtake[2], O Ichikawa[3], M Hata[3], T Mori[4], T Maeda[4] and T Yasuda[4]

[1]Yakohama National University, Japan, [2]National Institute for Materials Science, Japan, [3]Sumitomo Chemical Co., Ltd., Japan, [4]National Institute of Advanced Industrial Science and Technology, Japan

InGaAs is one of the promising materials for the metal-oxide-semiconductor field-effect transistors (MOSFETs) with high electron mobility. The ternary alloys such as InGaAs and InGaP exhibit cation ordering, or natural superlattice structures, under certain crystal-growth conditions, which induces anisotropy in their electrical and optical properties. In this study, the extent of the cation ordering in the InGaAs epitaxial layers grown on InP(100) substrates were investigated by measuring reflectance difference (RD) near the critical-point energies of InGaAs (2.6 and 2.9 eV) as well as by observing transmission electron diffraction (TED). Epitaxial growth of InGaAs layers of 50-300 nm thickness were carried out by MOCVD at two different temperatures. We have found that the InGaAs layer grown at the higher temperature shows ordering near the InGaAs/InP interface but not in its bulk. On the other hand, the InGaAs layer grown at the lower temperature shows rather uniform ordering throughout the thickness direction. In these measurements, depth distribution of the ordering-induced optical anisotropy was evaluated by thinning the InGaAs layer from both top and bottom sides of the layer. The existence of such interface-induced ordering, which was observed for the first time to our knowledge, needs to be considered in examining the InGaAs MOSFET performance when the ultrathin channel structures (~10 nm) are formed by the wafer-bonding technique. A part of this study was carried out in Nanoelectronics Project supported by NEDO.

P1.122 Photoemission and ellipsometry measurements of GeO_2 and Y_2O_3 films on Ge substrates

D Hesp, M Althobaiti, V R Dhanak, I Z Mitrovic, W M.Davey, N Sedghi and S Hall

University of Liverpool, UK

The continuous downscaling of devices to nanoscale dimensions, following Moore's law, means silicon based complimentary metal-oxide-semiconductor (CMOS) devices, which currently dominate the device industry, are reaching fundamental limits. Germanium is seen as a possible replacement for the Si p-MOSFET channel material because of its high hole mobility and as a result there has been much interest in developing Germanium based MOS technology[1,2]. There are particular challenges for the Ge/high-permittivity (k) oxide stack, which is now actively studied. Unlike Si, the native oxide of Ge is volatile and so an important issue in establishing Ge MOS technology is to develop a stable metal-insulator semiconductor (MIS) gate stack. To this end, attention has focused on the GeO_2/Ge interface control layer, which has the advantage of low interface state density and La_2O_3/Ge high-k oxide as an alternative[3,4].

Our focus is on using X-ray photoemission (XPS) and Variable Angle Spectroscopic Ellipsometry (VASE) to systematically study the surface and interface of GeO_2 and Y_2O_3 passivation layers thermally grown on Ge under differing conditions of temperature and thickness. Y_2O_3 was grown in-situ by co-deposition of Y and atomic oxygen. The thickness of the oxide layers, determined from the VASE measurements, varied from 3-12 nm. The composition and structure of the layers were determined by XPS and show that there is some reaction at the interface between Y_2O_3 and Ge, suggesting that a stable $YGeO_x$ is favored. The valence band offset, interfacial structural changes and the origin of the Ge^{2+} defects at the interface are discussed.

[1] R. Zhang et al., IEEE VLSI 2011, Tech. Dig., pp. 56-7, 2011.
[2] T. Sasada et al., J.Appl. Phys. 106, 073716 (2009).
[3] G. Mavrou et al., J. Appl. Phys. 103, 014506 (2008).
[4] J. Song et al., Microelectron. Eng. 86, 1638 (2009).

P1.123 Polaronic effect on impuritiy state in Wurtzite Nitride Semiconductor Quantum Dot under an electric field and hydrostatic pressure

Z Yan, M Dalai and L Shi

Inner Mongolia Agricultural University, China

The wide band-gap nitride semiconductors have attracted much attention for optoelectronic applications in the blue to ultraviolet spectral range in recent years. Nitrides have both wurtzite and blende as their nature crystalline structure, and exhibit highly unusual properties in III-V compounds of semiconductors. In recent years, the electron-optical phonon mode interaction mechanism in crystals with wurtzite structure has been considered.

The binding energy hydrostatic impurity state in a finite potential spherical quantum dot including an applied electric field and hydrostatic pressure are studied. Interaction between the charge carriers (electron and impurity) with the optical phonons has been taken into account in our study using a Lee-Low-Pines (LLP) variational treatment. The results for the binding energy as well as polaronic correction are obtained as functions of the dot size and the hydrostatic pressure, respectively. Numerical calculation shows that the interaction of the charge carriers (electron and impurity) with the optical phonons is greatly decreases the binding energy on the $GaN/Al_xGa_{1-x}N$ quantum dot. The correction induced by the charge carriers-LO-phonons interaction increases as the electronic confinement increases. On the other hand, the binding energies hardly change with respect to the applied electric field in the regime of strong geometric confinement. Moreover, the binding energies increase with the pressure for any size of dot.

P1.124 Aharonov-Bohm quantum rings in microcavities

A Alexeev[1], I A Shelykh[2] and M E Portnoi[1]

[1]University of Exeter, UK, [2]University of Iceland, Iceland

Progress in nanolithography and epitaxial techniques has resulted in burgeoning developments in the fabrication of semiconductor nanostructures and optical microcavities. Cavity quantum electrodynamics addresses the interaction of an emitter embedded inside a microcavity with the cavity modes and the emission spectrum of the system. The luminescence spectrum of a microcavity coupled to a single quantum-dot-based emitter under incoherent continuous pumping has been studied both theoretically and experimentally [1,2]. This system possesses a rich spectrum, which maps transitions between quantized photon-dressed states of the light-matter coupling Hamiltonian.

There is a considerable current interest in non-simply-connected nanostructures, quantum rings, which have been obtained in various semiconductor systems. The fascination in quantum rings is partially caused by a wide variety of purely quantum mechanical effects, which are observed in ring-like nanostructures, including the celebrated Aharonov-Bohm effect resulting in magnetic-flux-dependent oscillations of various physical quantities. It has been shown recently that an external lateral electric field, which is known to reduce the ring symmetry and suppress the energy oscillations for the low-energy states, modifies optical properties of the ring [3]. Namely, the application of a weak electric field leads to magneto-oscillations of frequency and the degree of polarization of THz transitions between the ground and first excited states.

In the present work we examine a microcavity with an embedded quantum ring pierced by a magnetic field and subjected to a lateral electric field. We calculate the luminescence spectrum of the system using the Lindblad master equation approach and demonstrate that it is strongly influenced by the pumping intensity and the quality factor of the cavity. An additional degree of control can be achieved by changing the angle between the polarization plane of the pump and the external electric field. Optical properties of the considered system demonstrate a rich behaviour which can be controlled by external electric and magnetic fields. These fields govern the electron spectrum and optical selection rules in a ring, which can be tuned to match the cavity modes.

[1] E. del Valle et al., Phys. Rev. B 79, 235326 (2009).
[2] K. Hennessyet al., Nature (London) 445, 896 (2007).
[3] A.M. Alexeev and M.E. Portnoi, Phys. Status Solidi C 9, 1309 (2012).

P1.125 Effect of weak magnetic fields treatment on photoluminescence of gallium arsenide and gallium phosphide single crystals

R Red'ko and S Red'ko

The National Academy of Sciences of Ukraine, Ukraine

The samples of GaAs and GaP under investigation were Cz-grown with orientation (111) and n-type doped with Te up to $1 \cdot 10^{16}$ and $8 \cdot 10^{16}$ cm^{-3} carriers concentration, respectively. The defect structure of our samples was studied using the photoluminescence (PL) method. The PL spectra of semiconductors were measured in the 0.5–2.0 eV spectral range at temperatures between 77 and 300 K. Two groups of samples were treated in the single-pulse regime (I) of weak magnetic treatment (WMF) with different values of B: 8 and 60 mT. The duration of WMF pulse in this case was τ_I = 30 ms. The multi-pulse regime (II) with parameters B = 60 mT, f = 10 Hz, τ_{II} = 1.2 ms, t = 60 s was the second.

Exposure to MF in regime I resulted in decrease of the intensity of almost all observed bands (1.01 and 1.21 eV for GaAs and 1.7 and 1.3 eV for GaP). The pulse of MF with B_2 = 60 mT results in other features. After exposure, the intensity of PL peaks does not vary essentially. But after some period of time (5–8 days), the transformation of recombination spectra was detected. The MF exposure in regime II results in small decrease in observable emission intensity with synchronous changes until reaching some quasi-steady state appeared.

The energy of WMF is very low to induce the observed transformations. Therefore, we used the spin mechanism to explain the obtained results of experiments. WMF causes reorientation of electron spin. This can result in weakening of chemical bonds and destruction of the complex formed by this atom. As a result, non-equilibrium native point and impurity defects appear that induce local quasichemical reactions.

P1.126 Charge carrier density at the (Na/K)TaO$_3$ /SrTiO$_3$ interfaces

S Nazir and U Schwingenschlogl

King Abdullah University of Science and Technology (KAUST), Saudi Arabia

The formation of a quasi two-dimensional electron gas between the band insulators NaTaO3 and SrTiO3 as well as KTaO3 and SrTiO3 is studied by means of the full-potential linearized augmented plane-wave method of density functional theory. Optimization of the atomic positions points to only small changes in the chemical bonding at the interface. The creation of metallic interface states thus is not affected by structural relaxation but can be explained by charge transfer between transition metal and oxygen atoms. It is to be expected that a charge transfer is likewise important for related interfaces such as LaAlO3/SrTiO3. The effects of O vacancies are discussed. Spin-polarized calculations point to the formation of isolated O 2p magnetic moments, located in the metallic region of the p-type interface.

P1.127 High mobility of the strongly confined hole gas in AgTaO$_3$/SrTiO$_3$

S Nazir and U Schwingenschlogl

King Abdullah University of Science and Technology (KAUST), Saudi Arabia

A first principles calculation is used to study the electronic structure of AgTaO$_3$/SrTiO$_3$ (001) heterostructure. Formation of a two-dimensional hole gas at the (AgO)/(TiO$_2$) p-type interface is presented. The Ag 4d states strongly hybridize with the O 2p states and contribute to the hole gas. It is demonstrated that the holes are confined to an ultra thin layer (~4.9 A) with a considerable carrier density of ~ 10^{14} cm^{-2} . We estimate a hole mobility of 18.6 cm^2 V^{-1} s^{-1}, which is high enough to enable device applications.

P1.128 The interface of the ferromagnetic metal CoS_2 and the non-magnetic semiconductor FeS_2

S Nazir and U Schwingenschlogl

King Abdullah University of Science and Technology (KAUST), Saudi Arabia

The electronic and magnetic properties of the cubic pyrite CoS_2 /FeS_2 interface are studied using the all-electron full-potential linearized augmented plane wave method. We find that this contact between a ferromagnetic metal and a non-magnetic semiconductor shows a metallic character. The CoS_2 stays close to half-metallicity at the interface, while the FeS_2 becomes metallic. The magnetic moment of the Co atoms at the interface slightly decreases as compared to the bulk value and a small moment is induced on the Fe atoms. Furthermore, at the interface ferromagnetic ordering is found to be energetically favourable as compared to anti-ferromagnetic.

P1.129 Oscillator strengths for intersubband transitions in the multi-layered nano-antidots with haydrogenic impurity

Y Naimi and A Jafari

Islamic Azad University, Iran

In this study we have obtained the exact solutions of Schrodinger equation for a multi-layered quantum anti-dot (MLQAD) within the effective mass approximation and dielectric continuum model for the spherical symmetry. The MLQAD is nano-structured semiconductor system that consists of a spherical core (e.g. $Ga_{1-x}Al_xAs$) and a coated spherical shell (e.g. $Ga_{1-y}Al_yAs$) as the whole anti-dot is embedded inside a bulk material (e.g. *GaAs*). The dependence of electron energy spectrum and its probability density on nano-system radius are studied. The numeric calculations and analysis of oscillator strength of intersubband quantum transition from ground into first excited state at the varying radius, for both finite and infinite confining potentials as well as constant thickness, are performed. It is shown that, in particular, the binding energy and the oscillator strength of the hydrogenic impurity of a MLQAD at different shell thickness behave differently from that of a single-layered quantum anti dot. At large core radius, our results are closed to respective values for a single-layered quantum anti-dot that previously reported.

P1.130 Ion beam analysis for Hall Scattering Factor measurements in antimony-implanted silicon

T Alzanki[1], R Gwilliam[2] and B Sealy[2]

[1]Public Authority for Applied Education and Training (PAAET), Kuwait, [2]University of Surrey, UK

A viable way to produce ultra-shallow n^+-p junctions for the next generation of Complementary Metal Oxide Semiconductor (CMOS) devices (10-20nm node or logic technology) will be presented. The study of the electrical characteristics of the antimony implanted at energy level of 2 keV into silicon layer as a function of annealing conditions lover the range 600°C to 1100°C for various periods. Doping profiles will be investigated at a depth resolution of 2nm with junction depths of about 20nm. A comparison between Differential Hall Effect (DHE) measurements of carrier concentration and mobility profiles and Secondary Ion Mass Spectroscopy (SIMS) measurements will be presented. The atomic profiles for different annealing temperatures will be done using Rutherford Back Scattering (RBS) method to calculate the retained dose of the samples both as implanted and after thermal treatment. Information relating to atomic distribution of the dopant inside the layer, in terms of its lattice location, and of the damage induced by the injection will be studied.

Theory/computational physics

P1.131 Strain dependence of polarization and dielectric response in epitaxial (Ba_xSr_{1-x})TiO_3 thin films

S Binomran
King Saud University, Saudi Arabia

The potential of ferroelectric thin films for many applications, such as dynamic random access memories, nonvolatile ferroelectric random access memories and integrated devices, has recently attracted a lot of research attention on these low-dimensional systems. Intense effort has been made recently to determine if (and understand how) properties of these low-dimensional systems can differ from those of the corresponding three-dimensional bulk. As a result, recent studies revealed that electrical boundary conditions and mechanical boundary conditions play a dominant role in changing the properties of ferroelectric films.

A first-principles-derived schemes is used to use a first-principles-derived technique to construct the temperature-versus-misfit strain phase diagrams for the whole BST composition rang (i.e., x=0.00,0.20,0.40,0.60,0.80,1.00). Moreover, we investigate the dependence of their dielectric and ferroelectric properties on the strain and the concentration.

We calculate the temperature-versus-strain phase diagram of (Ba_xSr_{1-x})TiO_3 ultrathin films having a thickness of 48 Å (as modeled by 12x12x12 supercell) and under ideal short-circuit conditions for selected composition. It shows that five crystallographic exists in the: the p paraelectric phase (in which $P_x=P_y=P_z=0$) at high temperature; the c tetragonal phase (for which $P_x=P_y=0$, $P_z\neq0$) at high compressive strains; the r monoclinic phase ($P_x=P_y=P_z\neq0$) at intermediate strains; the aa orthorhombic phase ($P_x=P_y\neq0$, $P_z=0$) at high tensile strains. Interestingly, we found that the multiphase point where all four phases meet depends on the composition. It ranges from η=1.7% at T=580 K (for pure $BaTiO_3$) to η=0.8% at T=204 K (for $SrTiO_3$). Also, we will present the dependency of dielectric constants on the misfit-strain and composition at room temperature. Our results reveal that the predicated phase diagrams show a topology similar to those calculated by Shirokov et. al. Phy. Rev. B. 79 144118 (2009) with quantitative discrepancies that will be revealed and explained.

Our results also indicate that in-plane strain increases (respectively, decreases) the in-plane (respectively, out-of-plane) dielectric constants. Furthermore, the out-of-plane component of dielectric permittivity ε_{33} enhances with lowering x in (Ba_xSr_{1-x})TiO_3 films. We hope that our results will be benefits to many scientists and will lead to new strategies for material design.

P1.132 Charge-transfer excitations in oxo and peroxo dicopper complexes modelled within TDDFT and MBPT

M Rohrmüller[1], W G Schmidt[1] and S Herres-Pawlis[2]

[1]Universität Paderborn, Germany, [2]Ludwig-Maximilians-Universität München, Germany

The activation mechanism of oxidation by enzymes containing as active part binuclear Cu complexes, relevant e.g. for biological systems, is up to now not completely understood [1]. Therefore we study μ-η^2:η^2-peroxodicopper(II) species and the bis-μ-oxodicopper(III) species within a experimental characterized model system [2]. Understanding the properties of such molecules, which lead to oxidation and reduction, is crucial for further investigation and understanding of such systems.

We present a detailed investigation of $[Cu_2(dbdmed)_2(O_2)]^{2+}$ ground- and excited-state properties using time dependent density functional theory and many body perturbation theory [3], plane waves or gaussian-type localized orbital basis sets and different exchange-correlation functionals. We also take care of a possible broken symmetry character of the structure and shed light on the influence of solvents and the ligand system.

We found that the accuracy of the various DFT flavors used in the present study is comparable for ground state properties like geometries. This includes properties, which can be calculated as differences of ground state properties of a subspace using the Δ-scf method (e.g. ionization energies).

Calculated optical spectra depend strongly on the physical approximations and numerics. In particular the amount of exact exchange in the XC functional and is decisive for the agreement with experiment data. The tested long-range corrected functional performs best due to the delocalized character of the involved transition orbital. We provide a detailed comparison between TDDFT calculations and results obtained from many-body perturbation theory, i.e. self-energy corrections obtained in the GW approximation and optical spectra from the Bethe-Salpeter equation approach.

[1] Solomon, et al., Chem. Rev., 96, 2563, (1996).
[2] Mahadevan, et al., J. Am. Chem. Soc., 122, 10249, (2000).
[3] Onida , et al., Rev. Mod. Phys., 74, 601, (2002).

P1.133 Ferroelectric transition in $LiNbO_3$ calculated from first principles

S Sanna and W G Schmidt

Universität Paderborn, Germany

Lithium niobate ($LiNbO_3$, LN) belongs to the most important ferroelectric materials. It is furthermore one of the most important optic materials, being the equivalent in the field of non-linear optics and optoelectronics to silicon in electronics [1]. Despite the extensive technological usage, the knowledge of the mechanisms underlying the ferroelectric phase transition is rather poor. The nature of the phase transition itself (displacive or order-disorder) is still argument of debate [2]. In this contribution we report on our first-principles theoretical studies of the ferroelectric transition, which is described in detail at the microscopic level. Total energy calculations as well as long-run molecular dynamics simulations are used to understand the driving forces and mechanisms of the phase transition. Our calculations show that the structural phase transition is not an abrupt event, but rather a continuous process occurring over about 100 K and involving different ionic species at different temperatures. Because of the different behavior of the Li and Nb sublattice, the ferroelectric transition displays both displacive and order-disorder character. In addition to pure materials, the role of the widely used dopant Ti is investigated, and the results of existing experiments explained in the light of our theoretical models. The mechanisms underlying the polarization reversal process (required for example for the realization of periodically poled structures) are discussed.

[1] A. Räuber, Chemistry and Physics of Lithium Niobate North-Holland Publ. Company, Current Topics in Mat. Sci., (1978).
[2] I. Inbar and R. E. Cohen, Phys. Rev. B 53, 1193 (1996).

P1.134 Break down of one-dimensional free fermion picture on equilibrium crystal shape for sticky steps I: PWFRG calculations

N Akutsu

Osaka Electro-Communication University, Japan

A restricted solid-on-solid model with point-contact type step-step attraction (p-RSOS model)[1] is considered to study the many-body problem of sticky steps, where the surface height differences of the nearest neighbor sites on the square lattice are restricted {1,0,-1}. An equilibrium crystal shape (ECS), which is a shape of a crystal particulate with the least surface free energy, around (001) facet is calculated by using the product wave-function renormalization group (PWFRG) method[2]. The method is a transfer matrix version of the White's density matrix renormalization group (DMRG) method[3]. From the analysis of the ECS, singularities in the surface free energy and anomalous shape exponents are obtained for the vicinal surface tilted from (001) surface towards <110> direction in a low temperature region[4].

[1] N. Akutsu, Appl. Surf. Sci. 256 (2009) 1205; J. Cryst. Growth 318 (2011), 10.
[2] T. Nishino and K. Okunishi, J. Phys. Soc. Jpn. 64 (1995) 4084. Y. Hieida, K. Okunishi and Y. Akutsu, Phys. Lett. A 233 (1997) 464; New J. Phys. 1 (1999) 7.1.
[3] S. R. White, Phys. Rev. Lett. 69 (1992) 2863.
[4] N. Akutsu, J. Phys.: Condens. Matter 23 (2011) 485004.

P1.135 Structure and IR spectra of $Na_8[AlSiO_4]6$ $(BH_4)2$ sodalite: comparison between theoretical predictions and experimental data

M Marcus[1], T Bredow[1], L Schomborg[2], C Rüscher[2] and J Buhl[2]

[1]Rheinische Friedrich-Wilhelms Universtät Bonn, Germany, [2]Leibniz Universität Hannover, Germany

A new material has been developed, namely BH_4-SOD, which encloses and largely protects the BH_4-anion in the sodalite cage both in microcrystalline and in nanocrystalline form [1,2].For a better understanding of the hosting properties of the sodalite for the BH_4 molecule and its reaction products, quantum-chemical calculations of the BH_4-SOD structure were carried out. Here first results performed with the crystalline orbital package CRYSTAL09 [4] are presented.

Three Hartree-Fock-DFT-Hybrid functionals based on the Perdew-Wang '91GGA, Perdew-Burke-Ernzerhof GGA, and van-Barth-Hedin LSD functionals were tested with exchange mixings between 0 and 100%. For all three cases best agreement with experimental atom parameters [1] were obtained for about 20-35% mixing. The optimised positions of framework and cagefilling atoms were used to calculate all IR active modes within space group P -43n. The intensities were calculated by a Barry phase approach [5]. Best agreement between peakpositions of measured and calculated spectra was obtained for about 20% of mixing within all three methods.

The two IR active stretching and bending vibrations of the tetrahedral BH_4-anion were theoretically predicted at about 2385-2418 cm^{-1} and 1122-1150 cm^{-1}, respectively, in very good agreement with experimentally observed peaks assigned to the BH_4-anion. Here two additional modes can be seen in the spectra in the range between 2200 and 2400 cm-1, which are known, however, to correspond to combination modes. Such contributions were not included in the calculations which are based on the harmonic approximation.

Also the possibility of symmetry reduction by displacements of sodium ions and the effects on the IR spectrum is investigated and results will be presented.

[1] J.-Chr.Buhl, T.M.Gesing, C.H.Rüscher, Microporous Mesoporous Mater. 80 (2005) 57-63.
[2] J.-Chr.Buhl, L.Schomborg, C.H.Rüscher, Microporous Mesopourous Mater. 132 (2010) 210-218.
[4] R.Dovesi, R.Orlando, B.Civalleri, C.Roetti, V.R.Saunders, C.M.Zicovich-Wilson, Z.Kristallogr. 220 (2005)571.
[5] A.F.Izmaylov,G.E.Scuseria,Phys.Rev.B77(2008),165131.

P1.136 Phase transitions pressure and lattice dynamical properties of lead polonide

B Yamina, F Mohamed and B Abdelaziz

University of Mostaganem, Algeria

In the present work we investigate the structural, electronic, dynamical and thermodynamics proprieties of lead polonide (PbPo) compound. To find the pressure-induced structural transitions phases, we consider the zinc-blende, wurtzite, rocksalt, CsCl, GeS and orthorhombic Pnma structures. Our results show that the intermediate phase transition for this compound is the orthorhombic Pnma phase. The PbPo undergo from the rocksalt to Pnma phase at about 4.20 GPa . Further structural phase transition from intermediate to CsCl phase has been found at about 8.49 GPa. The stability or metastability of predicted phase at high pressure is determined by studying the phonon spectrum. We examined the effect of pressure on the dynamical charges, the longitudinal optical (LO) branch, transverse optical (TO) branch and the splitting of (LO)-(TO) branches. The variation of partials heat capacity and the entropy of each constituent's atoms versus the temperature are also considered.

P1.137 Scalable coarse-grained spin dynamics simulation

F Buijnsters, M Katsnelson and A Fasolino

Radboud Universiteit Nijmegen, The Netherlands

Many phenomena in magnetism and spin dynamics are strongly multiscale in nature. At macroscopic system sizes, even classical atomistic spin-dynamics simulations become unfeasible and matched atomistic–coarse-grained simulation techniques are called for. Previous work [1] described a method for spin-system simulation that, while being based directly on (classical) microscopic Heisenberg Hamiltonians, allows a coarse-grained treatment of bulk regions. It thus goes beyond continuum micromagnetics simulations. We present a computational approach to this type of simulation that promises to be efficient and highly scalable.

[1] V. V. Dobrovitski, M. I. Katsnelson, and B. N. Harmon. Phys. Rev. Lett. 90, 067201 (2003).

P1.138 Progress in the development of the Cyclic Cluster Model at ab initio level

M F Peintinger and T Bredow

University of Bonn, Germany

The cyclic cluster model (CCM) is an alternative to the supercell model for the quantum-chemical description of solids. Periodic boundary conditions (PBC) are directly applied to a finite free cluster corresponding to a non-primitive unit cell. The interaction range of every atom within the cluster is defined by its Wigner-Seitz supercell (WSSC). It is a Γ point approach and integration is carried out in real space. The CCM has been successfully implemented at semi-empirical level (MSINDO, DFTB) and an implementation at KS-ADFT level (deMon2k) exists.

We implemented the CCM in the Hartree-Fock formalism in AICCM, which is an object oriented, educational quantum chemical code written in the Python scripting language with C extensions. The progress in the development of the CCM at *ab initio* level is presented.

P1.139 Cyclic Cluster Implementation of DFTB/DFTB-SCC

T Claff, M F Peintinger and T Bredow

University of Bonn, Germany

The Cyclic-Cluster-Model (CCM) is an approach for the quantum chemical treatment of periodic structures. Periodic boundary conditions are applied to a free cluster. Interactions are taken into account between the reference atoms and their non-primitive Wigner-Seitz-Cells, defined by the translation vectors. The CCM has been implemented on semi-empirical wave-function methods such as MSINDO. We present an implementation of the CCM in the density-functional-tight-binding (DFTB) and self-consistent-charge-DFTB (SCC-DFTB) formalism in AICCM. AICCM is an object oriented quantum chemical code, written in the Python scripting language with C extensions. Applications to Polymers, Surfaces and solids are shown and compared to data available from the literature.

P1.140 The pressure coefficients of the superconducting transition temperatures of ferromagnetic superconductors

R Konno and N Hatayama

Kinki University Technical College, Japan

The pressure coefficients of the superconducting transition temperatures of ferromagnetic superconductors were investigated. We used the free energy of ferromagnetic superconductors, where the superconducting gaps were similar to those of the thin film of A2 phase in liquid ^{3}He, derived from the microscopic Hamiltonian by Linder et al. [1] in the context of the mean-field theory. We succeeded in obtaining the numerical results of the pressure coefficients of the superconducting transition temperatures by using the analytical results [2].

[1] J. Linder and A. Sudbo, *Phys. Rev.* B 76 (2007), 054511.
[2] R. Konno and N. Hatayama, *J. Phys.: Conf. Ser.* 344 (2012), 012016.

P1.141 Quantum chemical simulations of surface reactions

A Funk and H F Reinhard Trettin

University of Siegen, Germany

The simulation of chemical reactions in large systems is a challenge, especially within periodic boundary conditions. Restricted by system size, *ab initio* methods of high precision, like coupled cluster methods, can not be applied. Force field methods are very cheap in computational effort, but lack in accuracy needed for a description of chemical reactions.

A good compromise between necessary precision and computational cost is density functional theory (DFT). By addition of empirical corrections for dispersion (DFT-D) an exceptionally good description of a variety of chemical reactions can be achieved. A combination of Car-Parinello molecular dynamics (CPMD) and geometry optimisations further reduces computing time.

In this poster we present combined CPMD calculations and geometry optimisations for the description of reactions on calcium hydroxide surfaces. All results are calculated using the revPBE density functional with D3 empirical dispersion energies and a double zeta basis set. The calculations were performed with the program CP2K.

P1.142 Polarization-dependent methanol adsorption on lithium niobate Z-cut surfaces

A Riefer, S Sanna and W G Schmidt

Universität Paderborn, Germany

Lithium niobate (LN) is a ferroelectric material with a huge range of applications. The LN bulk properties are exploited in numerous optical and acoustic devices. Recently, surfaces of ferroelectric materials are attracting attention. For example chemical sensing based on adsorption-induced switching of ferroelectric thin films has been proposed. Temperature programmed desorption measurements of polar molecules, such as Water, Methanol [1], and 2-Propanol [2], on the LN Z-cut show stronger adsorption of these molecules on the positive compared to the negative surface. The reasons fore this polarization dependence are essentially unknown. Recently, structural models for the negative and positive LN Z-cut have been proposed on the basis of density-functional theory (DFT) calculations [3]. Here, we investigate the adsorption of Methanol on LN surfaces by means of DFT within the generalized gradient approximation (GGA). As a first step, we calculate the potential energy surface (PES) for both orientations. We find the preferred position of an adsorption of Methanol near the oxygen atoms on the positive or near the Lithium atoms on the negative surface, respectively and a adsorption energy difference of about 0.5 eV between the two surface orientations. Also, reaction paths leading to molecular dissociation are presented.

[1] J. Garra et al., Surf. Sci. 603, 1106 (2009).
[2] Y. Yun et al., J. Phys. Chem. C 111, 13951 (2007).
[3] S. Sanna and W.G. Schmidt, Phys. Rev. B 81, 214116 (2010).

P1.143 First-principles non-adiabatic molecular dynamics simulations using local basis DFT Fireball code

P Jelinek[1], E Abad[2], V Zobač[1], P Hapala[1], J P Lewis[3] and J Ortega[2]

[1]Institute of Physics of the Czech Academy of Science, Czech republic, [2]Universidad Autónoma de Madrid, Spain, [3]West Virginia University, USA

Ordinary first-principles Molecular Dynamics (MD) are based on the Born-Oppenheimer (BO) approximation. In this approximation, the nuclei follow classical trajectories defined on a single potential energy surface (PES). PES corresponds to the ground state electronic energy of the system, for “frozen” atomic configurations. There are many physical, chemical and biological phenomena that cannot be described properly within the BO approximation, e.g. when electronic transitions are relevant. Some examples are: non-radiative electron-nuclear relaxations, photochemical reactions, ultrafast dynamics of photo-excited molecular systems, electron and proton transfer in chemical and biological systems, etc. A particularly important class of phenomena that is not described properly by the BO approximation corresponds to those processes that involve inelastic energy transfer between electrons and nuclei.

In order to go beyond the BO approximation, we have implemented the time-dependent Kohn-Sham dynamics using the Fewest-switches Surface Hopping [1,2] and Mean Field Ehrenfest methods [2,3] in our local basis Fireball code [4]. Several applications of these techniques will be presented on selected testing systems.

[1] J. C. Tully, J. Chem. Phys. 93, 1061 (1990); C.F. Craig et al, Phys. Rev. Lett. 95, 163001 (2005).
[2] N. L. Doltsinis. in John von Neumann Institute for Computing (NIC) Series (ed. J. Grotendorst, D. M., and A. Muramatsu) 377-397 (2002).
[3] J. K. Tomfohr and O. F. Sankey, Physica Status Solidi B: 226, 115-123 (2001).
[4] www.fireball-dft.org

P1.144 Monte Carlo calculation of the final backscattering energy and the backscattering coefficient of electron in solids: the effect of the transport cross section

A Bentabet[1] and A Aydin[2]

[1]Centre Universitaire de Bordj Bou-Arréridj, Algeria, [2]Balıkesir University, Turkey

The transport electron beam normally incident impinging on solid targets is stochastically modeled within a Monte Carlo frame work.The purpose of our work is to show the hidden effect of the electron transport cross section in the beam electrons transport study impinging in solid targets by using Monte Carlo method. We think that this work is useful for those who develop semi empirical or analytical models of elastic cross sections. For this, our study is based on our semi empirical model of differential elastic cross section by leaving only one free parameter adjusted once to the elastic total cross section and to transport cross section on the other hand. The obtained results showed good agreement with the experimental data when discussed and compared to those of the literature.

P1.145 Developing a forward flux sampling plugin for multiple applications

R Allen[1], J Lintuvuori[1] and K Stratford[2]

[1]The University of Edinburgh, UK, [2]Edinburgh Parallel Computing Centre, UK

Forward Flux Sampling (FFS) is a conceptually simple and efficient method to simulate rare events in either equilibrium or non-equilibrium systems with stochastic dynamics. The structure of the FFS algorithm is independent of the precise details of the underlying simulation method. This means that it may be used with a wide variety of methods or programs providing stochastic sampling/dynamics. Our aim is to provide a generic (simulation method independent) implementation of FFS with an interface which can be easily coupled to existing simulation code(s). Further, we aim to achieve this using a parallel implementation employing the Message Passing Interface (MPI). In particular, we will consider the specific case of a serial FFS algorithm coupled to a parallel implementation of a molecular dynamics code, such as LAMMPS. In future, further possibilities will be considered, including parallel implementation of FFS with simulation in serial and parallel FFS coupled to parallel simulation.

P1.146 First-principle studies of phonons in wurtzite structure III-N compound semiconductors

G Zhao, J Zhang and X Liang

Inner Mongolia University, China

In the last few decades, the III-nitride semiconductor compounds have attracted considerable attention and been widely applied in optoelectronic devices, because of the considerable hardness, the high thermal conductivity and the direct energy gap[1-2]. In this work, based on the density of functional theory, we present a detailed investigation of the phonon dispersion relations and density of states of III-nitride semiconductor compounds in the wurtzite structure. All calculations are implemented by using the code of Quantum ESPRESSO[3]. The LDA and GGA exchange correlation potentials are used. The crystal structure of III-nitride semiconductor compounds is wurtzite structure with space group P63mc, and the lattice constants $a=b$, $c/a=1.6333$, and $a=\beta=90^\circ$, $\gamma=120^\circ$. The equilibrium lattice constants a, c and the internal geometrical constant u are obtained by fitting the energy versus volume curve to the Murnaghan equation of state. Based on the structural optimization results, we compute the phonon dispersion and the density of states of AlN, BN, GaN and InN. The results show that the width of the gap between LO and TO phonon frequencies increases with the element masses of B, Al, Ga and In, and the highest frequency of phonons depends on the mass of cations. The calculated results of phonon frequencies at Γ point are in good accordance with experimental data and other theoretical results[4-7].

[1] Khan, A., et al. (2008). Nat Photon 2(2):77-84.
[2] Kneissl, M., et al. (2011). Semicond. Sci. Technol. 26:014036.

[3] Giannozzi, P., et al. (2009). J. Phys.: Condens. Matter 21,395502.
[4] Gorczyca, I., et al. (1998). Phys. Rev B51(17):11936-11939.
[5] Kim, K., et al. (1996). Phys. Rev. B53(24):16310-16326.
[6] Davydov, V. Yu, et al. (1998). Phys. Rev. B58(19):12899-12907.
[7] Ranjan, V., et al. (2005). Phys. Rev. B72(8):085315.

P1.147 Dirac superplasmons in a honeycomb structure of metallic nanoparticles

C Woollacott

University of Exeter, UK

In this theoretical project we combine the physics of localised plasmonic resonances in metallic nanoparticles with the peculiar electronic properties of graphene. The project analyses a 2D array of metallic nanoparticles arranged in a honeycomb lattice similar to the crystallographic structure of graphene.

The localised plasmonic resonance in each nanoparticle interacts with those in the neighbouring nanoparticles, giving rise to a collective ‘Super-plasmon’ mode of the whole lattice. This interacting system of dipoles in the nanoparticle array can be mapped onto the equivalent problem of tight binding for electrons in graphene. The resulting superplasmon dispersion can thus show features reminiscent of the massless Dirac spectrum of electrons in graphene.

In particular, when the dipole moments in the nanoparticles are orthogonal to the 2D plane the resulting dipolar interactions are repulsive, leading to a gapless conical dispersion of the superplasmon in the vicinity of two inequivalent Dirac points. This analogy with the dispersion of electrons in graphene leads to the emergence of massless Dirac physics for the bosonic superplasmons, with observable consequences on the plasmonic response of the 2D metamaterial.

As the orientation of localised dipole moments is tilted slightly, the superplasmonic dispersion can be mapped to that of electrons in strained graphene, until a critical dipole tilt is reached, resulting in the appearance of a gap in the superplasmon spectrum.

Thin carbon layers/grapheme

P1.148 On the Quantum Hall Effect in graphene

M Cheremisin

A.F. Ioffe Physical-Technical Institute, Russia

Using the thermodynamic approach[1,2], we calculate both the transverse and longitudinal magnetoresistivity of 2D electron gas in mono- and bi-layer graphene[3]. In quantizing magnetic fields 2D electrons assumed to be dissipationless. Nevertheless, an extraneous longitudinal magnetoresistivity is generated in sample as a result of Peltier and Seebeck thermoelectric effects combined [1,2]. The current, *I*, causes heating(cooling) at the first(second) sample contact due to the Peltier effect. The contact temperatures are different, the constant temperature gradient is linear in current. The voltage measured across the sample is equal to the Peltier effect-induced thermoemf which is linear in current too. Finally, the longitudinal magnetoresistivity is nonzero as *I*-->0.

We examine [3] two different cases when 2D carrier density (magnetic field) is varied(fixed) and vice a versa. Similar to conventional 2D electron gas case[2], for mono- and bi-layer graphene the longitudinal magnetoresistivity is a universal function of magnetic field and temperature, expressed in fundamental units h/e^2.

Our special interest concerned the magnetoresistivity peak observed experimentally in the vicinity of the Dirac point. We attribute this peak to the splitting of the zeroth Landau level in graphene. The existing experimental data allow us to deduce [3] the B-dependence of zeroth-LL split sublayers for both the mono- and bi-layer graphene cases.

[1] Kirby and M.J. Laubitz, Metrologia 9, 103, 1973.
[2] M.V.Cheremisin, Physica E, 28, 393, 2005.
[3] M.V.Cheremisin, arXiv:1110.5778, 2011.

P1.149 Na induced changes in the electronic band structure of graphene on C-face SiC

L Johansson, S Watcharinyanon, C Xia and C Virojanadara

Linköping University, Sweden

The effects of deposited Na on monolayer graphene on Si-face 6H-SiC were recently investigated in detail [1,2,3] using PES, ARPES, STM, LEEM, XPEEM and selected area PES and LEED. The results showed that after deposition at room temperature some of the Na atoms preferred to adsorb on the graphene layer. Some intercalated in between the graphene and the carbon buffer layer and some went in even further and intercalated at the interface between the buffer layer and the SiC substrate. The latter was clearly revealed by pronounced shifts of the substrate C 1s and Si 2p core level peaks. Heating the sample at around 100°C was found to promote intercalation while higher temperatures resulted in a gradual desorption of Na. The ARPES spectrum showed initially only a lowering of the Dirac point, indicating an increased n-type doping. Upon heating the buffer layer was transformed into a second graphene layer and the ARPES spectrum then exhibited two π-bands. We recently carried out a similar ARPES investigation of the effects induced by deposited Na in the band structure of C-face graphene grown on 6H-SiC. Those findings will be presented and discussed in view of the earlier findings.

[1] S. Watcharinyanon, et al, J. Appl. Phys. in press.
[2] A. Sandin, et al, Phys. Rev. B 85, 125410 (2012).
[3] C. Xia, et al, submitted for publication.

P1.150 Coupling epitaxy and chemical bonding at the local scale in transition metal supported graphene

C Bromley, B Wang, M Caffio, H Früchtl and R Schaub

University of St Andrews, UK

Graphene has been hailed the new super material due to its host of fascinating properties. The possible applications for these have grabbed the attention of large electronic and technological companies. It is now possible to produce large sheets of graphene on copper foils and successfully transfer them to polyethylene terephthalate (PET) for possible touch screen applications and more. The basic technology is there but more research is required to optimise growth and quality of graphene to take full advantage of its amazing properties. A popular synthesis method is Chemical Vapour Deposition (CVD) on transition metal surfaces due to the ability of producing large graphene sheets and the relative ease of transferring it to other substrates. To understand the epitaxial relationship between graphene and the metal support, we have used low temperature STM, coupled to DFT calculations, to study graphene on two very different surfaces: Rh(111)[1] and Cu(110).

[1] B. Wang, M. Caffio, C. Bromley, H. Früchtl and R. Schaub, ACS Nano 2010, 4, 5773-5782.

P1.151 Adhesion of graphene on rough substrates, and substrates with nanoparticles

P-L Olivier

CNRS/ LPMCN, France

We discuss the adhesion of graphene on rough substrates and on nanoparticles, based on theory and experiments.

A generic elastic model for graphene on nanopatterned substrates indicates the presence a complex sequence of partial unbinding transitions, ended by a complete unbinding transition[1].

On rough SiO_2 substrates, we find an unbinding transition between two and three layers graphene [2]. Quantitative agreement is found between experiments in LPMCN (Lyon France) and our model based on continuum elasticity [1].

In the presence of Silica nanoparticles intercalated between graphene and the substrate [3], we observe experimentally (UMD College Park, USA) a wrinkling transition, and a wrinkle percolation transition when increasing the nanoparticle density. Increasing the number of layers in graphene, we observe the unbinding transition. A simple elastic model is found to be in good agreement with these results.

[1] O. Pierre-Louis Phys Rev E 78, 021603 (2008).
[2] J Nicolle, D. Machon, P. Poncharral, O. Pierre-Louis, A. San Miguel, NanoLetters 13 043017 (2011).
[3] M. Yamamoto, O. Pierre-Louis, J. Huang, M. S. Fuhrer, T. L. Einstein, W. G. Cullen, submitted (2012).

P1.152 Effective interaction between hydrogen atoms adsorbed on graphene

Y Saito, H Kaji and K Kakitani

Okayama University of Science, Japan

Recent ARPES and theoretical studies show that some energy gap and gap states on the hydrogenated graphene.[1] These additional electronic structures depend on the concentration of hydrogen atoms. However, the atomic arrangement of the H atoms on the graphene is not well-defined. In this paper, we discussed the interaction between adsorbed H atoms on the single graphene layer.

We perform the first principles calculation for the hydrogen adsorbed graphene. We employ the generalized gradient approximation within the density functional theory. We use Dacapo package that can handle the plane wave expansion and the ultra-soft pseudo-potential.[2] We consider a 6x6 super cell to describe the single graphene layer. Two H atoms are adsorbed on the super cell.

Calculated density of states show that the H atom behaves as a donor and additional states appear at the Fermi level. We obtain the complicated effective interaction between adsorbed H atoms depending on the arrangement of the adsorbed H atoms. Analysing wave functions of the electronic states near Fermi level, the effective interaction is determined by the symmetry of the electronic states induced by hydrogen adsorption.The attractive and repulsive interaction between H atoms are originated by the indirect bonding and anti-bonding characters of the graphene electronic states, respectively. These effective interaction should be key parameters to study the dynamical hydrogenation process of the graphene.

[1] D. Haberer, et al. Phys. Rev. B83 (2011) 165433.
[2] CAMD, Technical University of Denmark.

P1.153 Electronic properties of super-periodic structures due to dislocated graphene on HOPG

D Yıldız[1], Ş Şen[2], O Gülseren[2] and O Gürlü[1]

[1]Istanbul Technical University, Turkey, [2] Bilkent University, Turkey

Highly oriented pyrolytic graphite (HOPG) is a commonly used crystal in surface science. It is widely employed as a calibration sample for scanning tunneling microscopy (STM) studies. HOPG is composed of stacked two dimensional hexagonal lattices formed by carbon atoms, popularly named as graphene layers. Due to the weak van der Waals bonding between the layers of HOPG, the topmost layers may be shifted or rotated by mechanical or chemical means. Due to the rotation of the top layer, super-periodic structures called as Moiré patterns form on HOPG. These formations were investigated in numerous studies; however, they are rediscovered in graphene research. We used different solvents to see their effects on the HOPG samples and the resulting super-periodic structures on these surfaces. Morphological and electronic properties of these structures are investigated by using scanning tunneling microscopy and spectroscopy (STM and STS) under ambient conditions. Observed properties of Moiré patterns with different periodicities are compared. Particularly some of the Moiré patterns are found to be more stable electronically than the clean HOPG surfaces. The correlation between the patterns and the procedures applied to attain those patterns are looked upon. In order to shed light onto the observed electronic structures we also performed ab initio calculations on these super periodic structures.

P1.154 Gap opening of graphene by dual doping method

J W Yang, G Lee, J S Kim and K S Kim

Pohang University of Science and Technology, South Korea

The band gap opening of graphene is the most desired property in the device industry because it is vital to the application of graphene as a logical device of semiconductors. Here, we show how to make a reasonably wide band gap in graphene. This is accomplished with bilayer graphene (BLG) dual-doped with $FeCl_3$-acceptor and K-donor. To elucidate this phenomenon, we employed the first-principles method taking into account van der Waals interaction. For the $FeCl_3$ adsorbed BLG, the optimal distance between the adjacent graphene and $FeCl_3$ layers is 4.6~4.8 Å, consistent with experiments. Due to the high electronegativity of $FeCl_3$, these graphene layers are hole-doped. The dualdoped BLG gives a band gap of 0.27 eV due to broken symmetry, with a Dirac point shift by 0.09 eV. This increased band gap and proper Dirac point shift could make the dual-doped BLG useful for applications toward future field effect transistor devices.

[1] J. W. Yang, G. Lee, J. S. Kim, and K. S. Kim, JPCL 2, 2577 (2011).

[2] J. Park, S. B. Jo, Y. Yu, Y. Kim, J. W. Yang, W. H. Lee, H. H. Kim, B. H. Hong, P. Kim, K. Cho and K. S. Kim, AM 24, 407 (2012).

P1.155 Graphene/h-BN heterostructures: shaping Dirac fermions for applications and testing QED_{2+1}

J Slawinska, P Kosinski, P Maslanka and I Zasada

University of Lodz, Poland

Combining graphene and hexagonal boron nitride (h-BN) into multilayers as well as hybrids containing nanoribbons and nanotubes provides systems with amazing electronic properties, promising both for fundamental studies and novel applications. By means of tight-binding and density functional theory methods, it is demonstrated that in graphene/h-BN analogue of AB bilayer graphene a substrate-induced energy gap of about 50 meV is opened in the spectrum and can be tuned by external electric field perpendicular to the layers up to 130 or 250 meV depending on the configuration. In the ABC h-BN/graphene/h-BN trilayer the Dirac cones are exactly preserved in the band-structure being the consequence of the intact symmetry between graphene's sublattices. The electric field lifts this symmetry, thus the band-gap is created in the biased system [1-2].

Graphene is called a bridge between condensed matter physics and quantum electrodynamics (QED_{2+1}) [3], in particular the Klein tunneling is observed as the electron propagation through potential barriers with the graphene as the effective medium. TB Hamiltonians describing graphene/h-BN heterostructures enable straightforward analysis of the massive/massless Dirac equation as well as chiral and charge conjugation symmetries. Properties different from free-standing graphene make the hybrids complementary systems elucidating which symmetries are related to anomalies in Klein tunneling phenomenon.

[1] J. Slawinska, I. Zasada, Z. Klusek, PRB 81, 155433 (2010).
[2] J. Slawinska, I. Zasada, P. Kosinski, Z. Klusek, PRB 82 085431 (2010).
[3] P. Kosinski, P. Maslanka, J. Slawinska, I. Zasada, arxiv:1203:4094 submitted to PRB.

P1.156 Lattice spin in graphene and spin from isospin

P Maślanka, P Kosiński, J Sławińska and I Zasada

University of Lodz, Poland

It is well-known that the dynamics of low energy electron in graphene honeycomb lattice near the K-points can be described, in tight-binding approximation, by 2+1 massless Dirac equation. Graphene's spin equivalent, "pseudospin," arises from the degeneracy introduced by the honeycomb lattice's two inequivalent atomic sites per unit cell. Mecklenburg and Regan (Phys. Rev. Lett. 106 (2011), 116803) have shown that, contrary to the common view, the pseudospin has all attributes of real angular momentum. It seems that, in some circumstances, the internal symmetries can produce an important contribution to angular momentum.

This phenomenon has been known for many years in particle physics and called „spin from isospin". Consider the gauge theory with isospin group as a gauge group. Assume all particles entering the theory are bosons so, superficially, there is no spin one-half contribution to angular momentum. Assume further one is quantizing the small oscillations around the monopole solution. The symmetry group includes, generically, the direct product of rotations and isospin group. However, due to the specific monopole configuration, this group is broken down to its diagonal subgroup. Now, if the matter bosons have isospin ½, they give spin ½ contribution to the total angular momentum.

We show that similar mechanism works in the case of lattice pseudospin. The Hamiltonian exhibits a symmetry which results from simultaneous lattice rotations and atom exchange. In the low-energy regime it is promoted to the continuous symmetry which yields, in quite analogous to „spin from isospin", the spin ½ contribution to total angular momentum.

P1.157 Hot carrier relaxation in HOPG probed at the H-point by means of time-resolved XUV photoemission

A Stange, G Rohde, C Sohrt, T Rohwer, S Hellmann, K Hanff, L Kipp, K Rossnagel and M Bauer

Christian-Albrechts-Universität zu Kiel, Germany

Time- and angle-resolved XUV photoelectron spectroscopy (tr-ARPES) is applied to study the relaxation dynamics of excited hot carriers in HOPG. The XUV probe used in the experiment allows us to record electronic structure transients at large momentum values so that in particular the boundary of the first Brillouin zone becomes accessible. In the case of HOPG this capability provides a most direct access to the momentum region relevant for optical excitation and subsequent relaxation of the hot carriers. Our data are indicative for the presence of carrier relaxation channels which act asymmetric onto the hot electron and hole distribution, at least within the first picosecond after excitation. On this time-scale a clear difference in the corresponding carrier temperatures is observed. The results are discussed with respect to other time-resolved experiments which in the past were restricted to probes in the visible/NUV regime.

P1.158 X-ray photoelectron study (XPS and XPD) of few-layer graphene (FLG) on ^{6}H-SiC (0001)

F Djawhar[1], P Jose[1], G Genevieve[1], B Claude[1] and O Abdelkarim[2]

[1]Université de Lyon, France, [2]CNRS, France

Graphene is presently the subject of intense investigation due to its interesting electronics properties. In this context, we have investigated the atomic arrangements of few layers of graphene (FLG) on ^{6}H-SiC (0001) by X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD). C1s core level exhibits several components which can be related to bulk SiC, graphene and interfacial carbon atoms. These C1s components - plus Si2p core level from bulk SiC and O1s from contamination - have been recorded as a function of azimuth angle for different polar angles. As expected, C1s and Si2p XPD curves exhibit a clear six-fold symmetry. For all polar angle except at the 53° polar angle (for which 12-fold is observed), the graphene component exhibits also a clear 6-fold symmetry with the intensity maxima shifted by 30° from the bulk SiC ones. Therefore, we assume that the direct epitaxial relationship between graphite and SiC is defined by SiC [10-10]//graphene [11-20]. We have also determined the O location by comparing O1s and C1s core level XPD azimuth curve background. This background is different for a surface and an interface contamination. We have found evidence for an oxygen migration from FLG surface to the more reactive FLG/SiC interface.

P1.159 Growth and atomic structure of graphene on Ir(332)

V Mikšić Trontl, I Šrut, M Petrović, I Delač, P Pervan and M Kralj

University of Zagreb, Croatia

The growth of large-scale uniform graphene on flat Ir(111) is today well established. The graphene produced by thermally activated catalytic decomposition of ethylene forms a (9.32 x 9.32) moiré superstructure. The moiré structure gives rise to superperiodic potential which forms replica bands and opens minigaps in the π-band of graphene (Dirac cone). Motivated by the possibility to further modify the Dirac cone, e.g. by additional 1D periodic potential introduced by substrate, we have studied the growth and performed scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) investigation of graphene on vicinal Ir(332) surface. The structural properties of graphene grown by temperature controlled growth (TPG) and chemical vapour deposition (CVD) by varying sample temperature and ethylene pressure have been characterized.

LEED results show that the growth process alters the long-range uniformity and 1.1 nm periodicity characteristic for a pristine Ir(332) surface, which is upon graphene growth characterized by new periodicity of much smaller length. STM study of the topology shows that periodic narrower steps are formed but also flat (111) areas, indicating the reshaping of the substrate by step bunching. The width of new formed terraces and degree of step order can be influenced by sample temperature during CVD. We have identified at least three distinct rotational variants of graphene resulting in different moiré patterns. With the insight in the atomic arrangement of carbon lattice on terraces and at the step edges a link between moiré pattern and edge properties is established.

P1.160 Diamond Like Carbon (DLC) film by laser ablation for industrial application

M Khalid[1], M Waqar[1], M Maqsood[1] and M Arif[2]

[1]National Institute of Vacuum Science and Technology (NINVAST), Pakistan, [2]University of Engineering and Technology (UET), Pakistan

Thin film of amorphous carbon (DLC) was deposited on 316 steel using Nd:YAG laser having energy 300mJ. Pure graphite was used as a target. The vacuum in the deposition chamber was generated in the range of 10-6 mbar by turbo molecular pump. Ratio of sp3 to sp2 content shows amorphous nature of the film. This was confirmed by Raman spectra having two peaks around 1300 cm-1 i.e. D-band to 1700 cm-1 i.e. G-band. If sp3 bonding ratio is high, the films behave like diamond-like whereas, with high sp2, films are graphite-like. The ratio of sp3 and sp2 contents in the film depends upon the deposition method, hydrogen contents and system parameters. The structural study of the film was carried out by XRD. The hardness of the films as measured by Vicker hardness tester and was found to be 28 GPa. The EDX result shows the presence of carbon contents on the surface in high rate and optical microscopy result shows the smoothness of the film on substrate. The film posses good adhesion and can be used for industrial purpose.

P1.161 Characterization of graphene growth on commercial available cubic-SiC(001)/Si standard wafers

V Aristov[1], O V Molodtsova[2], A A Zakharov[3], B Thiagarajan[3], O Yu Vilkov[4], D V Vyalikh[5], C Laubschat[5], V V Kveder[1] and M Knupfer[6]

[1]Institute for Solid State Physics (ISSP), Russia, [2]Deutsches Elektronen-Synchrotron (DESY), Germany, [3]Lund University, Sweden [4]BESSY Berlin, Germany, [5]Institute für Photogrammetrie (IFP), Germany, [6]Institut für Weltwirtschaft (IFW), Germany

The best method to produce graphene until now is graphene synthesis on alpha-SiC under high pressure of argon [1,2]. Nevertheless it does not meet the requirements of industrial mass-production because of the limited size and the costly nature of alpha-SiC wafers sliced from the single crystal ingots. If graphene layers can be fabricated on the surface of thin SiC film grown on a large-diameter standard Si wafer (SiC virtual substrate), its industrial impact would be enormous. Such graphene/cubic-SiC(001)/Si wafer could be easily adapted for graphene-based electronic technologies and thus could be directly patterned by standard Si-electronic lithographic processes. The possibility of graphene synthesis on the surface of cubic-SiC(001) thin film (about 1 μm) deposited on standard Si wafer was already demonstrated in Refs. [3-5]. Here we show our recent data of investigation of graphene grown on SiC(001) virtual substrate. It seems that the results represent a realistic way of bridging the gap between the outstanding graphene properties and their technological applications.

[1] K.V. Emtsev et al., Nat. Mater. 8, 203(2009).
[2] M. Sprinkle et al., Phys. Rev. Lett. 103, 226803 (2009).
[3] V.Yu. Aristov et al., Nano Letters 10, 992. (2010).
[4] V.Yu. Aristov at al., Tenth International Conference on the Structure of Surfaces & e-Conference (Hong Kong, China, August 2011), p. 9.
[5] A. Ouerghi et al., Phis. Rev. B 83, 205429 (2011).

P1.162 Chemical termination of graphene nanoribbons – simulation and experiment

L Talirz, J Cai, P Ruffieux, D Passerone, R Fasel and C Pignedoli

Swiss Federal Laboratories for Materials Science and Technology, Switzerland

In order to use graphene as a channel material for electronic switching devices one must first introduce a sizeable band gap into its electronic structure. Such a gap opens naturally in ribbons of graphene when their width is decreased to the nm scale. At this scale the chemical termination of the ribbon edges plays a major role in determining their electronic properties, thus demanding control over the edge termination on the atomistic level.

Recently, atomically precise armchair graphene nanoribbons have been produced in our laboratory via thermally induced polymerization on a metal surface. The chemical termination of their free ends remained an open question. Here we address this question via DFT simulations accompagnied by STM experiments. We find that the outermost carbon atoms of the free zigzag ends are singly hydrogenated. The decay length of the localized end state is compared with simulations.

P1.163 Electronic transport in quasiperiodic graphene p–n–p junctions

M Vasconcelos and E Albuquerque

Universidade Federal do Rio Grande do Norte (UFRN), Brazil

Since the pioneering work of Novoselov *et al.* [1], graphene has been hailed as a promising candidate material for future microelectronic devices. Graphene is a sheet of crystal carbon that behaves as a ballistic conductor with a long mean free path that can be locally gated. In addition, graphene can carry spin currents, and supercurrents at room temperature. Although graphene is similar to carbon nanotubes, from the experimental standpoint the planar character of this material makes it more amenable to microelectronics and nanoelectronic applications. Hence, the researches about the electronic structure and electronic tunneling in arrangements of this material could affect the engineering of computers, mobile phones, security devices and medical applications devices.

On the other hand, the interaction of carriers with electrostatic barriers in this system is strongly influenced by Klein tunneling (i.e. the perfect transmission of carriers through potential barriers at normal incidence). This effect has been studied for periodic potentials and the effect of disorder on the charge transport through multiple barriers has been considered. These results have highlighted the interplay between disorder and resonance effects on the carrier transmission through multiple barriers, which can influence the overall conductivity of graphene-based devices [2].

In this work we investigate the interaction of charge carriers in graphene with a series of p–n–p junctions arranged according to a deterministic quasiperiodic substitutional Fibonacci sequence. Quasiperiodic systems are structures that can be classified as intermediate between ordered and disordered systems. Among the examples of quasiperiodic systems are artificial nanostructured materials with deterministic disorder. The quasiperiodic sequence of p–n–p junctions in graphene gives rise to a potential landscape with quantum wells and barriers of different widths, allowing the existence of quasi-confined states. Spectra of quasi-confined states are calculated for several generations of the Fibonacci sequence as a function of the wavevector component parallel to the barrier interfaces. Our results show that, as the Fibonacci generation is increased, the dispersion branches form energy bands distributed as a Cantor-like set. Besides, we obtain the electronic tunneling probability as a function of energy, obtain large transmission peak for small incidence angles, typical of Klein tunneling.

[1] K. S. Novoselov *et al.*, *Science* 306, 666 (2004).
[2] S.H.R. de Sena et al, JPCM 22, 465305 (2010).

P1.164 Adsorption energy of metal-phthalocyanines on graphene/Ir(111)

C Mariani[1], M Scardamaglia[1], C Struzzi[2], S Lizzit[2], A Baraldi[3], P Lacovig[2], M Dalmiglio[2] and M Grazia Betti[1]

[1]Università di Roma La Sapienza, Italy, [3]Sincrotrone Trieste, Italy, [4]University of Trieste, Italy

Metalorganic molecules deposited on graphene can form ordered architectures. Metal-phthalocyanine (MPc, M-$C_{32}N_8H_{18}$) molecules build up ordered layers on graphene/metal surfaces, thanks to the nanostructured long-range ordered moiré structure deriving from the C-metal substrate lattice mismatch [1]. Recent experiments have shown that different MPc molecules adopt a flat-lying orientation on the graphene moiré superstructure on Ni(111) [2] and Ir(111) [3], with a molecule-graphene interaction strength depending on the central metal atom [2].

In this work, we present Near-Edge X-ray Absorption Fine Structure (NEXAFS) measurements across the N K-edge and X-ray Photoemission Spectroscopy (XPS) core-level data for FePc and CuPc single layers (SLs) adsorbed on graphene/Ir(111). In particular, fast-XPS data as a function of annealing temperature taken at the ELETTRA synchrotron radiation facility (Trieste, Italy) and Thermal Desorption Spectroscopy (TDS) measurements, show a different desorption temperature for FePc and CuPc single-layer on graphene (about 875 K for FePc and about 675 K for CuPc). The higher adsorption energy of the FePc SL on graphene/Ir with respect to the CuPc SL is discussed considering the role of the differently occupied d-states, which contribute to the interaction strength.

[1] J. Mao, H. Zhang, Y. Jiang et al., J. Am. Chem. Soc. 131, 14136 (2009).
[2] W. Dou, S. Huang, R.Q. Zhang, C.S. Lee, J. Chem. Phys. 134, 094705 (2011).
[3] M. Scardamaglia, G. Forte, S. Lizzit, A. Baraldi, P. Lacovig, R. Larciprete, C. Mariani and M.G. Betti, J. Nanop. Res. 13, 6013-6020 (2011).

P1.165 Stamp transferred suspended graphene mechanical resonators for radio frequency electrical readout

X Song[1], M Oksanen[1], M Sillanpää[1], H Craighead[2], J Parpia[2] and P Hakonen[1]

[1]Low Temperature Laboratory of Helsinki University of Technology, Finland, [2]Cornell University, USA

We present a simple micromanipulation technique to transfer suspended graphene flakes onto any substrate and to assemble them with small localized gates into mechanical resonators. The mechanical motion of the graphene is detected using an electrical, radio frequency (RF) cavity readout scheme where the time-varying graphene capacitor modulates a RF carrier at f=5−6 GHz producing sidebands at $f \pm f_m$. A mechanical resonance frequency up to f_m=178 MHz is demonstrated. We find both hardening/softening Duffing effects on different samples and obtain a critical amplitude of ~ 40 pm for the onset of nonlinearity in graphene mechanical resonators. Measurements of the quality factor of the mechanical resonance as a function of dc bias voltage V_{dc} indicates that dissipation due to motion-induced displacement currents in graphene electrode is important at high frequencies and large V_{dc}. Besides the normal metal low-Q LC tank, superconducting circuits are developed as high-Q RF cavities to improve the detection sensitivity, aiming at the thermal motion and quantum limit of the graphene mechanical resonators.

P1.166 Conductance anomaly near the Lifshitz transition in strained bilayer graphene

D Gradinar, H Schomerus and V I Fal'ko

Lancaster University, UK

Strain qualitatively changes the low-energy band structure of bilayer graphene, leading to the appearance of a pair of low-energy Dirac cones near each corner of the Brillouin zone, and a Lifshitz transition (a saddle point in the dispersion relation) at an energy proportional to the strain [M. Mucha-Kruczynski, I.L. Aleiner, and V.I. Fal'ko, Phys. Rev. B 84, 041404 (2011)]. In this work, we show that in the vicinity of the Lifshitz transition the conductance of a ballistic n-p and n-p-n junction exhibits an anomaly: a non-monotonic temperature and chemical potential dependence, with the size depending on the crystallographic orientation of the principal axis of the strain tensor. This effect is characteristic for junctions between regions of different polarity (n-p and n-p-n junctions), while there is no anomaly in junctions between regions of the same polarity (n-n' and n-n'-n junctions).

Topological insulators

P1.167 Interpretation of 2DEG states in topological insulators

T Menshchikova[1], S Eremeev[2], M G Vergniory[3] and E Chulkov[4]

[1]Tomsk State University, Russia, [2]Institute of Strength Physics and Materials Science, Russia, [3]Max Planck Institute for Microstructure Physics, Germany, [4]Donostia International Physics Center (DIPC), Spain

Recently the emergence of two types of 2D electron gas (2DEG) states at the $Bi_2Se_3(0001)$ surface was observed by angle resolved photoemission measurements. These states form a parabolic band in the energy gap just below the conduction band and M-shaped band in the local gap of bulk projected valence band. The 2DEG states can influence charge and spin transport, excited electron and hole lifetimes, electron-phonon interaction as well as induced superconductivity and magnetism on TI surfaces. The 2DEG states arise upon deposition of various magnetic and non-magnetic atoms and molecules. There is well-known fact that atoms deposited on the surface of different layered compounds diffuse into the van der Waals (vdW) spacing and thus induce the expansion of these spacing. In this work, we show that the formation of both parabolic and M-shaped bands in Bi_2Se_3 is caused by the effect of the broadening of the vdW spacing rather than by the chemical nature of the impurities. We show that this effect should be common for all layered topological insulators.

P1.168 Impurity induced electronic scattering in the protected surface state of Bi(111)

C Klein[1], D P Acharya[2], P Zahl[2], P Sutter[2] and M Horn-von Hoegen[3]

[1]University Duisburg-Essen, Germany, [2]Center for Functional Nanomaterials, USA, [3]University of Duisburg-Essen, Germany

Bi(111) shows a pronounced 2d conductivity in the surface state, which for epitaxial Bi(111) films on Si substrate does not depend on the film thickness between 6 nm and 60 nm. Due to the large spin orbit coupling electron backscattering is strongly suppressed. In order to identify possible scattering mechanism we performed low temperature scanning tunneling microscope (LT-STM) measurements in which sub-ML amounts of Fe and Co were directly deposited into the STM at 5K. After deposition of 0.01% of a monolayer ($1ML = 5.6 \times 10^{14}$ Bi atoms cm^{-2}) the deposited metal atoms are embedded in a sub surface site, as they are not visible in topology. However, in dI/dV images the embedded impurities become apparent as they are surrounded by a pronounced anisotropic threefold scattering pattern with dimensions of more than 10 nm. The pattern has an amplitude of ±0.2 Å in constant current mode and is visible at energies ±0.5 V around the Fermi energy, where the pattern shows the strongest corrugation. Large changes of the scattering pattern as function of the tunneling bias reflects the dispersion of the occupied and unoccupied surface states of Bi(111). In our experiments, we find the scattering pattern in the case of Co and Fe impurities to be more than 10 times larger than that of single Bi atoms. During co-deposition of different impurities an identification of the embedded elements is possible due to a slightly different size of the scattering pattern. We attribute this effect to different sub-surface embedding levels which seems to be specific for the individual element.

P1.169 Electronic structure of Fe and Co magnetic adatoms on Bi_2Te_3 surfaces

L Shelford[1], T Hesjedal[2], L Collins-McIntyre[2], S Dhesi[1], F Maccherozzi[1], G Van Der Laan[1]

[1]Diamond Light Source, UK, [2]Oxford University, UK

Topological insulators (TI) have gained strong interest from the scientific community as a new class of materials with fascinating yet exotic physics which offers a large potential for applications in the field of spintronics. TIs host a gapless topological surface state which exhibits a Dirac-cone like dispersion. The topological surface state is protected by time reversal symmetry (TRS) which leads to a variety of interesting effects.

We investigate the influence of low coverages (~0.5% monolayer) of ferromagnetic adatoms on a substrate of the TI Bi_2Te_3 via x-ray magnetic circular dichroism (XMCD). We find that the magnetization curve obtained for Fe atoms deposited at ~1.5K is qualitatively indicative of paramagnetic behavior of the individual atoms with no evidence of long range magnetic ordering. We find a spin magnetic moment ratio of 0.46 for Fe and 0.42 for Co. The line-shape of the XMCD profile indicates that the impurity adatoms hybridize weakly with the substrate material; a state somewhere between that expected for a single atom and a delocalized metal. Our results suggest that magnetic impurities on the surface of the sample do not break the time-reversal symmetry in topological insulators.

Poster abstracts

Poster session ECOSS/ECSCD (C/D)
Wednesday 5 September and Thursday 6 September

Biological interfaces

P2.001 Electron spectroscopic analysis of stratum corneum lipids: Plasma-induced changes in lipid composition

M Marschewski[1], J Hirschberg[2], T Omairi[2], O Höfft[1], S Emmert[3], W Viöl[2] and W Maus-Friedrichs[1]

[1]TU Clausthal, Germany, [2]HAWK Göttingen, Germany, [3]Universitätsmedizin Göttingen, Germany

The lipids of the stratum corneum loom large for the barrier function of human skin. Recently several important findings related to mutations of the fillaggrin-gen and according to this, diseases like ichthyose and atopic dermatitis were made but not yet completely understood. Cold plasma treatment on e.g. skin diseases causes in an abatement of diseases by the assured disinfected effect of plasma [1].

In addition to cholesterol, the basic structure of the stratum corneum lipids consists of ceramides and free fatty acids. We correlated these three components with the binding states of the lipid probes under the prediction that we only detect these three components and compared our measurements to previous works [2,3,4]. Based on these procedure we were able to fix binding energies, distances between the Gaussian's curves and also full widths of half maximum (FWHM) for all following measurements which finally led to considerably reproducible results.

Here, we present our results on the characterisation of skin lipids, studied with X-ray photoelectron spectroscopy. Furthermore we have investigated the change in plasma treated skin samples to understand the basic effects of plasma treatment of biological systems.

[1] Morfill G E, Shimizu T, Steffes B and Schmidt H-U New Journal of Physics 2009: 11: 115019.
[2] Goddard E D, Harris W C. J Soc Cosmet Chem 1987: 38: 295-306.
[3] Michel R, Subramaniam V, McArthur S L. Langmuir 2008: 24: 4901-4906.
[4] Yang D Q, Sacher E. Surface Science 2003: 531: 185-198.

P2.002 Mechanistic control of amyloid fibril oligomer populatiions

K Eden, R Morris, C MacPhee and R Allen

The University of Edinburgh, UK

Filamentous protein aggregates such as amyloid fibrils have been associated with a wide variety of degenerative diseases. Evidence increasingly suggests that it is not the fibrils but rather their early precursor oligomers which are responsible for cell damage. Using kinetic Monte Carlo simulations, we explore modifications to existing auto-catalytic polymerisation models and demonstrate a variety of aggregation pathways which lead to differences in the oligomer load on the system.

Complex systems: large organic molecules, self-assembly and self-organisation

P2.003 Monte Carlo simulation of the self-assembly of cross-shaped molecules adsorbed on a solid surface

A Kasperski and P Szabelski

Maria Curie-Skłodowska University, Poland

We use the Monte Carlo simulation method to examine the effect of size and aspect ratio of a cross-shaped molecular building block on the morphology of the resulting self-assembled overlayer. The simulations were performed on a square lattice using the conventional canonical ensemble MC technique with Metropolis sampling. The adsorbed molecules were modeled as rigid structures composed of a central segment called core connected with two pairs of orthogonal arms [1]. We considered different molecular structures obtained by a suitable shortening/elongation of one arm or of a pair of collinear arms of the parent C_4 symmetric molecule. Additionally, we studied the influence of chemical composition of the molecules on the symmetry of the simulated assemblies. It was observed that, depending on geometrical features and chemistry of the building block, the self-assembly can lead to the formation of ordered chiral and achiral porous networks with largely diversified pore shape and size. The insights from our theoretical studies can be useful in designing two-demensional molecular architectures in which such molecules as porphyrines and phthalocyanines are used as building blocks.

[1] P.Szabelski, A.Kasperski, Top. Catal. 54 (2011) 1368.

P2.004 Nanopatterning of Si(001) by a self-organized bottom-up process

H Hosseinzadeh, Y Hu, A Kumar Das and R Koch

Johannes Kepler University of Linz, Austria

By means of scanning tunneling microscopy (STM) and Monte Carlo simiulation, we have investigated the epitaxial growth of Si on Si(001) under conditions at which the (2×n) superstructure is forming. Our STM investigations reveal that the morphology of the surface periodically changes with the surface coverage of Si. A regular (2×n) stripe-pattern is observed at coverages of 0.7-0.9 monolayers that periodically alternates with less dense surface structures at lower Si surface coverages. The Monte Carlo simulations evidence that the growth of Si is affected by step-edge barriers, which favors the formation of a rather uniform two-dimensional framework- like configuration. Finally, deposition of Ge onto this nanopatterned Si(001) template has been investigated.

P2.005 Properties of Asp, Glu, Gly and Leu on the Fe_3O_4-(111)-surface: A forcefield simulation study

A Bürger, U Magdans and H Gies

Ruhr-University Bochum, Germany

Magnetite (Fe_3O_4) crystallises in the inverse spinel structure[1]. In nature magnetite is an important biomineral. Magnetotactic bacterias, e.g., use magnetite single-crystals to orientate themselves in the earth magnetic field. The connection between the inorganic magnetite-(111)-surface and the organic parts of the animals is the magnetosome membrane (MM). The composition of the MM of the magnetotactic bacteria *Magnetospirillum gryphiswaldense* has been analysed[2, 3]. The MM is built by different magnetosome membrane proteins (MMPs). Two of these MMPs are the proteins MamJ and MamG. The structure of MamJ is dominated by the amino acids aspartic acid (Asp) and glutamic acid (Glu) whereas MamG is dominated by glycine (Gly) and leucine (Leu). Forcefield simulations of the interaction of the magnetite-(111)-surface and the membrane offer the possibility to investigate if and how the amino acids interact with the surface. Additionally, it is possible to investigate the interactions and the adsorption distances between the surface atoms and the functional groups of the amino acids.

We have chosen the COMPASS-forcefield because all parameters of the surface and of the amino acids are defined in this forcefield. As simulation software we used Forcite which is integrated in the Materials Studio 5.0 software package. In addition to that we use the magnetite-(111)-surface that had already experienced relaxation[4]. Based on the assumption the surface has been defined as a constraint.

The amino acids may adsorb in a docking box built by a 47.49 Å x 47.77 Å magnetite-(111)-surface and a 27 Å vacuum slab. For every amino acid 10000 frames has been calculated. The results show that it is energetically favourable for the amino acids to adsorb on the surface. All of them adsorb in Fe-O-distances between 2.6 and 2.7 Å. The involved O-atoms belong to the carboxyl-group (Asp) or to the carboxylate-group (Gly, Glu and Leu). From this it follows that electrostatic interactions dominate. This conclusion can be proven by the results.

Summing up we can show that it is energetically favourable for all of the amino acids to adsorb on the magnetite-(111)-surface and that the electrostatic interaction dominates during adsorption.

[1] Fleet ME (1981) Acta Crystallogr B 37:917-920.
[2] Grünberg K, Müller EC, Otto A, Reszka R, Lindner D, Kube M, Reinhardt R, Schüler D (2004) Appl Environ Micro 70:1040-1050.
[3] Schüler D (2004) Arch Microbiol 181:1-7.
[4] Ritter M, Weiss W (1999) Surf Sci 432:81-94.

P2.006 Ordering of copper phthalocyanine adsorbed on Ag-passivated Si(111)-$\sqrt{3}$x$\sqrt{3}$R30° studied by SPALEED and STM

T Wilkens, T Schmidt and J Falta

University of Bremen, Germany

Organic semiconductors are very promising materials for the use in electronic and opto-electronic devices as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), or even organic solar cells. The ordering of copper phthalocyanine (CuPc) thin films on substrates like silicon is mainly influenced by the molecule´s mobility on the surface. In case of Si(111) it is essential to passivate the surface before CuPc adsorption in order to achieve ordered films, because on unpassivated Si(111)-7x7 the CuPc molecules are unable to diffuse which leads to the formation of disordered films [1].

High-purity CuPc was evaporated on the silver-passivated Si(111) surface at room temperature. The adsorption of CuPc on the Ag/Si(111)-$\sqrt{3}$x$\sqrt{3}$R30° surface was investigated by STM and SPALEED. The SPALEED pattern shows that the CuPc molecules are ordered in three rotational domains. The lattice in these domains could be determined to be non-square but rhombic with measured angles of about 88° and 92°, respectively. The dimension of the unit cell of the CuPc layer is close to the size of the molecule from which one can conclude that the molecules lie flat on the surface.

These results are in reasonable agreement with the results obtained from STM measurements of cobalt phthalocyanine adsorbed on Ag/Si(111)-$\sqrt{3}$x$\sqrt{3}$R30° by Upward et al. [2], who suggest a model with 3x3 molecules forming one unit cell with characteristic angles of 87.8° and 92.2°, respectively.

[1] J. Gardener et al.; Surf. Sci. 602, 843-851 (2008).
[2] M. D. Upward et al.; Surf. Sci. 441, 21-25 (1999).

P2.007 Interface state formation at the PTCDA/Ag(100) interface studied with 2PPE

M Marks, M Galbraith and U Höfer

Philipps-Universität Marburg, Germany

The formation of interface states at metal-organic interfaces has huge influence on the interfacial electron dynamics and the injection of free charge carriers into the organic layers. Due to the complex interactions at such interfaces, the underlying mechanisms of the formation of unoccupied metal-organic interface states can best be investigated for well ordered organic thin films on single crystal surfaces. Using time- and angle-resolved 2-photon photoemission (2PPE) an unoccupied interface state was characterized for the interfaces between monolayers of PTCDA and NTCDA and a Ag(111) surface [1]. The state emerges from an upshifted Shockley surface state that interacts with molecular states. The binding energy of the interface state is mainly determined by the adsorption height of the organic molecules and the relative density of molecules per unit cell area [2]. The wave function overlap with molecular states is mainly modified by the bending of the carboxyl end groups.

In contrast to the Shockley surface state of the Ag(111) surface which lies in the projected band gap of the substrate, an unoccupied Shockley resonance degenerate with the lower sp-band forms on the Ag(100) surface. In our contribution we show, that with adsorption of PTCDA on Ag(100) a strongly-dispersing interface state forms at $E-E_F= 2.25 \pm 0.03$ eV. The main contribution to the interface state stems from the Shockley resonance which shifts to 0.95 eV higher energies. The energy shift is 250 meV larger compared to the PTCDA/Ag(111) model system. As PTCDA is stronger bound on Ag(100) and a smaller adsorption distance is found, the stronger shift corroborates our results for PTCDA and NTCDA on Ag(111). An effective decay of excited electrons via electron-hole pair leads to an inelastic lifetime between 3 and 18 fs. Our results indicate that Shockley-type interface states are a more general phenomenon for a larger class of metal-organic interface model systems and do not depend on an occupied Shockley state of the bare surface.

[1] C. H. Schwalb et al., Phys. Rev. Lett. 101, 146801 (2008).
[2] M. Marks et al., Phys. Rev. B 84, 081301(R) (2011).

P2.008 Interaction between metal-phtalocyanines and metallic substrates

E Rauls and W G Schmidt

Universität Paderborn, Germany

Phtalocyanines (Pc) with or without metal center are currently under intense investigation in surface physics. The biocompatibility of these molecules together with their electronic structure makes them highly interesting for energy transfer processes in medical applications. In nanotechnology, they are especially useful due to their flexibility, since the basis of these molecules can easily be varied with different functional groups substituting parts of the molecule or simply attached to the core of the molecule. Upon exchanging the center atom, the binding energy to a substrate, the molecular deformation or the spin state can be tailored.

In this work, we present our first principles investigations of Co-Pc and Cu-Pc on Au(100)-surfaces. In contrast to our previous studies of similar porphyrins on Au(111) [1] or Au(110) [2], the flat surface geometry does not induce the strong deformations observed in these cases. A comparatively strong interaction of the complete molecule with the substrate is observed. We, furthermore, investigated the formation of multiple molecular layers, as are needed e.g. for organic transistors. In experiment, a structural transformation is observed, with the molecules lying flat in the beginning and moving to a standing arrangement for higher Pc film thicknesses. Most probably, a buried interface structure is formed, the structure of which we address by our calculations.

[1] S. Müllegger, E. Rauls, et al. ACS Nano 5, 6480 (2011).

[2] E. Rauls, W.G. Schmidt, T. Pertram, K. Wandelt, Surf. Sci. (submitted, 2012).

P2.009 Adsorption of PTCDA on KCl and NaCl Surfaces

E Rauls, H Aldahhak and W G Schmidt

Universität Paderborn, Germany

The ability to grow self-assembled supramolecular nanostructures on solid surfaces has important implications in both basic science and nanotechnology.

In recent years, metal surfaces were used as the most common substrate. However, the surfaces of alkali salts like sodium or potassium chloride, open up new possibilities. Surface symmetry and ionicity as well as technological reasons, like e.g. simple mechanisms for the desorption of grown supramolecular assemblies, make these surfaces a worthwile alternative to metal substrates.

We present our investigations of the adsorption of PTCDA on KCl and NaCl (100) surfaces. In AFM investigations, arrangements of both flat-lying (P-type) [1] as well as standing molecules (S-type) [2] have been observed experimentally depending on preparation conditions. In order to understand the different mechanisms of the formation of these structures on the atomic scale, we have performed first principles density functional theory calculations, focussing on both the geometric and electronic structure of single molecules as well as a large variety of different molecular assemblies at varying coverages. Especially the charge transfer plays an important role in these systems.

[1] M. Möbus, N. Karl, T. Kobayashi, Journal of Crystal Growth116 (1992) 495-504.
[2] Thomas Dienel, “Molekulare Systeme im Wechselspiel von Struktur und Ladung”, Dissertation TU Dresden (2009).

P2.010 Adsorption of diindenoperylene on Cu(111) Surfaces

E Rauls, H Aldahhak and W G Schmidt

Universität Paderborn, Germany

Thin films of organic molecules like diindenoperylene (DIP) on metal substrates are of great interest for the further miniaturization of organic optoelectronic devices. As recently reported, films of DIP molecules on Cu(111) surfaces behave ambipolarly. In contrast to deposition on largely extended terraces, deposition of DIP molecules on narrow terraces (<15 nm) of Cu(111) leads to an interesting structure with co-directionally oriented molecules, the symmetry of which is not dictated by the hexagonal substrate symmetry [1].

In order to clarify this behavior, we investigated the balance between intermolecular and molecule-substrate interactions in this system. We performed first principles density functional theory calculations for various adsorbate structures. For isolated DIP molecules, the calculation of the potential energy surface (PES) allows us to determine the activation energy for the mobility of the molecules as a prerequisite for self organisation. At higher coverages, the molecules are found to organise in adsorbate structures which agree well with the experimental findings in [1].

[1] De Oteyza et al., Phys. Chem. Chem. Phys. 11, 8741 (2009).

P2.011 Monte Carlo modelling of molecular rhombus tilings

A Stannard, Juan Garrahan, Peter Beton

University of Nottingham, UK

Recent experiments have demonstrated the formation of entropically-determined 2D self-assembled molecular networks formed by tetracarboxylic molecules at the solid/liquid interface between highly-ordered pyrolytic graphite and alkanoic acids [1,2]. Each molecule forms up to four intermolecular hydrogen bonds and may be mapped onto a lozenge rhombus tile, having common edges with up to four other rhombi. These molecular rhombus tilings are imaged using scanning tunnelling microscopy (STM) in liquid.

Using a simple Monte Carlo (MC) model [2-4], the equilibrium properties of these systems may be determined and compared to experimental results, permitting quantification of randomness in these molecular networks. The degree of intermolecular disorder may be adjusted to create tilings which are more, or less, random. This can achieved through multiple routes: changing the solvent; modifying certain intramolecular distances; or using additional adsorbates to stabilize particular structural motifs. By a combination of STM and MC modelling, a range of elementary structural motifs arising due to intermolecular disorder can be studied.

[1] M.O. Blunt et al, Science 322, 1077 (2008).
[2] A. Stannard et al, Nature Chem. 4, 112 (2012).
[3] J.P. Garrahan et al, Proc. Natl. Acad. Sci. USA 106, 15209 (2009).
[4] A. Stannard et al, Phys. Rev. E 82, 041109 (2010).

P2.012 Chain-length and temperature dependences of the structures of alkylthiolate self-assembled monolayers on metal (111) surfaces

Y Wang[1], M Alcamí[1], F Madrtín[1], J G Solano Canchaya[2] and H Fabio Busnengo[2]

[1]Universidad Autonoma de Madrid, Spain, [2]Instituto de Física Rosario (CONICET-UNR)

During the last decades, self-assembled monolayers (SAMs) of alkylthiolates $S(CH_2)_{n-1}CH_3$ (hereafter C_n for short) on metal surfaces have been the focus of numerous experimental and theoretical studies, owing to their convenience of preparation, relatively high stability, high structural ordering, good adhesion to the surface and easiness of functionalization.

Here we present our systematic studies on C_n ($n = 3 \sim 20$) SAMs on various metal (111) surfaces at different temperatures using large-scale atomistic molecule dynamics (MD) simulations. One of the advantages in our simulation over other previous ones is the use of more reliable force field exclusively for the chain-chain interaction among alkylthiolates which was recently developed by us based on high-level quantum chemical (MP2) computations [1,2]. The present study focuses on C_n SAMs hexagonally packed at saturation coverage on various metal (111) surface. We aim to clarify the dependence of chain-length, lattice spacing of the SAM, and temperature on the structure of C_n SAMs, which also makes this study unique. Furthermore, an ordered-to-ordered phase transition of C_n SAMs due to temperature variation is also discovered. The MD simulations results are further understood by proposing a simple model, which gives us some important conclusions with more clear physical meanings.

[1] J. S. Canchaya, Y. Wang, M. Alcamí, F. Martín, and H. Busnengo, Phys. Chem. Chem. Phys. 12, 7555 (2011).
[2] P. Abufager, J. S. Canchaya, Y. Wang, M. Alcamí, F. Martín, L. A. Soria, M. Martiarena, K. Reuter, and H. Busnengo, Phys. Chem. Chem. Phys. 13, 9353 (2011).

P2.013 Ordering of Schiff base diamines on Au(111)

M Räisänen[1], M Buck[2], M Leskelä[1] and T Repo[1]

[1]University of Helsinki, Finland, [2]University of St Andrews, UK

Well-ordered two-dimensional nanostructures on surfaces are of immense interest as they have potential applications in various fields, e.g. molecular electronics, biomaterials and catalysis [1]. In preparation of the nanostructures so called bottom-up approaches, such as self-assembled monolayers (SAMs), have an advantage over conventional top-up methods as smaller feature sizes are accessible [2]. Various Schiff bases have been found to form spontaneously a monolayer on the metal surface and thus act as an effective corrosion inhibitor [3]. Schiff bases are also an important class of ligands for metal complexes which have for example interesting catalytic, structural and magnetic properties [4]. Despite of their significance in numerous fields of applications, surface structures of Schiff base compounds on a metal surface have been only rarely studied on (sub)molecular level [5]. Here we report SAMs of two Schiff base diamines, 2,2'-[(3,3'-diamino[1,1'-biphenyl]-4,4'-diyl)bis[(E)-nitrilomethylidyne]]bis[4,6-bis(1,1-dimethylethyl)-phenol (1) and 2,2'-[(3',4-diamino[1,1'-biphenyl]-3,4'-diyl)bis(nitrilomethylidyne)]bis[4,6-bis(1,1-dimethylethyl)-phenol (2), on Au(111)/mica studied by means of scanning tunneling microscopy under ambient conditions. Both compounds formed well-ordered highly crystalline structures when deposited on the surface from dilute solutions at 65 °C. SAM of 1 was prepared also at 25 °C resulting in the same structure as at elevated temperature which indicates that the formed structure is stable within this temperature range.

[1] (a) F. Schreiber, J. Phys. Condens. Matter 2004, 16, R881. (b) D. Vuillaume, S. Lenfant, Microelectron. Eng. 2003, 70, 539.
[2] V. Balzani, Small 2005, 1, 278.
[3] (a) S. Şafak et al.,Corros. Sci. 2012, 54, 251. (b) H. Keleş, Mater. Chem. Phys. 2011, 130, 1317–1324.
[4] (a) P. G. Cozzi, Chem. Soc. Rev. 2004, 33, 410. (b) K. C. Gupta, A. K. Sutar, Coord. Chem. Rev. 2008, 252, 1420. (c) H. Miyasaka et al., Coord. Chem. Rev. 2007, 251, 2622.
[5] (a) S. Kuck et al., ChemPhysChem 2009, 10, 2008. (b) S. Weigelt et al., Angew. Chem., Int. Ed. 2007, 46, 9227. (c) Q. Zhenlan et al., Chinese Sci. Bull., 2002, 47, 990. (d) D.-S. Kong et al., Electrochim. Acta 2002, 48, 303.

P2.014 Bonding configurations of C_{60} molecules on Au(111)

L Tang, Y Xie and Q Guo

University of Birmingham, UK

By using scanning tunneling microscopy (STM), we have studied the orientation and adsorption site of C_{60} molecules on Au(111) [1], and furthermore probed the buried C_{60}/Au(111) interface with Au atoms.

A complex orientational ordering has been observed for molecules inside the “in-phase” (R0°) domain. A 7-molecule cluster consisting of a central molecule sitting atop of a gold atom and 6 tilted surrounding molecules is identified as the structural motif. The $2\sqrt{3} \times 2\sqrt{3}$-R30° phase consists of molecules bonding to a gold atomic vacancies with a preferred azimuthal orientation. The quasi-periodic R14° phase is composed of groups of similarly oriented molecules with the groups organized into a $4\sqrt{3} \times 4\sqrt{3}$-R30° like super-lattice unit cell.

To characterize the C_{60}/Au(111) interface, we send Au atoms “diving” through the C_{60} layer and observe their behavior at the interface. The interfacial diffusion of gold atoms and the nucleation of small Au islands at the interface are found to be strongly dependent on the local C_{60}-Au(111) bonding which varies from one domain to another. The same probing method can be extended to study C_{60} bonding on other metal surfaces such as Ag(111) where dim and bright molecules have also been observed in STM images.

[1] L. Tang, Y. Xie and Q. Guo, The Journal of Chemical Physics 135 (2011) 114702.

P2.015 Construction of 2-D metal organic architectures on Au{111}

C Baddeley, R Seljamäe Green, J Greenwood, S Francis, H Fruchtl, K Wilson and A Trant

University of St Andrews, UK

The growth of 2-D metal organic architectures on metal surfaces has been an area of considerable recent interest. We are particularly interested in the growth of chiral 2-D architectures for potential application in the field of enantioselective heterogeneous catalysis. Our strategy has been to use well established methods (1) to grow arrays of 2D nanoclusters of Ni in the elbows of the Au{111} herringbone reconstruction via metal vapour deposition in ultrahigh vacuum. The metallic nanoclusters are then exposed to chiral amino acids such as glutamic acid (2), aspartic acid, lysine and proline. Scanning Tunnelling Microscopy (STM) has revealed the formation of a rich array of 1- and 2-D metal organic architectures on Au whose structures are strongly influenced by the Ni cluster size, the herringbone reconstruction, thermal treatment and the nature of the amino acid. In addition, we have examined the interaction of the catalytically important pro-chiral molecule, methylacetoacetate (3), with the metal organic structures to identify docking, chiral recognition and chiral amplification effects which may be exploitable catalytically.

[1] D.D. Chambliss, R.J. Wilson, S. Chiang, Physical Review Letters 66 (1991) 1721-1724.
[2] A.G. Trant, T.E. Jones, C.J. Baddeley, Journal of Physical Chemistry C 111 (2007) 10534-10540.
[3] A.G. Trant, C.J. Baddeley, Langmuir 27 (2011) 1788-1795.

P2.016 Organic heteroepitaxy of PTCDA and SnPc on single crystalline metals

R Forker, M Gruenewald, K Wachter, F Sojka and T Fritz

Friedrich-Schiller-University Jena, Germany

We report on the optical/electronic interaction at metal-organic and organic-organic interfaces in highly ordered ultrathin layers of the organic molecules 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and tin(II)-phthalocyanine (SnPc) on Ag(111) and Au(111). The thin films were characterized optically by *in situ* Differential Reflectance Spectroscopy (DRS), followed by an extraction of the related optical constants. For the first monolayer of PTCDA or SnPc, respectively, the metal-organic interaction is manifested in broad and structureless absorption spectra. The degree of broadening and the spectral position differ remarkably for both metals. This is explained by the much stronger chemisorptive interaction between both molecular species and Ag(111) as compared to the physisorptive interaction with Au(111). Further layers of PTCDA or SnPc, however, are efficiently optically decoupled from the respective first monolayers. This is deduced from the observation of vibronically resolved monomer signatures until aggregation occurs, thereby forming molecular stacks. Decoupling effects are also observed for stacked heterostructures. This means that the optical spectra of the second layer of a given molecule are similar, regardless of whether they are deposited on a PTCDA or on a SnPc wetting layer. Yet, certain characteristic differences will be discussed: For PTCDA on SnPc a small additional feature occurs in the spectra. This is tentatively explained by a stronger hybridization of the SnPc contact layer due to the adsorption of PTCDA. For SnPc the aggregation behavior on the PTCDA monolayer and on the SnPc monolayer differ noticeably which is evidenced by the spectral development and further corroborated by low-energy electron diffraction (LEED).

P2.017 Adsorption of EP-PTCDI films grown on Cu (100) studied by STM, LEED and DFT calculations

J C Moreno-López[1], L Salazar-Alarcón[1], O Grizzi[1], V A Esaulov[2], M L Martiarena[1] and E A Sánchez[1]

[1]Centro Atómico Bariloche - Comisión Nacional de Eneregía Atómica and CONICET, Argentina, [2]Université Paris Sud 11, France

We present results of the initial stages of the adsorption of N,N'-bis(1-ethylpropyl)-perylene-3,4,9,10-tetracarboxdiimide (EP-PTCDI) on Cu(100).

Scanning tunneling microscopy results show that, contrary to the case of Si(111)7x7 [1] and Ag(111) [2], the EP-PTCDI molecule adsorbed in Cu(100) presents an intermediate lateral mobility, where the adsorption starts somewhere in the middle of the terraces. The molecules form ordered islands with a unique arrangement, oriented in four different directions. This growth proceeds until completion of the first monolayer. The experimental results and the simulations of LEED patterns suggest that the molecular arrangement can be explained by a commensurate superstructure and its four rotational equivalents.

On the other hand, dual-scan-mode STM images obtained in both forward and backward scan directions with inversed bias polarities show different features. These results are discussed in terms of the simulation of occupied and un-occupied electron state images performed by density functional theory calculations including Van der Waals interactions.

[1] L.N. Serkovic Loli, J. E. Gayone, E.A. Sánchez, O. Grizzi, and V.A. Esaulov, Acta Microscopica 18 Supp. C, 295-296 (2009).

[2] L.N. Serkovic Loli, J.E. Gayone, M.L. Martiarena, E.A. Sánchez, O. Grizzi, L. Pasquali, B. Doyle, S. Nannarone, H. Hamoudi, C. Dablemont and V.A. Esaulov, Journal of Physical Chemistry C 113, 17866-17875 (2009).

P2.018 1,4-benzenedimethanethiol self assembled monolayers on Au(111) and Ag(111) from vapour phase: stability with surface temperature

L Salazar Alarcon[1], L J Cristina[1], J Shen[2], L Chen[2], V Esaulov[2], J E Gayone[1], M L Martiarena[1], E A Sánchez[1] and O Grizzi[1]

[1]Centro Atómico Bariloche - Comisión Nacional de Eneregía Atómica and CONICET, Argentina, [2]Universite Paris Sud and CNRS, France

We present results of a vacuum evaporative absorption method of assembly of the conjugated dithiol molecule 1,4-benzenedimethanethiol on the surfaces of Au(111) and Ag(111). Direct recoil spectroscopy with time-of-flight analysis shows in both cases formation of a standing up self-assembled monolayer (SAM) with S atoms available at the SAM-vacuum interface. Investigation of the adsorption kinetics shows that a lying down phase is formed at low exposures, which precedes the SAM phase. At room temperature, optimal conditions for standing up SAM formation require exposures of the order of a mega Langmuir, while around 250 K, a few kilo Langmuir are sufficient to form the dense layer. Multilayer formation is observed when the adsorption is performed below 250 K. A study of the SAM stability with temperature shows: i) the multilayer desorbs around 265 K, ii) the S terminated layer survives up to ~370 K, above this temperature a reordering of the layer takes place where S atoms are no longer available at the vacuum interface, iii) final desorption occurs around 500K. Analysis of the products remaining after surface annealing reveals C and S for the SAM phase and only S for the lying down phase. The C content left at the Ag surface is higher than that left at the Au surface. The scattering features are discussed in terms of DFT calculations that show the changes occurring in the molecule geometry during both phases.

P2.019 Long range ordered binary monolayers of sulphur containing donor molecules and TNAP on Au(111) investigated by LEED and STM

B Fiedler, E Rojo-Wiechel, J Klassen, S Gärtner and M Sokolowski

Universität Bonn, Germany

Binary mixtures of electron accepting and electron donating substances are interesting materials for use in organic electronics, since these mixtures can be isolators, semiconductors, or even metallic conductors. The electrical properties of these materials are strongly related to their structure. For organic electronics thin films of these materials are of particular interest. Therefore we prepared pure and mixed monolayers of the electron acceptor tetracyanonaphthoquinodimethane (TNAP) and two electron donating molecules, namely tetrathiotetracene (TTT) and tetrabenzothianthrene (TBTA), on Au(111). The films were studied by LEED and STM. Pure TTT shows a complex film growth with a disordered phase at low coverage and an ordered phase at high coverage. The deposition of TTT leads to a lifting of the Au(111) surface reconstruction, while for TBTA as well as for TNAP the Au(111) surface reconstruction is preserved after deposition. In case of TBTA, the adsorbate domains are aligned with the reconstruction domain of the Au(111) surface. The unit cells of the ordered monolayers of TTT and TNAP exhibit similar size and shape, with molecules arranged in brick wall type structures. Quite differently, in the mixed film the molecules are arranged in alternating parallel rows of one type of molecule. Interestingly, the two dimensional arrangement of TTT and TNAP is rather similar to that in alternating stacks of TTF/TCNQ bulk charge transfer crystals. The row like arrangement is also found for TBTA/TNAP, but unlike TTT/ TNAP we also found more complex porous arrangements.

P2.020 Comparison of self-assembly of TMPyP and TTMAPP porphyrin molecules on an iodine-modified Au(100) surface

T Kosmala, M Schneider and K Wandelt

University Bonn, Germany

The self-assembly of Tetra(N-methyl-4-pyridyl)-porphyrin molecules (TMPyP) and Tetra(4-trimethylammoniophenyl) porphyrin molecules (TTMAPP) on an iodide-modified Au(100) electrode surface has been studied by means of in-situ Electrochemical Scanning Tunneling Microscopy (EC-STM) with submolecular resolution. This enables unprecedented insight into such self-assembly phenomena at solid-liquid interfaces in the presence of anions and organic molecules as a function of electrode potential.

Porphyrins are well-known to play a very important role in natural vital processes such as in heme for transfer and storage of oxygen in blood or chlorophyll for the photosynthesis of green plants. Furthermore they open a range of potential applications in cancer therapy, or as catalysts and sensors.

The I/Au(100) surface was found to be a good substrate for the self-assembly of highly ordered layers of porphyrin cations. Furthermore iodide-modified Au(100)-surfaces show several phase transitions (from $(2\sqrt{2}xp\sqrt{2})$over $(2\sqrt{2}x\sqrt{2})$to $(4x\sqrt{129})$) and electrocompression dependent on the electrode potential.

Results of the investigations of TMPyP and TTMAPP molecules on an iodide-modified Au(100) surface in both cases show long-range periodic superstructures beyond the molecular arrangement with phase transitions between them which are dependent on the substrate structure and applied electrode potential.

P2.021 Effects of electron-beam irradiation on phospholipid/amino acid complexes

R Panajotovic[1], M Schnietz[2], A Turchanin[2], N Mason[3] and A Gölzhäuser[2]

[1]University of Belgrade, Serbia [2]University of Bielefeld, Germany, [3]The Open University, UK

The self-assembling property of lipids makes them an ideal substrate for studying radiation damage effects on molecules such as DNA, amino acids, proteins, etc. They are also used in biosensors, especially in the OFET configuration with the graphene layer [1] between lipids and SiO_2 substrate. Electrons, and especially the low-energy ones produced either as secondary particles or from the STM tip in high-resolution imaging, proved to produce significant alterations to the structure of such sensitive molecules and their complexes [2]. The latter is supported with a recent study of the effectiveness of a monoenergetic electron beam as a tool for shaping biosensors and biochips, as has been previously done with simpler aromatic molecules [3].

In this study we are using several experimental methods (XPS, FTIR, AFM, and STM) in assessing the level of degradation of thin phospholipid films (DPPC) alone and their complex with amino acid arginine, on different substrates – SiO_2, gold-coated silicon wafer, and CaF_2 crystal. DPPC was irradiated by electrons of energy between 10 and 500 eV and the shifts and intensity of the binding energies of C 1s, O 1s, P 2p, and N1s atoms are observed through analysis of the photo-electrons emitted from the target before and after electron irradiation. Similarly, the FTIR spectra were taken after irradiation with 20eV electrons, as this showed to be the energy for which the most damage to DPPC has been produced. It turned out that the most affected parts of our targets are the COO-group, which bridges the "head" of the lipid molecule to its tails. The least effect of electron irradiation is shown on the P 2p band, regardless of the incident energy. The reduced effect in lipid-arginine complex may be linked to the orientation of the DPPC molecules and additional molecular bonding, which will be discussed in a view of the way it can affect the efficiency and operation of the biosensor.

[1] Priscilla Kailian Ang, Manu Jaiswal, Candy Haley Yi Xuan Lim, Yu Wang, Jagadish Sankaran, Ang Li, Chwee Teck Lim, Thorsten Wohland, Ozyilmaz Barbaros, and Kian Ping Loh, ACS Nano 2010 4(12) 7387–7394.
[2] G. J. Köteles, Rad. Env. Biophys. 1982, 21(1), 1; K. P. Mishra, J. Environ. Path. Toxic.Onc, 2004, 23, 61.
[3] Turchanin A, Tinazli A, El-Desawy M, Grossman H, Schnietz M, Solak H H, Tampé R, and Gölzhäuser A,Adv. Mat.2008, 20, 471.

P2.022 Spectroscopic study of the orientation and electronic states of α-sexithiophene on chemically modified Si(001) surfaces

M Tanaka[1], H Toyoshima[1], K Hiraga[1], S-Y Ohno[1], K-I Ozawa[2], K Mase[3], K Mukai[4] and J Yoshinobu[4]

[1]Yokohama National University, Japan, [2]Tokyo Institute of Technology, Japan, [3]High Energy Accelerator Research Organization, Japan, [4]The University of Tokyo, Japan

The knowledge of the interaction between organic molecules and semiconductor surfaces is important to adapt organic semiconductors into the semiconductor technology. In this study, the processes of α-sexithiophene (α-6T) thin layer formation on passivated Si surfaces have been investigated in situ by means of surface differential reflectance spectroscopy (SDRS), reflectance difference spectroscopy (RDS), synchrotron radiation photoelectron spectroscopy (SRPES) and ultraviolet photoelectron spectroscopy (UPS). Si(001)-(2x1) surface was exposed independently to H_2O, O_2, H_2, and C_2H_4 gas in an ultrahigh vacuum chamber. α-6T molecules were deposited on these passivated surfaces at room temperature to the thickness of 5.0 nm at most.

The main findings are as follows. α-6T molecules are upright-standing to form bulk-like islands or films from the first layer on oxidized Si(001) and monohydride Si(001). Carbon atoms of the standing molecules are combined with the substrate atoms. On water-adsorbed Si(001), isolated α-6T molecules are flat-lying and align parallel to the dimer row until the thickness becomes 3nm. Sulfur atoms of the lying molecules are combined with -OH of the surface. Above 3nm, most of molecules are standing and constitute well ordered islands or films. On ethylene-adsorbed Si(001), the majority of α-6T molecules are flat-lying, and isolated molecules and those in the islands or films tend to align parallel and perpendicular to the dimer row, respectively. Thus, the orientation and electronic states of the molecules depend on the method of passivation, which raises the possibility of controlling the molecular orientation by the surface modification.

P2.023 Orientation changes of n-Alkane in a monolayer on graphene modified Pt(111) studied by C K-NEXAFS

O Endo[1], M Nakamura[2], K Amemiya[3] and H Ozaki[1]

[1]Tokyo University of Agriculture and Technology, Japan, [2]Chiba University, Japan, [3]KEK-PF, Japan

The self-assembled monolayer of *n*-alkane molecules lying on an inert solid surface such as a graphite basal plane is an intriguing system to study the molecule-molecule and molecule-substrate interactions, which are important in order to understand surface and interface phenomena including wetting and lubrication. A monolayer graphene, which is grown on metal surfaces by the thermal decomposition of hydrocarbon, can be used to study several effects on the self-assembly of *n*-alkane molecules, which may not necessarily be observed for the bulk graphite, e.g.*,* defects, domain size, and metal substrate. In addition, the molecular orientation is analyzed in detail by polarization dependent near carbon K-edge X-ray absorption fine structure spectroscopy (C K-NEXAFS) for *n*-alkane on the monolayer graphene because of the lower presence of the substrate carbon atoms. In this study, we have measured the C K-NEXAFS spectra of *n*-$C_{36}H_{74}$ molecules in a (sub)monolayer on the Pt(111) surface modified with the monolayer graphene. The orientation is confirmed by the polarization dependence of the σ^*_{CH} and σ^*_{CC} resonances in the NEXAFS spectra. The molecules with the chain axis parallel to the graphene sheet form self-assembled lamellar structures, and the orientation of the CCC plane changes depending on temperatures. At around room temperature, the lamellae are in the smectic phase and most molecules adopt the parallel (flat-on) orientation. The smectic phase is transformed into an incommensurate crystalline phase on cooling, and at least half of the molecules in this phase adopt the perpendicular (edge-on) orientation. This molecular reorientation depends on the initial coverage.

P2.024 Optical properties of liquid crystal placed in nonuniform electrical field

M Boussoualem, J-F Tahon and J-M Buisine

University of Science and Technology of Lille (USTL), France

The combination of the high refractive-index variation of the liquid crystal (LC) molecules, achievable under electric control and the asymmetric structure of the cell (plane electrode and hole-patterned electrode) provides a spatially dependent electric field across LC layer. Such that the light wave experiences a centro-symmetric phase retardation when passing through the LC cell which act as glass lens. But, in addition and unlike the glass lens, the phase retardation profile is electrically controllable and so the focal length of the LC lens. In this work, LC lens with continuously tunable focal length obtained by placing LC layer between a planar electrode and a circularly hole-patterned electrode is demonstrated. The optical properties of this LC lens were characterized at various driving conditions (voltage, frequency).

P2.025 Adsorption height of benzene and azobenzene on Ag(111) and Cu(111)

M Willenbockel[1], G Mercurio[1], E R McNellis[2], C Bronner[3], B Stadtmüller[1], S Meyer[3], E Varene[3], M Schulze[4], I Martin[4], F Leyssner[3], J Meyer[4], S Soubatch[1], M Wolf[5], K Reuter[4], P Tegeder[4] and F S Tautz[1]

[1]Forschungszentrum Jülich, Germany, [2]Fritz-Haber-Institut Berlin, Germany, [3]FU Berlin, Germany, [4]TU München, Germany, [5]FU Berlin/FHI Berlin, Germany

Research focused on the interactions at organic/metal interfaces revealed that weak long-range van-der-Waals (vdW) forces play a significant role in the bonding mechanism. However, a clear experimental gauge is needed to judge to which extent the vdW interactions influence the adsorption strength. For molecules at surfaces the height of adsorption is known to satisfy this need.

Here we report the normal-incidence x-ray standing waves data on the adsorption height of the classical aromatic molecule benzene on Ag(111) and Cu(111) surfaces. In these systems the contribution of vdW interactions to the bonding is meant to be dominant. To identify the effect of additional chemical interaction channels, we furthermore studied the adsorption of azobenzene, a molecule containing two benzene rings linked by a diazo-bridge. Achieved experimental results are compared to density functional theory calculations.

P2.026 The adsorption of pentacene on quasicrystalline surfaces

J Smerdon, K Young, H R Sharma and R McGrath

University of Liverpool, UK

Quasicrystals are binary or ternary alloys that possess long range ordering but no translational symmetry [1]. They are materials that occupy a classically forbidden area of crystallography: one with no periodic space lattice and therefore no implicit restriction on the rotational symmetries permitted. Layered materials consisting of eight-, ten- or twelve-fold planes have been discovered, but the most prevalent structural symmetry is icosahedral.

Because of the novel properties of metamaterials ordered following the same principles, there is a good deal of potential in harnessing the self-assembly properties of epitaxial films to produce two-dimensional materials with quasicrystalline ordering. This has successfully been observed in metallic monolayers [2] and Cu [3] and Co multilayers. Cu multilayers are composed of vicinal domains of crystalline material, with the aperiodic ordering manifested as a small-scale step-terrace structure at the surface of the film [4].

To exploit the self-assembly phenomenon but simultaneously access other length scales, we attempt to perform molecular adsorption on quasicrystalline surfaces. The behaviour of Pn molecules when deposited on several quasicrystalline substrates has been tracked using scanning tunneling microscopy (STM). Pn is a molecule with 2-fold symmetry comprising 5 benzene rings fused along C-C bonds. This reduced symmetry allows the expression of quasicrystalline ordering through the orientation of the molecule as well as the location.

[1] Shechtman, D., Blech, I., & Gratias, D. (1984). Phys. Rev. Lett., 53, 1951.
[2] Franke, K.J., Sharma, H.R., Theis, W., Gille, P., Ebert, P., & Rieder, K.H. (2002). Phys. Rev. Lett., 89, 156104.
[3] Ledieu, J., Hoeft, J.T., Reid, D.E., Smerdon, J.A., Diehl, R.D., Lograsso, T.A., Ross, A.R., et al. (2004). Phys. Rev. Lett., 92, 135507.
[4] Pussi, K., & Gierer, M. (2009). J. Phys.: Condens. Matt. 21 474213.

P2.027 Charging and switching of metallo-organic complexes on ultrathin, insulating films sup- ported by a metal support: a density functional theory study based on a perfect conductor model

I Scivetti, J Sharp, F Hanke and M Persson

University of Liverpool, UK

The study of atoms and molecules deposited on ultra-thin, insulating and polar films supported by metal substrates by scanning probe microscopies is an emerging and exciting area of research, in which simulations based on density functional theory (DFT) play a key role. In fact, a further understanding of these systems by theory could lead to creation and design of novel functionalized nano structures or molecular devices for electronics, photo voltaics, information storage and processing, catalysis and chemical sensors. However, DFT calculations of these complex systems, exhibiting multiple charge states, are very challenging[1]. We have developed a simplified computational scheme in which the metallic support is replaced by a perfect conductor model. This new scheme allows us to speed up the calculations by two orders of magnitude and to treat various charge states of adsorbates readily by varying the chemical potential. We will plan to present a few most interesting applications of this scheme to different charge states of metal adatoms and switching of and reversible bond formation in metallo-organic molecules[2,3], being adsorbed on a sodium chloride bilayer supported by a copper substrate.

[1] J. Repp, et al., Science 305, 493 (2004).
[2] F. Mohn et. al., Phys. Rev. Letter 105, 266102 (2010).
[3] T. Leoni, et al., Phys. Rev. Lett. 106, 216103 (2011).

P2.028 Self-assembly of reactants for an on-surface click-reaction: Azides and Acetylenes on Cu(111)

S R Vadapoo, F Bebensee, C Bombis, J Cramer, K Gothelf, F Besenbacher and T Linderoth

Aarhus University, Denmark

The on-surface synthesis scheme process for forming molecular surface nanostructures where the molecular building blocks are joined by strong covalent bonds has received tremendous recent interest. In this context there is a need to identify suitable chemical reactions that will readily proceed under extreme UHV conditions.“Click-Chemistry” and in particular the 1,3-dipolar Huisgen cycloaddition reaction between azides and alkynes is a widely used reaction in organic chemistry and very interesting in this respect since it proceeds readily in the presence of a Cu-catalyst and is free of by-products. Here we study on-surface click chemistry on a Cu(111) surface under Ultra High Vacuum (UHV) conditions using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). This poster presents details on the adsorption of the reactants, i.e. the alkyne 9-ethynylphenanthrene and the azide 4-azidobiphenyl in which the alkyne and azide moieties are joined to different small aromatic systems allowing their facile identification in STM images. We find that the terminal alkyne adsorbs individually with distinct orientations believed to result from interaction of the alkyne group with the Cu surface. Although we find indication for mobility of the molecules even at low temperature, we have not found any self-assembled structures for this molecule. The azide shows a strong tendency for adsorption in a range of small clusters (involving 3-8 molecules) that express distinct motifs. The adsorption motifs identified for the individual reactants are compared to those formed after co-deposition and reaction.

P2.029 A molecule-like composite nanostructure by self-selective growth

Y Xie, T Lin and Q Guo

Nanoscale Physics Research Laboratory, China

Fabrication of two-dimensional molecular structures on top of a solid substrate is an important process towards the realisation of molecular electronics. There has been a rapid increase in research effort devoted to the study of molecular organisation on surfaces and the formation of various two-dimensional molecular networks. Most of the molecular structures obtained so far on surfaces are part of an extended two-dimensional lattice due to directional hydrogen bonding or the preferred metal-molecule coordination. A structure of 7-C_{60}/Au has been observed in our investigation of C_{60} adsorption on Au(111) where a group of seven C_{60} molecules coordinated with a two-dimensional Au cluster are found to behave as a discrete molecule.

In our experiment, the Au atoms and C_{60} molecules are sequentially deposited onto Au (111) when the sample is kept at 110K in an HV STM chamber. After the deposition, the temperature of the sample is gradually increased and STM is used to follow the changes of the C_{60}/Au complexes. At low temperature (110 K), the structures of C_{60}/Au are irregular with several C_{60} molecules partly or fully enclosing small Au islands at the elbow sites. With the increasing temperature, the C_{60} molecules and Au atoms on Au (111), due to thermal activation, reorganise into stable structures. A frequently observed structure is seen to consist of seven C_{60} molecules: one sitting above a small Au island and the remaining six attached to the edges of the Au island (7-C_{60}/Au complex). The closed-shell structure is stable up to 400 K during annealing process. The stability of such a complex arises from a mutual stabilization effect between the metal island and the C_{60} molecules. Besides the stable structure, there are also other structures with one C_{60} molecule missing (6-C_{60}/Au complex) or added (8-C_{60}/Au complex) to the closed-shell structure.

The interaction between the C_{60} and Au atoms, which unites the two to form a stable structure on Au (111), are supposed to come from charge transfer which is non-selective. The formation of the molecule-like structure demonstrates a different kind of selectivity and specificity where directional bonding is unnecessary.

P2.030 Aging of organic nanowires

F Balzer[1], M Schiek[1], A Osadnik[2], A Lützen[2] and H-G Rubahn[1]

[1]University of Southern Denmark, Denmark, [2]University of Bonn, Germany

Organic semiconductors formed by epitaxial growth from small molecules such as the *para*-phenylenes or squaraines promise a vast application potential as the active ingredient in electric and optoelectronic devices. Their self-organization into organic nanowires or "nanofibers" adds a peculiar attribute, making them especially interesting for light generation in OLEDs and for light-harvesting devices such as solar cells. Functionalization of the molecules allows the customization of optical and electrical properties. However, aging of the wires might lead to a considerable decrease in device performance over time. In this study the morphological stability of organic nanoclusters and nanowires from the methoxy functionalized quaterphenylene, 4,4'''dimethoxy-1,1':4',1''4'',1'''-quaterphenylene (MOP4), is investigated in detail. Aging experiments conducted by atomic force microscopy under ambient conditions already expose substantial changes in sample morphology within hours. Clusters show Ostwald ripening, whereas nanowires reveal strong faceting and even fragmentation. All these aging effects are ascribed to the influence of water vapor. Decay curves (cluster number vs. time) for clusters surrounded by other clusters or close to a nanowire reveal the mechanism behind the coarsening. Implications for device design are discussed.

P2.031 An STM and UPS study of thermally polymerised 5,10,15,20-tetrakis(4-aminophenyl)-porphyrin (TAPP) films.

H L Lee[1], L Giovanelli[2], M Abel[2], J-P Cunniffe[3], A Preobrajenski[4], L Porte[2] and A Cafolla[3]

[1]Dublin City University, Ireland, [2]Aix-Marseille Université, France, [3]Dublin City University, Ireland, [4]University of Lund, Sweden

The formation and characterisation of covalent polymeric networks on metal surfaces, in the monolayer coverage range, has recently received much interest due to their potential application in bottom-up device technologies. Here we report an STM, UPS and XPS study of the formation of stable molecular networks on the Au(111) and Cu(111) surfaces through covalent bonding of 5,10,15,20-tetrakis(4-aminophenyl)-porphyrin (TAPP) molecules. The molecules were deposited onto the metal surface which was subsequently annealed to 623 K causing thermal dissociation of the amine groups, producing an organic network on the surface. The ordering observed in the resulting structure is largely determined by the initial molecular coverage, substrate temperature and deposition rate. UPS measurements show a distinctive electronic structure at the interface with a modification in the position and width of the highest occupied molecular orbital when polymerisation occurs. A large negative work-function (WF) change was observed when TAPP was absorbed on both Au(111) and Cu(111) This decrease in the work function indicates the formation of a dipole layer at the interface with the molecule positively charged. This change in WF is in the opposite direction to that expected and may originate from the charge redistribution at the interface due to the induced image charge in the metal and the push back of electrons from the metal surface by the adsorbed molecules (pillow effect)[1].

[1] J. Fraxedas et.al., J. Phys. Chem. C. 115 (2011) 18640.

P2.032 Hybrid organic–inorganic systems: Al, Ag and Au nanoparticles self-assembled in CuPc

O Molodtsova[1], I M Aristova[2], O Y Vilkov[3], V V Kveder[2], C Laubschat[4] and V Y Aristov[2]

[1]DESY, Germany, [2]Institute of Solid State Physics, Russia, [3]BESSY Berlin, Germany, [4]Technische Universität Dresden, Germany

The basis for resistive random-access memory (RRAM) could become materials with a high on-off resistance ratio. Such a new “storage class memory” would revolutionize the information technology industry as outlined in [1-3]. One type of RRAM can be based on hybrid organic–inorganic systems, mainly consisting of inorganic nanoparticles (NP) blended into an organic matrix. Comparative studies of electronic properties and morphology of the hybrid organic-inorganic systems composed of aluminum, silver and gold NP’s, distributed in an organic matrix, copper phthalocyanine, as a function of nominal metal content was studied by transmission electron microscopy and by surface- and bulk sensitive photoelectron spectroscopy

[1] Z. Liu, et al., Science 302, 1543 (2003).
[2] J.C. Scott, Science 304, 62 (2004).
[3] J.C. Scott and L.D. Bozano, Adv. Mater. 19, 1452 (2007).

P2.033 Low temperature scanning tunneling microscopy study of Co-phthalocyanine molecules on graphene/Ir (111)

S Bouvron, P Erler, E Cavar and M Fonin

University of Konstanz, Germany

Because of its influence on the electronic and transport properties of a molecule, the interaction between a molecule and a substrate is of crucial importance for possible applications in molecular electronic devices. Furthermore, the adsorption behavior of molecules on surfaces is decisive in a bottom up approach to build molecular electronics.

Graphene grown by chemical vapor deposition on Ir(111) reveals a highly ordered hexagonal moiré superstructure resulting from the small mismatch between graphene and the Ir(111) surface lattice. This superstructure makes graphene/Ir(111) a promising template for molecular self-assembly.

We investigated Cobalt Phthalocyanine (CoPc) molecules deposited on Au(111) and Graphene/Ir(111) by means of low-temperature scanning tunneling microscopy(STM) and near-edge xray absorption. Here we present the analysis of the nucleation and the early stage growth of CoPc islands on graphene on Ir(111). We report on the competition between intermolecular interactions and substrate-adsorbate interaction for different coverages of CoPc molecules, varying from a submonolayer to a multilayer. Depending on the coverage, we observed different growth patterns. At a monolayer coverage, the CoPc molecules arrange in a monoclinic close-packed structure, whereas at lower coverage a moiré-supported hexagonal network consisting of ring-like units of six CoPc molecules is observed.

P2.034 Supramolecular self-assembly of 1,3,5-triethynyl-benzene and 1,3,5-triethynylphenyl-benzene molecules on Ag(111)

F Klappenberger[1], N Kepčija[1], M Kleinschrodt[1], Y Zhang[1], K Diller[1], J Björk[2], S Klyatskaya[3], M Ruben[3] and J Barth[1]

[1]Technische Universität München, Germany, [2]Linköping University, Sweden, [3]Karlsruhe Institute of Technology, Germany

The self-assembly of 1,3,5-triethynyl-benzene (TEB) and 1,3,5-triethynylphenyl-benzene (Ext-TEB) molecules on the Ag(111) surface was investigated by scanning tunneling microscopy (STM) and spectroscopy (STS) measurements and density functional theory (DFT) modeling. Both TEB and Ext-TEB molecules form highly regular chiral superstructures at low temperature (< 200 K). For TEB molecules, a dense-packed phase was observed, while for Ext-TEB molecules, two arrangements exist, i.e., a dense-packed and an open-pore phase. Based on high-resolution STM experimental data and computational modeling, the substrate registry of TEB and Ext-TEB molecules, and the supramolecular unit cell of different phases are examined. The analysis reveals that the acetylene group plays an important role in the attractive intermolecular interactions and expression of noncovalent nodal motifs. Moreover, STS data reveal distinct electronic characteristics at these nodes. Thus, building blocks with acetylene groups can be used for 2D supramolecular assembly, and even for tuning the electronic structure of the organic-metal hybrid interface.

P2.035 Bonding and reaction of self-assembled monolayers on ferromagnetic metal surfaces

F Blobner[1], F Allegretti[1], R Han[1], P Abufager[2], H Fabio Busnengo[2], K Reuter[1] and P Feulner[1]

[1]Technische Universität München, Germany, [2]Instituto de Física Rosario CONICET, Argentina

While thiolate bonded self-assembled monolayers (SAMs) on gold and other inert metal surfaces have been widely investigated in the past decades, studies of such SAMs on the more reactive 3d ferromagnetic metals are comparatively rare, despite the envisaged role of these interfaces in molecular spintronics [1]. Here, we report on the adsorption geometry and stability of aromatic SAMs with backbone composed of a single phenyl ring and different ligands as endgroups, deposited in ultra high vacuum (UHV) on single crystal surfaces and/or thin films of Ni(111) and Co(0001). By means of high resolution X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) and thermal desorption spectroscopy (TDS) in conjunction with density functional theory (DFT) calculations we get insight into the molecule integrity and bonding configuration and cast light onto decomposition reactions that may occur at different temperatures and coverages. In particular, we investigate systematically preparation induced effects, aiming to reconcile the puzzle of conflicting evidence on SAMs prepared in solution [2] and UHV [3]. Two molecules are investigated, where the ligands are one F atom and a CN group respectively, and the comparison with more ordinary benzenethiolate SAMs enables to highlight the influence of endgroups and of the charge redistribution in the aromatic ring on the stability of the thiolate-metal bond, the molecular conformation and packing.

[1] A.R. Rocha et al., Nat. Materials 4 (2005) 3.
[2] P.G. Hoertz et al., J. Am. Chem. Soc. 130 (2008) 9763, and references therein.
[3] T.S. Rufael et al., J. Phys. Chem. 98 (1994) 13022.

P2.036 2D adaptive nanoporous networks with random features from flexible molecular modules

S Vijayaraghavan[1], D Ecija[1], W Auwärter[1], S Joshi[1], K Seufert[1], C Aurisicchio[2], D Bonifazi[2] and J V Barth[1]

[1]Technische Universität München, Germany, [2]University of Namur, Belgium

Unraveling the nature of complex condensed matter systems including glasses, glassy crystals and amorphous materials is of paramount importance in actual material science. Traditionally, most insights into the structure of non-crystalline materials have been based on diffraction techniques that rely on space averaging. Only recently, the employment of self-assembly protocols on surfaces to create surface-confined supramolecular random networks and their in-situ visualization with Scanning Tunneling Microscopy (STM) [1,2,3] have provided crucial breakthroughs regarding the local order characteristics of the 2D glassy structures.

Here, we exploit the self-assembly route to organize on Cu(111) an inherently-flexible molecular module (1,3,5-tris(pyridin-4-ylethynyl)benzene), which presents three pyridyl groups connected to a central aryl ring through alkyne moieties. The functional terminal groups are programmed to steer metal-organic interactions through pyridyl-metal-pyridyl coordination motifs. We report the formation of two types of nanoporous 2D networks on Cu(111) incorporating simultaneously distinct random and regular features, regarding the pore shape on the one hand and arrangement of nodes on the other hand. Notably we address the role of molecular flexure and non-cooperative molecular rotational alignment in the structural characteristics of the expressed network phases. The supramolecular spatial organization can be considered as a surface analogue to 3D glassy crystals.

Furthermore, we probe the flexibility of an open network phase by locally inducing a flipping of the molecular terminal groups with an STM tip, which leads to subtle changes of the pore shape, while leaving the overall network organisation unaffected. This behaviour reveals their potential for an adaptive response towards molecular guests, a crucial property for exploitation in molecular recognition, and constitutes a demonstrator for a “soft porous crystal” in 2D. [4]

[1] Otero, R. et al. Elementary structural motifs in a random network of cytosine adsorbed on a gold(111) surface. Science 319, 312-315 (2008).

[2] Blunt, M. O. et al. Random tiling and topological defects in a two-dimensional molecular network. Science 322, 1077-1081 (2008).

[3] Marschall, M. et al. Random two-dimensional string networks based on divergent coordination assembly Nat. Chem. 2, 131-137 (2010).

[4] Horike, S., Shimomura, S. & Kitagawa, S. Soft porous crystals Nat. Chem. 1, 695-704 (2009).

P2.037 Adsorption of R,S-Phenylglycine on Au(111)

F Grillo, S Francis and N Richardson

University of St Andrews, UK

Self-organization of organic molecules appears as one of the most promising approaches to the further miniaturization of electronic devices. However, we are only beginning to understand the detailed mechanisms of molecular recognition and how self-assembly might be exploited for actual device production. In order to investigate the molecular self-organization, suitable model systems need to be found that allow the study of intermolecular and molecular-substrate interactions reproducibly and with high accuracy. Controlled choice of surface adsorbed molecules seems an obvious choice.

In this context, the adsorption of racemic phenylglycine, a simple chiral amino acid, on the 22x$\sqrt{3}$-Au(111) surface is studied via scanning tunneling microscopy and high resolution low energy electron spectroscopy under UHV conditions. Initial results show the presence of two distinct self-assembled ordered molecular domains, one of which exhibits 2-fold and the other 3-fold symmetry. The gold herringbone reconstruction is preserved and a strong interaction between phenylglycine molecules, revealed by vibrational spectroscopy, seems to suggest a weaker van der Waals interaction with the surface and the possibility of peptide bond formation. DFT modelling helps to describe the geometry and the energetics of this adsorption system.

P2.038 Thickness-dependent dielectric constant of organic ultra-thin films

C Albonetti[1], J de Silva[2], M Sferrazza[2] and F Biscarini[1]

[1]CNR-ISMN, Italy, [2] Université libre de Bruxelles (ULB), Belgium

The relative dielectric constant (ε_r) of organic ultra-thin films is assumed to be around 3 [1]. In general, the relationship between ε_r and the film thickness (h) is overlooked, especially for the first few monolayer (ML) of the film. Nevertheless this topic is strongly relevant for understanding the physics of Organic Field Effect Transistor [2]. For n-type organic film, positive gate-to-source voltage attracts electrons in proportion to its ε_r, then electrons are driven towards the SiO_2 surface to form the conductive channel. To clarify the relationship between ε_r and h, Scanning Capacitance Microscopy (SCM) is used for correlating the film morphology to ε_r.

We studied PDI8-CN2 ultra-thin films that have shown high electron mobility (~ 0.6 $cm^2/V\cdot s$) and stable electrical performance in air [3]. Films were grown on SiO_2 substrate kept to 80°C by sublimating molecules in vacuum. The films thickness h increases from 1ML (≈ 20 Å) to 6MLs (≈ 120 Å). In SCM measurements, the tip-sample capacitance of the layered structure SiO_2/PDI8-CN2/Air is measured by biasing the metal tip (Pt) and the heavily doped Si substrate (n-type). The bias is the sum of direct voltage (not exceeding 1V) and alternate voltage with low amplitude V_{ac} (typically 200mV) and frequency ω_{ac}. The second harmonic of the tip-sample capacitive force depends only on dC/dz and V_{ac} [4] therefore we can measure precisely the film capacitance because the SiO_2 thickness (570 Å) and the air gap (2nd pass technique) are known. From both capacitance and topographical images of the PDI8-CN2 film, ε_r has been extracted. This experimental procedure was applied to organic films with increasing h from 1ML to 6ML then ε_r was plotted with respect to h. The plot shows a plateau to $\varepsilon_r \approx 5$ for the first three MLs, then the graph decreases to ≈ 3 (expected value) for the next two MLs. SCM measurements are compared to ellipsometric one, referred as standard technique for the dielectric constant measurements. Ellipsometric measurements both confirm SCM results and stated ε_r measured by SCM as the real part of the dielectric constant.

[1] D. Faltermeier et al., Phys. Rev. B 74 (2006) p125416.
[2] M. Mottaghi et al., Org. Electr. 7 (2006) p528.
[3] B.A. Jones et al., Chem. Mater. 19 (2007) p2703.
[4] P. Girard, Nanotechnology 12 (2001) p485.

P2.039 Hierarchical assembly of keratin intermediate filament structures inside skin cells

D Bray[1], R Notman[1], T Walsh[2] and M Noro[3]

[1]University of Warwick, UK, [2]Deakin University, Australia, [3]Unilever, UK

Intermediate filament proteins such as keratins are an important structural component of skin, hair and nail giving elastic response and flexibility to these cells. The hierarchical assembly of keratin proteins into long filaments is key to their function. It is well known that these proteins bundle together first into dimers, then tetramers which elongate into proto-filaments. These then intertwine like rope to form the mature filament.

We are attempting to understand the cross-sectional arrangement of proto-filaments by describing the filament using a mesoscopic model describing the energy balance between untwisting the fibre and the inter-protofilament attractions that hold the filament together. We are also performing molecular dynamics simulations of the keratin proteins with the aim of providing insights into the assembly of keratin intermediate filaments at the molecular-level and determining key parameters with which to inform the mesoscopic model. Our overall objective is to understand how to control and optimise the assembly of keratin proteins into stable filaments for applications in healthcare.

P2.040 Covalent immobilization of molecularly imprinted nanoparticles on (3-glycidoxypropyl) trimethoxysilane functionalized glass

T Kamra[1], S Chaudhary[1], J Schnadt[1], L Ye[1] and L Montelius[1,2]

[1]Lund University, Sweden, [2]ENI AB, Malmö, Sweden

Our work is aimed at the development of highly active and selective surfaces for label free sensing of biomolecules [1]. There are various suitable supports which can be used, but glass surfaces have particular importance due to their usefulness in technical sensing applications. In the present work we have studied the immobilisation of molecularly imprinted nanoparticles (MIP) on glass specific to the sensing of propranolol molecule. One of the main problems is to produce a thin, uniform layer of the MIP nanoparticles, which should be very stable, have high detection efficiency for its target molecules, as well as a high selectivity. Preferably, this criterion requires an immobilization technique which results in a covalent linkage of the nanoparticles to the surface, and produces a reproducible, homogenous layer. One of such immobilisation method is the silanization of glass with 3-glycidoxypropyltrimethoxysilane (GPTMS), which is thought to create a uniform and stable layer with epoxide termination on the silica surface. The available epoxy group is expected to bind to the amine functionalised MIPs via a ring opening reaction. Here, we have studied the GPTMS surface using atomic force microscopy (AFM), scanning electron microscopy (SEM), contact angle measurements and x-ray photoelectron spectroscopy (XPS). We found that the MIP layers indeed are homogeneous and more hydrophilic than the underlying GPTMS surface. Moreover, the results confirm the covalence of the surface linkage. Future work will aim at the investigation of thickness and density of the layers using a Quartz Crystal Microbalance (QCM).

[1] S. Kumar, J. Singh, V. V. Agrawal, M. Ahamad and B. D. Malhotra,Anal. Methods.2011, 3, 2237-2245.

Electronic structure of surfaces

P2.041 Photoemission, ion scattering and electron diffraction studies of the CdO(001) surface

M Walker, J Mudd, L Fishwick and C McConville

University of Warwick, UK

Cadmium oxide (CdO) is one of a range of II-VI compounds which show promising properties as transparent conducting oxide (TCO) materials. CdO has been shown to be an n-type semiconductor which possesses a non-stoichiometric composition either due to interstitial Cd atoms or oxygen vacancies, which act as doubly-charged donors [1]. CdO possesses a rocksalt structure and several interesting optoelectronic properties [2], so an investigation of the surface structure is of interest in order to assist in the explanation of these characteristics.

In this investigation, a CdO(001) sample was cleaned under ultra-high vacuum conditions by simply annealing to 600 °C for one hour, with the levels of contamination before and after cleaning determined using a monochromated X-ray photoelectron spectroscopy (XPS) system. The surface structure was determined using low energy electron diffraction (LEED) and co-axial impact collision ion scattering spectroscopy (CAICISS) [3], revealing evidence for relaxations and oxygen vacancies in the near-surface region.

Following the quantitative surface structure determination, the sample was exposed to a series of molecular and atomic oxygen doses at a range of temperatures. Changes to the stoichiometry of the near-surface region were monitored with XPS, revealing only a small oxygen uptake after extended atomic oxygen exposure at elevated temperatures.

[1] T.P. Gujar, V.R. Shinde, W.-Y. Kim, K.-D. Jung, C.D. Lokhande and O.-S. Joo, Appl. Surf. Sci. 254 3813 (2008).
[2] M. Ortega, G. Santana and A. Morales-Acevedo, Solid-State Electronics 44, 1765 (2000).
[3] C.R. Parkinson, M. Walker et al., Surf. Sci. 545, 19 (2003).

P2.042 Strongly anisotropic surface conductivity of diamond(001) surfaces upon N-doping

N J Vollmers, U Gerstmann and W G Schmidt

Universität Paderborn, Germany

Diamond has a lot of outstanding qualities but the lack of a suitable n-type donor has hindered this material to gain broad technological application. Nevertheless, nitrogen doping was already successfully used to improve the emission behavior of field emission devices based on a-C:H diamond thin films [1, 2, 3].

In this theoretical work we want to propose a possible way to n-type surface conductivity at the clean diamond (001) (2×1) reconstructed surface which consists of flat dimer rows [4, 5].

Using density functional theory together with the Quantum ESPRESSO PWscf package [6], we compare the electronic and magnetic properties for different N incorporation depths. Built-in directly at the surface, N gives rise to localized surface states similar to intrinsic carbon dangling bond-like states. Otherwise N is able to introduce surface conductivity as demonstrated by ab initio calculated effective mass tensors. In addition, the extreme anisotropy of the effective mass tensor comparable with those of metallic indium-chains on silicon substrates indicates the possibility to achieve n-type 1D surface-conductivity along the dimer-chains. Our calculations show in accordance with recent STM measurements [7] that diamond offers potential for intrinsic surface conductivity but is so far insulating because of the lack of charge carriers. N doping in the subsurface region should provide solution of this problem.

[1] R.S. Balmer et al., J. Phys.: Cond. Matt. 21, 364221 (2009).
[2] J. Xu et al., Appl. Phys. A 80, 123 (2005).
[3] M. Kaukkonen et al., Phys. Rev. Lett. 83, 5346 (1999).
[4] C. Kresse et al., PRB 50, 17697 (1994).
[5] N. Nimmrich et al., PRB 81, 20140(R) (2010).
[6] Ch.J. Pickard, F. Mauri, Phys. Rev. Lett. 88, 086403 (2002).
[7] K. Bobrov et al., Nature 413, 616 (2001).

P2.043 Collapse of Shockley surface state by randomly adsorbed Bi atoms at Ag(111) surfaces

H Hirayama, Y Aoki and H Fukumoto

Tokyo Institute of Technology, Japan

We studied the collapse of the Shockley surface state by randomly adsorbed Bi atoms at Ag(111) surfaces. The E(k) relation of the surface state was deduced from the STM differential conductance images. It deviated from the intrinsic downward parabolic dispersion of the Ag(111) Shockley surface state at the low energy side close to the band bottom. The deviation became remarkable with the increase in the Bi coverage from 0 to 0.1 ML. It was also accompanied with the broadening of the onset of the surface electron's density of state in STS.

The deviation is attributed to the reduced coherent length of the surface state electron. We estimated the lifetime from STS, and numerically calculated the coherent length as the product of the lifetime and group velocity. The deviation of the E(k) relation is regarded to take place in the energy region where the coherent length becomes shorter than the wavelength of the intrinsic Shockley surface state electron. The group velocity reduces dramatically near the edge of the surface band. In addition, the lifetime reduces with the Bi coverage. These explain why the E(k) relation comes off the Shockley surface state dispersion from the low energy side with the Bi coverage quantitatively. We found that this concept also explains the way of the completion of the spin-split upward parabolic dispersion of the Bi/Ag(111)-root3 surface reconstruction, which happened in the higher energy side close to the band edge at the Bi coverage near 1/3 ML, consistently.

P2.044 Spatial mapping of surface plasmons in nanoscale Ag islands on graphite using scanning probe energy loss spectroscopy

K Bauer, S Murphy, L Tang and R Palmer

University of Birmingham, UK

A scanning STM tip operated at high voltage can be used to obtain localised spectroscopic information about surfaces via energy loss measurements [1,2]. In this technique, known as Scanning Probe Energy Loss Spectroscopy (SPELS), the STM tip is used as a localised source of field-emitted electrons, which, upon backscattering from a surface, are analysed by an energy-dispersive detector to obtain localised energy loss spectra. Characteristic surface excitations such as plasmons and excitons (as well as secondary electrons) can be probed with a spatial resolution below 50 nm and an energy resolution approaching 0.3 eV [3]. In principle the field-emitted electrons can also induce surface chemistry, e.g. dissociating the surface-adsorbate and intra-molecular bonds, to achieve reactive patterning of the surface in a way similar to the more conventional tunneling regime [4,5], but possibly at higher rates.

We report the development of a new generation SPELS instrument which includes a cylindrical sector analyser equipped with a 400-channel detector, allowing fast enough sampling of loss spectra, to allow us to obtain 2D spatially-resolved maps of energy loss features in a reasonable timeframe (minutes). We demonstrate the new instrument by mapping plasmons in (thermally evaporated) Ag nano-islands on the surface of graphite and illustrate the various mechanisms giving rise to the contrast obtained in the energy-resolved maps of the nanostructured Ag/graphite surface.

[1] J. J. Lawton, A. Pulisciano, and R. E. Palmer, J. Phys.: Condens. Matter, 21, 474206 (2009).
[2] A. Pulisciano, S. J. Park, and R. E. Palmer, Appl. Phys. Lett. 93, 213109 (2008).
[3] F. Festy and R. E. Palmer, Appl. Phys. Lett. 85, 5034 (2004).
[4] P. A. Sloan, S. Sakulsermsuk and R. E. Palmer, Phys. Rev. Lett. 105, 048301 (2010).
[5] S. Sakulsermsuk, P. A. Sloan and R. E. Palmer, ACS Nano 4, 7344 (2010).

P2.045 Photoemission study of the hydrogenated Si(111)-1x1 surface

W Srour[1], A Tejeda[2], A Nicolaou[1], B Kierren[2], A Taleb-Ibrahimi[1] and D Malterre[2]

[1]SOLEIL Synchrotron, France, [2]Institut Jean Lamour -Nancy, France

The adsorption of hydrogen atoms on the Si(111) surface is considered as a model for chemisorption study on the semiconductor surface. Hydrogenation is highly interesting from technological point of view [1] because it passivates the surface states of Si(111)-7x7 and stabilizes thus the surface. Moreover, it may serve as a template for the growth of artificial nanostructures or molecules decoupled from the substrate. Insight of the interaction with the substrate may be gained by watching at the eventual substrate surface states modification. It is therefore necessary to precisely determine experimentally the location of the surface states in the whole Brillouin zone. We present here different isoenergetic cuts of the whole electronic structure of H/Si(111)-(1x1) at a photon energy of 37 eV. We discuss the reciprocal space extension of the two states surface a and a' induced by hydrogen [2].

[1] International Technology Roadmap for Semiconductors, 2007.
[2] K. Hricovini, R. Giinther, P. Thiry, A. Taleb-Ibrahimi, G. Indlekofer, J. E. Bonnet, P. Dumas, Y. Petroff, X. Blase, Xuejun Zhu, Steven G. Louie, Y. J. Chabal and P. A. Thiry, Phys. Rev. Lett. 70,1992 (1993).

P2.046 Nanoscopic insight ino recombination active defects at silicon heterojunctions

U Gerstmann[1], M Rohrmüller[1], W Gero Schmidt[1], B George[2], A Schnegg[2], J Behrends[2], T F Schulze[2], M Fehr[2], L Korte[2], M Schmidt[2], K Lips[2] and B Rech[2]

[1]University of Paderborn, Germany, [2]Helmholtz-Zentrum Berlin, Germany

Semiconductor interfaces play an important role in solid state physics and are crucial for the function of countless devices [1,2]. Controlling the interface-derived electronic states, which lead to trapping or recombination of charge carriers, is a prime goal in modern semiconductor processing. The quality of the corresponding devices depends strongly on the microscopic details of the heterojunctions. Therefore, it is highly desirable to develop a sensitive method directly probing interface states *in a working device* and their electronic and atomic structure. In this context, electrically detected magnetic resonance (EDMR) has been improved towards a sensitivity approaching single spin detection [3].

In this work, we combine high-resolution EDMR with *ab-initio* calculations of the *g*-tensor of interface structures using the example of miniature *a*-Si:H/*c*-Si heterojunction solar cells. By this, we unambiguously identify the states responsible for the carrier recombination at the (111)-oriented interface, by their rotation pattern in an external magnetic field: Spin-dependent recombination is detected between a-Si:H/c-Si interface dangling bonds and conduction band tail states of - at first view - unknown origin. For these quasi-metallic electronic states perturbation theory is not applicable. As an alternative, we derive the *g*-tensor in a non-perturbative way via a Berry phase formula [4]. By this, we are able to show that the conduction band tails do not originate from (*a*-Si:H) bulk material, but from a 2D electron gas close to the interface. Having demonstrated the feasibility of combining high-resolution EDMR measurements on real devices with ab-initio calculations, it is straightforward to apply this method to other systems and devices.

[1] E. Yablonovitch, Science 246, 347 (1989).
[2] H.J. Queisser, Science 281, 945 (1998).
[3] M. Xiao, I. Martin, E. Yablonovitch, and H.W. Jiang, Nature 430, 435 (2004).
[4] D. Ceresoli, U. Gerstmann, A.P. Seitsonen, and F. Mauri, Phys. Rev. B81, 060409R (2010).

P2.047 Stability of In/Si(111)-(4x1) nanowires

M Babilon, U Gerstmann, S Wippermann, S Sanna and W G Schmidt

University of Paderborn, Germany

Quasi one-dimensional structures, such as artificial atomic-scale wires, have attracted considerable attention recently [1]. They do not only show fascinating physical properties, but also have a large technological potential, e.g., as atomic-scale interconnects. Highly anisotropic surface superstructures are suitable model systems to explore atomic-scale wires both experimentally and computationally. The In/Si(111)-(4x1) surface [2, 3] is probably the most intensively investigated system in this context. Experimentally, a reversible phase transition from the metallic Si(111)-(4x1)-In zigzag chain structure to an insulating (8x2) reconstruction below 125 K is observed [4]. Here, we investigate the influence of relativistic effects and the treatment of the In core electrons on the phase transition temperature T_C. Whereas a classical, non-relativistic treatment overestimetes the critical temperature T_C by about 100 K, a scalar-relativistic treatment of the core electrons reduces this discrepancy between theory and experiment considerably. The remaining difference can be attributed to the neglection of spin-orbit coupling within the scalar-relativitic approximaton. Further steps towards a desired full-relativistic treatment are presented.

[1] N. Nilius, T. M. Wallis and W. Ho, Science 297, 1853 (2002).
[2] O. Bunk et al., Phys. Rev. B 59, 12228 (1999).
[3] S. Wippermann, N. Koch, W. G. Schmidt, Phys. Rev. Lett. 100, 106802 (2008).
[4] A. A. Stekolnikov, K. Seino, F. Bechstedt, S. Wippermann, W. G. Schmidt, Phys. Rev. Lett. 98, 026105 (2007).

P2.048 The surface electronic structure of Al(100) revisited with the first-principle calculation

D-A Luh

National Central University, Taiwan

Adapting the first-principle calculation to study the surface electronic structures have yielded many successes, but not without difficulties. The geometry of the periodic slabs separated with vacuum layers is often employed in the calculations. One important feature in the surface electronic structures is the surface state locating within the projected bulk band gap. The split in the surface states resulting from the interplay between the surfaces of the slabs can be significant when the sizable slabs are not used. The problem may become unacceptable especially when the surface state locates closely near the band edge. In addition, the surface states may reside within the symmetry gap and overlap with the bulk states, making the determination of the surface states difficult. In this work, the Al(100) surface, possessing narrow and symmetry gaps, was revisited with the first-principle calculation. The interplay between the split in the surface states and the thickness of the slab was investigated. A criterion based on the distribution of the wave functions was proposed to classify the eigenstates into the categories of the bulk state, surface state, or surface resonance. Our calculation, showing evidently the converged surface states and resonance, is in an excellent agreement with the recent high-resolution ARPES measurement on Al(100), and demonstrates that the sizable slabs are mandatory to obtain correct surface electronic structures with the first-principle calculation.

P2.049 Image potential states on manganese phthalocyanine thin films

I Yamamoto, K Mizoue, J Azuma, M Imamura, K Takahashi and M Kamada

Saga University, Japan

Image potential states (IPS) have attracted growing interest due to its fundamental physical properties such as two-dimensional free-electron-like behavior and quantum confinement. In order to clarify essential details of the IPS, a large number of experimental and theoretical studies have been performed. For the IPS on organic thin films, however, details of the influence of hybridization with unoccupied molecular orbitals and/or morphology of organic thin films is not clear. In this study, we have investigated IPS on manganese phthalocyanine (MnPc) films of 1 monolayer (ML) coverage prepared on graphite (HOPG) and Cu(100) substrates by angle-resolved two-photon photoemission spectroscopy. A MnPc molecule is one of the interesting and fundamental molecules, and has received much attention due to its rich applications to electronic devices.

The first IPS(n=1) on the MnPc(1 ML)/HOPG film shows a free-electron-like parabolic dispersion parallel to the surface, and the effective mass is $1.9m_e$, which is about twice as large as that for the HOPG clean surface. Moreover, the backfolding of the IPS(n=1) was observed clearly and coincided with the Brillouin zone boundaries for the phthalocyanine unit cell. On the other hand, such backfolding of the IPS(n=1) was not observed in the MnPc(1 ML)/Cu(100) system, although the IPS(n=1) shows the free-electron-like parabolic dispersion. The effective mass is $0.97m_e$, which is rarely different from the Cu(100) clean surface. These different behavior of the IPS(n=1) may be due to the difference of the molecular ordering and the wavefunction overlap between the IPS(n=1) and the MnPc molecule-derived unoccupied states.

P2.050 Atomic and electronic structure of the $(2\sqrt{3}x2\sqrt{3})$R30° reconstruction of Sn/Ge/Si(111)

A Tejeda[1], W Srour[1], M Stoffel[1], M Abuín[2], Y Fagot-Révurat[1], P Le Fèvre[3], F Bertran[3], A Taleb-Ibrahimi[3] and D Malterre[1]

[1]CNRS/Institut Jean Lamour, France, [2]Universidad Complutense de Madrid, Spain [3]Synchrotron Soleil, France

Mott transitions where discovered on Sn/Ge(111) [1,2] and on Sn/Si(111) [3,4]. These correlated surfaces appear for a Sn coverage of 1/3 ML, where all the T4 sites are occupied [5,6]. Despite this similarity, there are some differences in these two systems. Sn/Ge shows a structural transition from a (3x3) towards a $(\sqrt{3}x\sqrt{3})$R30° at 30 K, concomitantly with the Mott transition [1]. In turn, Sn/Si exhibits conductivity changes below 100 K [4], but no structural transition has ever been observed down to 6 K [7]: a $(\sqrt{3}x\sqrt{3})$R30° symmetry is always observed, which is indicative of a flat surface and equivalent Sn atoms. Since the Sn 4d core level exhibits more than one component even at low temperatures, quantum fluctuations between two configurations have been evoked [8].

The different behaviors observed between Sn/Si and Sn/Ge are not understood yet. In particular, the driving force of the transition, which may be different in these two systems, is still not clarified. For Sn/Ge, we have evoked two possible mechanisms for the transition that will modify the delicate balance between elastic and electronic energies [1]. Sn/Ge and Sn/Si differ both on their elastic properties and on the electronic correlation U. In order to disentangle the elasticity and electronic effects, we aimed to tailor a surface of Sn/Ge (2 ML)/Si, where we expect to obtain the correlation of Sn/Ge and a similar elasticity to Sn/Si. We will present the atomic structure and the electronic properties of the $(2\sqrt{3}x2\sqrt{3})R30°$ reconstruction that we have tailored.

[1] R. Cortés, A. Tejeda, J. Lobo, C. Didiot, B. Kierren, D. Malterre, E.G. Michel, and A. Mascaraque, Phys. Rev. Lett. 96, 126103 (2006).

[2] S.C. Erwin, Nature 441, 295 (2006).

[3] G. Profeta and E. Tosatti, Phys. Rev. Lett. 98, 086401 (2007).

[4] S. Modesti, L. Petaccia, G. Ceballos, I. Vobornik, G. Panaccione, G. Rossi, L. Ottaviano, R. Larciprete, S. Lizzit, and A. Goldoni, Phys. Rev. Lett. 98, 126401 (2007).

[5] A. Tejeda, R. Cortes, C. Didiot, B. Kierren, D. Malterre, E.G. Michel, and A. Mascaraque, Phys. Rev. Lett. 100, 026103 (2008).

[6] J. Lobo, A. Tejeda, A. Mugarza, and E. G. Michel, Phys. Rev. B 68, 235332 (2003).

[7] H. Morikawa, I. Matsuda, and S. Hasegawa, Phys. Rev. B 65, 201308(R) (2002).

[8] F. Ronci, S. Colonna, and A. Cricenti and G. Le Lay, Phys. Rev. Lett. 99, 166103 (2007).

P2.051 Quantum degeneracy revealed by the relation between the tunneling current and the chemical force.

P Jelinek[1], M Ondráček[1] and F Flores[2]

[1]Institute of Physics of the Czech Academy of Science, Czech Republic, [2]Universidad Autónoma de Madrid, Spain

Recent progress has allowed merging AFM and STM into a new experimental setup where tunneling current and atomic forces are recorded simultaneously. The possibility to collect both quantities simultaneously opens new horizons in understanding fundamental relations between the electron transfer and formation of the chemical bond between two bodies.

Actually, there is a long-standing debate in the scientific community about the relation between the chemical force and the tunneling current (see e.g. [1]) on the atomic scale. Both the tunneling current and the short-range component of the force, induced by the formation of the chemical bond, exhibit in atomic contacts an exponential decay with increasing distance in the range of several angstroms. As the quantities depend directly on the wave-function overlap between outermost atoms of tip and surface, the corresponding exponential functions should have similar characteristic decay length. The relation between the chemical force F and the tunneling current I follows the law $F^n \sim I$, where n is an integer number. Over the last 10 years, different scaling factors n, varying from 1 to 4, have been proposed by different groups based on both theoretical and experimental analysis (see reference in [2]).

In this contribution, we explain the relation between the tunneling current and the interaction force at the atomic scale using a simple analytical model [2]. The model unveils the existence of two characteristic scaling regimes, where the tunneling current is either proportional to the chemical force $I \sim F$ or to the square, i.e. $I \sim F^2$. We show that the existence of a given regime is basically controlled by two parameters: (i) the electronic level degeneracy and (ii) the hopping between electronic levels involved in the interaction process. Finally, we will collate our theoretical prediction with experimental AFM/STM measurements of single-atom point contacts and complex DFT simulations [3] to confirm the existence of these two characteristic regimes.

[1] W. Hofer and A.J. Fisher, Phys. Rev. Lett. 91, 036803 (2003) and the reply in by C.J. Chen.

[2] P. Jelinek et al, J. Cond. Mat. Phys. 24, 084001 (2012).

[3] M. Ternes et al Phys. Rev. Lett. 106, 016802 (2011).

P2.052 The role of van der Waals potential on the electronic spectra of solids and interfaces

A Ambrosetti[1], N Ferri[1], R A Di Stasio Jr.[2], R Car[2] and A Tkatchenko[1]

[1]Fritz-Haber-Institut der MPG, Germany, [2]Princeton University, USA

Van der Waals (vdW) interactions are known to be important in determining the structure and stability for a wide variety of systems. However, little is known regarding the influence of vdW interactions on the electronic spectra of molecular and solid state systems[1].

We address this problem by developing a self-consistent implementation of the Tkatchenko-Scheffler[2] method (SC-TS) for computing the vdW energy and the electronic structure. Remarkably, the SC-TS method allows for a clean and direct comparison between standard and vdW-inclusive DFT using the same underlying exchange-correlation functional.

The influence of vdW interactions on the electronic spectra will be illustrated for a number of condensed matter systems, such as molecular crystals, semiconducting solids, and hybrid inorganic--organic interfaces.

[1] T. Thonhauser, Valentino R. Cooper, Shen Li, Aaron Puzder, Per Hyldgaard, and David C. Langreth, Phys. Rev. B 76, 125112 (2007)
[2] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009)

P2.053 Theoretical reconstruction of MIES spectra

W Beenken, J Preiß, M Reinmöller and S Krischok

Ilmenau University of Technology, Germany

Metastable induced electron emission spectroscopy (MIES) is a very surface sensitive method, which utilizes the exchange interaction between a metastable excited Helium atom and a molecular orbital at the surface. For the extreme short-ranging exchange interaction MIES extends the scale of surface sensitive methods from XPS, which for normal emission is almost bulk sensitive, over UPS He I and He II, to sub-Ångström sensitivity depth. Since we are able to reconstruct XPS and UPS spectra of ionic liquids [1] and other molecular systems [2] by means of quantum-chemical calculations quite precisely, we are now interested to do the same for MIES spectra. However, the calculation of MIES spectra is more complicated than that for UPS or XPS, where photoemission cross sections from literature may be taken. For example, it is necessary to estimate the approach of the metastable He atom to the surface, and gauge the respective parameters of the mean trajectory. Therefore, we will demonstrate the calculation method first on the simple and experimentally wellstudied molecule benzene adsorbed in different orientations on an arbitrary substrate.

[1] Theoretical reconstruction and elementwise analysis of photoelectron spectra for imidazolium-based ionic liquids, M. Reinmöller, A. Ulbrich, T. Ikari, J. Preiß, O. Höfft, F. Endres, S. Krischok, W. J. D. Beenken, Phys. Chem. Chem. Phys. 13, 19526 (2011).
[2] Valence band structure of cellulose and lignin studied by XPS and DFT, T. Haensel, M. Reinmöller, P. Lorenz, W. J. D. Beenken, S. Krischok, S. I.-U. Ahmed, Cellulose (2012) DOI: 10.1007/s10570-012-9681-9.

P2.054 Cs doping of organic semiconducting monolayers: probing the electronic and geometric structure with Angle Resolved UPS

E M Reinisch[1], T Ules[1], G Koller[1], P Puschnig[1], M Ostler[2], S Berkebile[1], T Seyller[2] and M Ramsey[1]

[1]Karl-Franzens-University, Austria, [3]University Erlangen Nürnberg, Germany

Cesium-deposition on ordered organic semiconducting thin films induces changes in the electronic structure and geometric orientation of the molecules.The current investigation is focused on rodlike Sexiphenyl (6P) and Pentacene (5A) molecules adsorbed on Ag(110) and Cu(110) substrates. In an undoped 6P monolayer on Cu(110), we observe flat lying molecules with the LUMO being filled by hybridisation with the surface. Upon Cs deposition first the molecules are tilted and decoupled from the surface, thus the LUMO is emptied. Further Cs deposition subsequently leads to electron charge transfer from the alkali metal to the molecular orbitals, filling first the LUMO, then LUMO+1, with increasing amounts of Cs. In contrast, in an undoped 6P monolayer on Ag(110) the LUMO is empty. Upon Cs deposition the 6P molecules on Ag(110) are doped similar to 6P on Cu(110). Significantly, prior to charge transfer doping, the initial Cs exposure azimuthally reorients the molecules of the 6P and 5A monolayer on Ag(110) from perpendicular to parallel to the substrate corrugation. This constrasts to Cu(110) where both molecules lie parallel to the Cu-rows before and after Cs deposition. This suggests a strong influence of the Cs atoms on the molecule-substrate bonding. The results will be discussed in the light of comparison between the experimental band (E, k) and momentum map (k_x, k_y) of ARUPS with DFT calculations.

P2.055 Optical vibration modes and electron-phonon interaction in spherically capped core-shell quantum dots

X Liang, Y Xing and Z Wang

Inner Mongolia University, China

Optical vibrations of the lattice and the electron-phonon interaction are investigated in the case of a spherical core-shell quantum dots in the framework of the dielectric continuum approach. The essential model is a spherical shell of material “1” sandwiched between a spherical core dot of material “2” and a cap in the form of an additional concentric spherical layer of material 2. It is assumed that the whole heterostructure is imbedded in a host matrix considered as an infinite dielectric medium which does not participate of the polar optical vibrations. The confined longitudinal-optical phonon modes, surface optical (SO) phonon modes, as well as the corresponding electron-phonon (e-p) interaction Hamiltonians are derived. Numerical calculations are performed on a CdS/HgS/CdS heterostructure which is surrounded by the water, and the results reveal that there are five branches of SO phonon frequencies in the system. The SO phonon frequencies dependence on the geometrical size is studied and interesting results concerning the growth parameter are analyzed. The contributions of different angular momentum quantum numbers to the electron-SO phonon potential are given. A detailed discussion of the e-p interaction strength is also made.

Liquid-solid interfaces incl. water and electrochemistry

P2.056 The (100)-pyrite-water interface: A molecular dynamic simulation study supporting GIXRD-experiments

S Meis, U Magdans and H Gies

Ruhr-University Bochum, Germany

The interaction of bio-polymers, monomers and water with surfaces of biominerals is of particular importance for biomineralization and many natural processes. Especially, the mineral pyrite plays an important role in geological, biological and environmental processes. Its surface adsorption properties for water and organic molecules in hydrothermal settings were shown by Lindgren et al. [1] and are important in the Iron-sulphur-world scenario, that describes one possibility for the origin of life, proposed by Wächtershäuser et al. [2]

Previous grazing incidence X-ray diffraction (GIXRD) experiments under environmental conditions resulted in an adsorption model for water at the (100)-pyrite surface [3]. The surface cell is bulk terminated with a defect structure resulting from S- and Fe-vacancies, with only small relaxations and no reconstruction pattern. Three layers of H_2O-molecules are adsorbed to the surface in a distance of 1.9(1)Å, 3.0(3)Å and 5.4(4)Å, followed by a transitional zone between adsorbed and bulk water. Additionally H_2O-molecules occur at Fe-vacancies. An electrostatic interaction along the x-direction of the surface cell leads to an ordered in-plane structure, whereas the interaction along the y-direction is more dynamic, caused by the anisotropy of the (100)-pyrite surface.

In this study we present the results of molecular dynamic simulations of a water layer on the experimentally determined surface structure of the (100)-pyrite surface. Simulations were carried out with the program package Materials Studio 5.0 from Accelrys Inc. In good agreement with results of other molecular dynamic simulations [4], ab-initio simulations [5] and the determined experimental model, three layers of H_2O-molecules are adsorbed to the pyrite surface. Probable positions of the water H-atoms could be mapped. Also, the dynamic positions of H_2O-molecules in y-direction of the experimental model could be explained with an extended positional probability. The combination of molecular simulation techniques with GIXRD-experiments is shown to be a powerful tool to obtain further details of the atomic structure of the (100)-pyrite water interface.

[1] P. Lindgren, J. Parnell, N.G. Holm, C. Broman, Geochemical Transactions (2011), 12:3.
[2] G. Wächtershäuser, C. Huber, Science 281 (1998) 670-672.
[3] S. Meis, U. Magdans, X. Torrelles Acta Cryst. A67 (2011), C338-C339.
[4] M.R. Philpott, I.Y. Goliney, T.T. Lin, J. Chem. Phys. 120(4) (2004), 1943-1950.
[5] A. Stirling, M. Bernasconi, M. Parrinello, J. Chem. Phys. 118(19) (2003), 8917-8926

P2.057 Water-hydroxyl phases on Cu(110): breaking the ice rules

J Carrasco[1], M Forster[2], R Raval[2], A Michaelides[3] and A Hodgson[2]

[1]Spanish National Research Council (CSIC), Spain, [2]University of Liverpool, UK, [3]University College London, UK

Hydroxyl is a key reaction intermediate in many surface catalyzed redox reactions, yet establishing the phase diagram for water-hydroxyl adsorption on metal surfaces remains a considerable challenge for interfacial chemistry, in particular on reactive, open metal surfaces. Based on scanning tunnelling microscopy and density functional theory calculations, we report the phase diagram for water-hydroxyl on Cu(110), providing a complete molecular description of the complex H-bonding structures formed [1]. Three distinct phases are observed as the temperature is decreased and the water-hydroxyl ratio increases: pure OH dimers, extended $1H_2O{:}1OH$ chains, aligned along the close-packed Cu rows, and finally a distorted 2D hexagonal c(2x2) $2H_2O{:}1OH$ network [2]. None of these phases obey the conventional "ice rules", instead their structures can be understood based on weak H donation by hydroxyl, which favours H-bonding structures dominated by water donation to hydroxyl, and competition between hydroxyl adsorption sites. Hydroxyl binds in the Cu bridge site in the 1D chain structures, but is displaced to the atop site in the 2D network in order to accommodate water in its preferred atop binding geometry. The adsorption site and stability of hydroxyl can therefore be tuned simply by changing the surface temperature and water content, giving a new insight as to how the open metal template influences the water-hydroxyl structures formed and the activity of hydroxyl.

[1] M. Forster, R. Raval, J. Carrasco, A. Michaelides, and A. Hodgson, Chem. Sci. 3, 93 (2012).
[2] M. Forster, R. Raval, A. Hodgson, J. Carrasco, and A. Michaelides, Phys. Rev. Lett. 106, 046103 (2011).

P2.058 Use of multivariate analysis in optimization process of black electroplated Cu-Ni coatings preparation

G Czerniak, Ł Skowroński, A Wronkowski and A A Wronkowska

University of Technology and Life Sciences, Poland

The black Cu-Ni coatings are becoming promising for application as absorbers in the solar collector panels. The process of the coatings preparation using deposition techniques like electrochemical deposition resulted in a variety of parameters to be examined eg. pH, temperature, bath composition etc. Thus the optimization process of sample preparation is essential to ensure optimum selectivity and sensitivity.

The series of samples with Cu-Ni layers were prepared under a different combination of parameters. The properties of the produced samples were analysed using standard absorptance (α_s) [1] derived from the diffusive reflectance spectra (DRS). Therefore, two types of data sets are expected to be analysed – the first one contains the bath composition and plating parameters and the second type collects the reflectance R spectra.

The multivariate analysis (MVA) is a statistical approach to help the study and monitor the absorptive quality of the prepared layers [2]. Two classified method such as cluster and principal component analyses (CA and PCA) were undertaken to provide a statistical graphical representation of samples. These applications allowed to compare the generated optimum spectrum of the ideal solar selective coating (SSC) with experimental data and to find the similarities and differences between the samples. The results indicated that these methods are efficient for testing if the sample with the expected properties was properly selected. Moreover, the more detailed understanding of an influence of the bath composition and plating conditions on reflectance spectra was achieved. Besides, some of the applied MVA techniques allowed to demonstrate the correlations between two types of data sets. These analyses provided the information which of the plating parameters are statistically significant in the coatings preparation process.

In most cases, optimization process is performed by sequential analysis of experimental parameters. In this work an alternative approach, using statistical method called factorial design, was adopted to extract the most important parameters (factors) and to search for the optimal preparation conditions [3].

[1] J.A.Duffie, W.A.Beckman, Solar Engineering of Thermal Processes, John Wiley & Sons, 2006.
[2] P.Simeonova, S.Tsakovski, P.Mandjukov, V.Simeonov, and V.Lovchinov, Mikrochim. Acta 124, (1996) 151.
[3] C.M.Ronconi, O.L.Alves, R.E.Bruns, Thin Solid Films 517, (2009) 2886.

P2.059 Interaction of some atmospheric oxygenated volatile organic compounds (OVOCs) with H_2O, $HNO_3.3H_2O$, and pure HNO_3 ice surfaces

J Lasne[1], C Laffon[2] and P Parent[2]

[1]Heriot-Watt University, UK, [2]CNRS and Universite Pierre et Marie Curie, France

Oxygenated volatile organic compounds (OVOCs) influence the oxidative properties of the atmosphere. Their transport from the ground may occur by scavenging by the nitric acid-rich supercooled water droplets found in polluted convective air masses. On the other hand, their reaction with nitric acid (HNO_3) at the surface of aerosol particles catalyses the formation of secondary organic aerosols. With infrared spectroscopy, we have studied the interactions of four typical atmospheric OVOCs (acetone, hydroxyacetone, acetaldehyde and benzaldehyde) with water, $HNO_3.3H_2O$ (nitric acid trihydrate, NAT) and pure HNO_3 ices. We show that these molecules adsorb weakly by hydrogen bond interaction with the surface of water ice or that of NAT film whereas they strongly react with anhydrous HNO_3, the proton of the acid being transferred to the carbonyl group of the OVOCs. These results suggest that the formation of the hydrogen bond complexes with H_2O or NAT favours the OVOCs atmospheric transport during which they remain intact in contact with hydrated HNO_3 in atmospheric ice clouds.

P2.060 Effect of Ions Y_{3+} inhibitor on mild steel corrosion in 0.5 N NaCl

S Abderrahmane, S Ouchenane and A Himour

University of Badji-Mokhtar, Algeria

The corrosion inhibition of mild steel by Yttrium salt $Y(NO_3)_3$ $6H_2O$ at different concentrations in 0.5 N NaCl, has been carried out by potentiodynamic tests and electrochemical impedance spectroscopy (EIS).In ions Y_{+3} presence, the ions OH^- formation at the interface (electrode / electrolyte) by water and oxygen reduction ,precipitates oxide and hydroxyde composite in passive film. The current density decreases as a function of the inhibitor concentration; it varies from the value without inhibitor (i = 0.2139 m A /cm^2) to the minimal value (i = 7.4.10^{-4}m A/cm^2) for 600 ppm concentration; the corresponding inhibitive efficiency reaches 99.65 %. On laminar hydrodynamic regime ($\omega \leq$ 3000 rpm), steel inhibition depends on rotation speed. It has been showed that passive film formation is all the more slowly than the rotation speed increases.

P2.061 Water adsorption on lithium niobate studied from first principles

R Hölscher, M Witte, S Sanna and W G Schmidt

Universität Paderborn, Germany

$LiNbO_3$ (LN) is a frequently used material for optical and acoustic applications due to its strong piezoelectric, pyroelectric, and photorefractive properties. As for other ferroelectric materials, manipulating the polarization can change the surface reactivity. This opens the possibility for the realization of molecular detectors and other devices[1].

Unfortunately, only few data about the structure of the surface are available. Most studies do not refer to clean surfaces in UHV conditions, but are rather performed in ambient conditions, where the adsorption of foreign species like water might modify the LN surface properties. Here we present ab initio calculations on the adsorption of H2O monomers and thin water films on the positive (0001) and negative (0001) surface of LN. The adsorption is modelled by means of density functional theory (DFT) within the generalized gradient approximation[2,3]. From the thermodynamic grand-canonical potential calculated from first principles we determine the stable adsorption configurations as a function of the water chemical potential, which itself is given in dependence on temperature and pressure.

The present calculations indicate that at ambient conditions a thin water film may cover the LN surface. The interface atomic structure is calculated both from first principles, as we all using a solvent model.

[1] D. Li, et al., Nature Materials 7 (2008) 473.
[2] W.G. Schmidt, et al., Phys. Rev. B 77 (2008), 035106.
[3] S. Sanna, A.V. Gavrilenko, W.G. Schmidt, Phys. Stat. Sol. C 7 (2010) 145.

P2.062 From HCl oxidation to the formation of water on the Cu(100) Surface

M Gladys[1], I Suleiman[2], M Radny[2], J Mackie[2], P Smith[2], E Kennedy[2] and B Dlugogorski[2]

[1]University of Newcastle, UK, [2]The University of Newcastle, Australia

Using density functional theory and a p(2×2) periodic slab, we have studied the water formation via HCl oxidation on the Cu(100) surface. We show that the interaction of HCl with oxygen on the Cu(100) surface lead to water formation according to two different pathways depending on the applied temperature, however, both obey the Eley-Rideal mechanism. We also show that while chlorine increases the stability of water on the Cu(100) surface, water dissociates immediately when located next to oxygen atom.

P2.063 Adsorption and desorption of SO_2 on the ionic liquids $[C_2C_1C_1Im][Tf_2N]$ and $[C8C_1Im][BF_4]$

M Buckley, R Jones, K Syres and R Stainer

University of Nottingham, UK

Due to strong coulombic forces between their constituent ions ionic liquids (ILs) have extremely low vapour pressures. This allows the use of ultra-high vacuum techniques in our aim to study their applicability as selective gas capture agents. Here we study the interaction of SO_2 with two ILs which are expected to form different types of surface. Line of sight mass spectrometry was used for temperature programmed desorption and absolute sticking probability (S) measurements.

$[C_2C_1C_1Im][Tf_2N]$ surfaces are expected to be comprised of charged imidazolium cations and bulky $[Tf_2N]^-$ anions, partially covered by the rather small ethyl, methyl and CF_3 groups. At 300 K the absolute sticking probability of SO_2 on this surface was found to be zero, while adsorption onto the IL glass at 100 K showed mono and multilayer adsorption consistent with relatively strong $SO_2 \ldots SO_2$ interactions.

By comparison, $[C_8C_1Im][BF_4]$ surfaces are expected to form a layer of octyl chains above an ionic underlayer of the imidazolium cations and small $[BF_4]^-$ anions. SO_2 adsorption at 100 K exhibited unusual behaviour, where a threshold pressure of $\approx 5\text{x}10^{-8}$ mbar was required before adsorption commenced. This is interpreted as due to a particularly short $SO_2 \ldots$octyl chain surface life-time requiring SO_2/SO_2 collisions on the surface to produce nucleation centers.

P2.064 Continuum solvent model for adsorption processes on periodic surfaces

M Witte, U Gerstmann, E Rauls and W G Schmidt

University of Paderborn, Germany

Systems in solution play an important role in physical chemistry and are often difficult to calculate from first-principles methods such as density functional theory (DFT). In order to study adsorption processes on the solid-liquid interface, for example, a solvent model implementation that allows for periodic boundary conditions would be very helpful. We implemented the continuum solvent model proposed by Fattebert et al. [1] in the plane wave DFT code PWscf [2] and the modified Poisson equation is solved with the Parallel algebraic MultiGrid (PMG) solver [3]. Instead of the suggested zero-Dirichlet boundary conditions we use a different approximation using the screened Hartree potential. This model is applied to small model systems to compare their behaviour in solution and their dependence of the surrounding. We present a detailed analysis of the various contributions to molecular solvation energies and study the impact of the solvent on the surface atomic and electronic structure.

[1] J.L. Fattebert et al., Int. J. Quantum Chem., 23 (2002) 662.
[2] P. Giannozzi et al., J. Phys.: Condens. Matter 21 (2009) 395502.
[3] M.J. Holst et al., J. Comput. Chem. 14 (1993) 105.

P2.065 Adsorption of cysteine modified silicon substrates in electrolyte solution studied by means of surface differential reflectance spectroscopy

Y Fujimori[1], S Ookawara[1], M Tanaka[1], T Sekiya[1], T Momose[1], S Ohno[1], C Smith[2] and P Weightman[2]

[1]Yokohama National University, Japan, [2]University of Liverpool, UK

Interaction between biomolecules and semiconductor substrates is not well understood, although the knowledge of the interaction is important to develop biodevices compatible with the semiconductor electronics. In this study, the structure of cysteine adsorbed on modified Si substrates and its potential dependence in electrolyte solution have been investigated by means of surface differential reflectance spectroscopy (SDRS). Au thin film with thickness of 20nm or Au nanoparticles with mean diameter of 100nm is formed on Si(001) covered with native oxide. The substrates were then introduced into an electrochemical cell which was filled with 0.1 M H_2SO_4 solution containing 10 mM L-cysteine. Applied potential was ranged from -0.4 to +0.4V.

SDR spectra of cysteine/Au-film/Si show that a feature at 2.5eV ascribed to Au-S bond and a feature at 4.7eV ascribed to cystine increase in intensity at negative and positive potential, respectively. The former indicates that more cysteine molecules are combined with Au due to the electric field, while the latter indicates that cysteine is oxidized to form cystine. Similar result was obtained from SDR spectra of cysteine/Au(110). The result of SDRS is not only consistent with that of reflectance difference spectroscopy but also provides us with new findings. In addition to the above result, a red shift of the plasmon peak due to cysteine overlayer is found in SDR spectra of cysteine/Au-nanoparticles/Si. Thus, it has been shown that the behavior of biomolecules is revealed by SDRS even at in-plane isotropic solid-liquid interface.

P2.066 Metal-induced anisotropic etching of Ge(100) surfaces in water with dissolved oxygen

K Arima, T Kawase, A Mura, Y Kawai, K Kawai, J Uchikoshi and M Morita

Osaka University, Japan

Germanium (Ge) is a promising channel material for future metal-oxide-semiconductor (MOS) devices because of its higher carrier mobility than silicon (Si). It is generally accepted that the microroughness of a substrate surface greatly affects the performance and reliability of gate insulators in MOS devices. The surface microroughness of a substrate is mainly determined by wet cleaning prior to the formation of the gate insulator. Contrary to the sophisticated RCA cleaning for Si surfaces, wet cleaning processes for Ge surfaces have not yet been well established. To realize such processes, it is necessary to understand the interaction of various solutions with Ge as well as the behavior of contaminants on Ge in solutions from the viewpoint of electrochemistry. We reveal that Ge(100) surfaces containing metallic particles are etched anisotropically even in water. This originates from the catalytic reduction of dissolved oxygen (O_2) in water to water molecules (H_2O) on the metallic particles, which is followed by the enhanced oxidation of Ge around the particles. The soluble nature of the Ge oxide (GeO_2) in water promotes the formation of etch pits composed of (111) microfacets. From these results we propose strategies for avoiding unwanted surface roughening during the wet cleaning of Ge. Furthermore, we apply this catalytic reaction in water for novel surface processes such as micropatterning and flattening of Ge.

P2.067 Atomic surface structure of Cs-terminated muscovite mica determined using SXRD

S Pintea[1], W de Poel[2], A de Jong[3], F van den Bruele[2], V Vonk[2], P van Asdonk[2], O Balmes[3], R Felici[3], E Vlieg[2]

[1]European Synchrotron Radiation Facility, France, [2]Radboud University Nijmegen, The Netherlands, [3]European Synchrotron Radiation Facility, Grenoble, France

The atomic surface structure of Cs-exchanged muscovite mica in dry and wet conditions was determined using surface x-ray diffraction (SXRD). Specular and non-specular crystal truncation rods, measured in the stationary mode, were performed at the ID03 beamline of the European Synchrotron Radiation Facility (ESRF). Data, rapidly collected using a 2D pixel detector, were analyzed using a specially written plug-in of PyMca software. Fitting was carried out using an improved version of the ROD software.

The cleavage of muscovite mica along the (001) plane can occur at two specific heights within the unit cell. This leads to the appearance of two surface domains, which are symmetry related by the glide plane of the muscovite's crystalline structure (space group C2/c). Averaging over the X-ray footprint on the sample of about 1 x 5 mm^2, the occupancy of surface domains is expected to be 50% each. Fitting the data, however, revealed that the ratio of occupancies of the two domains is very different from 50:50. This means that either the terrace size is bigger than expected, or one of the domains occurs with higher probability.

The surface structural model proposed uses as fitted parameters the relaxations, occupancies and Debye-Waller parameters for atoms that are located at less than 5 Å deep in the bulk muscovite and for the partly ordered water layers located on the top of the mica.

P2.068 Characterization of ionic liquid interfaces with metastable induced electron spectroscopy (MIES) and photoelectron Spectroscopy (UPS/XPS)

O Höfft[1], A Ulbrich[2], M Marschweski[1], A Zühlsdorff[2], W Maus-Friedrichs[1], F Endres[1] and S Krischok[2]

[1]TU Clausthal, Germany, [2]TU Ilmenau, Germany

Ionic liquids (IL) are a highly interesting group of solvents for electrochemical processes; mainly due to the combination of their high electrical conductivity, their electrochemical stability and their ability to dissolve a wide range of compounds [1]. Due to the low vapour pressure ionic liquids interfaces can be investigated with electron spectroscopic methods like metastable atom induced electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS, HeI/II)) and X-Ray photoelectron spectroscopy (XPS) [2] . Here we use the different surface sensitivity of these methods to investigate the molecular composition of the vacuum interface of [XMIm]Cl (X = Octyl, Hexyl, Butyl, and Ethyl alkyl chain) ionic liquids in detail. We will show that the increasing of the cation chain length is connected with a decrease of the chlorine signal in the UPS spectra. For the [OMIm] cation no chlorine is visible in the MIES spectra at all.

In addition we present for the first time the interaction of cesium with thick films and monolayers of imidazolium based ILs. Here we will focus on the solvation of cesium in these ionic liquid films. For the IL monolayers, grown on Si(100), we find a shift of the IL valence band states to higher binding energies during Cs adsorption.

[1] F. Endres, S. Zein El Abedin, Phys. Chem. Chem. Phys., 8 (2006) 2101.
[2] H.-P. Steinrück, Surface Science, 604 (2010) 481.

P2.069 Amplitude-modulation AFM-derived heights under suspicion

J Fraxedas[1], G Sauthier[1], J J Segura[1], S Santos[2], M Chiesa[2] and A Verdaguer[1]

[1]Centre d' Investigació en Nanociència i Nanotecnologia, Spain, [2]Masdar Institute of Science and Technology, United Arab Emirates

The determination of the true height of water films on surfaces at ambient conditions as determined by atomic force microscopy operated in true noncontact operation modes has been recently discussed based on theoretical models taking into account capillary forces [1]. A dependency of the measured water height on operational parameters has been identified. The ratio between the apparent and true heights spans from values well above one to even negative values thus, challenging the determination of the true heights of objects on surfaces under the action of water [2]. Here, we present a systematic study of the variation of step heights of stearic acid islands grown on freshly cleaved mica surfaces by sublimation. The contrasting behavior of the exposed surfaces, mica is hydrophilic while the island are hydrophobic because they are methyl-terminated, makes this system an ideal benchmark for investigating the variation of the measured heights as a function of the operational parameters with noncontact AFM.

[1] S. Santos, A. Verdaguer, T. Souier, N. H Thomson and M. Chiesa, Nanotechnology 22, 465705 (2011).
[2] S. Santos, A. Verdaguer and M. Chiesa J. Phys. Chem. C (under review).

P2.070 Electrochemical oscillation in the additives-assisted copper electroplating: a mechanistic study on the role of intermediate species at the copper/electrolyte interface

H Nguyen, J Odermatt, V Grimaudo, K W Krämer and P Broekmann

University of Bern, Switzerland

Additives are mandatory for the industrial copper electroplating in context of the Copper Damascene Process. It is well-known that the presence of additives could guarantee the free-defect bottom-up fill of the vias and trenches. However, the mechanistic details of those additives are not well understood due to the synergistic and antagonistic interplay among them. In this study we present a study on the copper deposition in the presence of an accelerator additive SPS (bis(sodium sulfopropyl) disulfide) and a leveler additive (polymerizate of imidazole and epichlorohydrin (Imep)). A potential oscillation is commonly observed during the galvanostatic copper electroplating. A combination of various methods such as potentiometry, STM, elementary analysis, UV-VIS, SQUID, SIMS allowed us to identify the active suppressor ensemble at the copper/electrolyte interface. SPS adsorbs and dissociates under reactive conditions leading to the formation of co-adsorption MPS/Cl phase on copper surface and MPS formation at the copper/electrolyte interface. MPS coordinates with Cu(I) intermediate species forming stable H_2O-Cu(I)-MPS complexes which subsequently coordinate with the OH-group of the Imep polymer. The introduction of negatively charged MPS species into the positively charged Imep polymer leads to the neutralization of the complex and finally to its precipitation on the copper surface. This precipitate acts as effective physical barrier for the further copper deposition. It is discussed that the formation/precipitation and the dissolution of the Imep-Cu(I)-MPS complex on at the copper/electrolyte interface result in the appearance of the potential oscillation. This precipitate incorporates into in the growing copper deposit as proven by SIMS measurements.

P2.071 Redox-active Safranine/Janus Green B leveler additives at Cu(100)/electrolyte interface: EC-STM and electrochemical studies

H Nguyen and P Broekmann

University of Bern, Switzerland

Copper electroplating is one of the key steps in the formation of the internal wiring in integrated logic and memory devices. The bottom-up fill of vias and trenches can be only achieved by using additives such as accelerators, suppressors and levelers which control the copper deposition faster at the bottom of the features compared to the suppressed copper deposition at the upper-side walls and on the surface of the wafer. Janus Green B and Safranine are used as model leveler systems for the bottom-up fill of 3D-Through Silicon Vias (3D-TSV). Our combined electrochemical an in-situ STM study demonstrates the role of these levelers at the copper/water interface. Both two molecules are proven to be redox-active at the potential range of copper deposition in which their aromatic cores undergo a reduction process involving two electron transfer processes. STM study demonstrates that an ordered layer of mono-reduced Safranine is formed on the chloride modified Cu(100) surface. A further reduction step leads to a phase transition of this layer on copper/chloride surface from an ordered 2D monolayer to a film of 3D-clusters. It is the reduction process which makes these levelers more hydrophobic as prerequisite for the formation of 3D-clusters. This hydrophobic layer of clusters is discussed as the actual suppressor film with respect to the copper film.

P2.072 LEED - IV study of the co-adsorption of chlorine and water on Cu (100)

M Puisto[1], K Pussi[1], M Alatalo[1], D Hesp[2], V R Dhanak[2], C A Lucas[2] and Y Grunder[3]

[1]Lappeenranta University of Technology, Finland, [2]University of Liverpool, UK, [3]The University of Manchester, UK

Halogens adsorbed on metals are known to inhibit catalytic reactions by blocking reactive species, i.e. spectator anions. At the electrochemical interface, where reactions take place in an aqueous environment understanding how the presence of water perturbs the substrate is of fundamental interest. Studies on other systems of the adsorption of water on single metal crystals has found the interaction of water to the surface to be a weak one, comparable in strength to the hydrogen bonding between adjacent water molecules[1,2].

The co-adsorption of chlorine and water on the Cu (100) surface was studied using LEED -IV and photoelectron spectroscopy. The aim of this work was to investigate the influence of water on the charge distribution at the Cl/Cu interface. When chlorine is adsorbed on a metal a strongly bound stable adsorbate system is produced [3]. This system had been studied previously and the chlorine is found to form a c(2x2) chemisorbed layer where the Cl atoms occupy the energetically favourable four-fold hollow sites[3].

Consistent with previous work the XPS data showed no detectable perturbation of the substrate when the water was adsorbed. There were no new spots in the LEED pattern after adsorption although the IV curves did show a change. The data we present here is based on the modeling of these IV curves which showed that water molecules form chains bonding to the copper sites of the substrate through the its oxygen atom.

[1] Henderson, SUR. SCI. REP. 46 (2002) p1.
[2] Thiel, SUR. SCI, REP. 7 (1987) p211.
[3] Westphal, Goldmann, SOL. ST. COMMUN (1982) p308.

P2.073 Gly-Cys-Gly-Cys immobilization on porous silicon nanostructure for electrochemical detection of metals

S Sam[1], C Yaddadene[1], A C Gouget-Laemmel[2], J-N Chazalviel[2], F Ozanam[2], A Etcheberry[3], N Chiboub[1] and N Gabouze[1]

[1]Unité de Développement de la Technologie du silicium (UDTS), Algeria, [2]CNRS, France, [3]Institut Lavoisier de Versailles, France

Hybrid nanomatrials based on organic layer covalently grafted on porous silicon PSi nanostructure appear as promising systems for innovative applications. In this work, we focused on the functionalization of the PSi nanostructure by the peptide Gly-Cys-Gly-Cys, which forms stable complexes with metal ions. This property is exploited to realize toxic metal recognition in water.

The immobilization was achieved using multi-step reactions: Gly-Cys-Gly-Cys was anchored on a previously prepared carboxyl-terminated PSi surface using EDC/NHS coupling agents. This scheme is compatible with the mild conditions required for preserving the probe activity of the peptide.At each step of the functionalization, the surface was monitored by infrared spectroscopy Fourier transform (FTIR) and X-ray photoelectron spectroscopy (XPS).

Electrochemical behaviour of such prepared electrodes was carried out in the presence of copper or Nickel ions by means of cyclic voltammetry. The recorded cyclic voltammograms showed a quasi-irreversible processes corresponding to the Cu(II)/Cu(I) or Ni(II)/Ni(0) couples, respectively.

These results demonstrate the potential role of peptide-modified PSi nanostrutures in developing strategies for simple and fast detection of metal ions in solution.

P2.074 Electrochemical study and mechanical investigation of zinc alloy electrodeposition in the presence of solanum tuberosum juice extract as additive.

O S Fayomi, A Patricia, I Popoola and O Popoola

[1]Tshwane University of Technology, South Africa

This study focuses on the effect of co-deposition of zinc alloy particles in the presence of solanum tuberosum juice extract additives on zinc alloy electrodeposition bath. The characterization of the resultant microstructure was carried out by SEM and XRD on the morphology of Zn alloy coating. Abrasive wear tester and potentiodynamic polarization tests were used to study the tribological and corrosion properties of the coatings, respectively. Results of hardness analysis revealed that the hardness of electrodeposited sample in the presence of solanum tuberosum juice show better performance. Wear investigations showed that simultaneous co-deposition of theparticles into the zinc coating increased the wear resistance of the coating by about 80%. Corrosion studies illustrated that in the presence of solanum tuberosum reduction in corrosion resistance was achieved compared to ordinary zinc deposition.

Metal surfaces

P2.075 Growth of perfect metallic nanowires on Cu (100) vicinal surfaces: a kinetic Monte Carlo study

A Ben Haj Hammouda, S Blel and B Oujia

Faculy of Science of Monastir, Tunisia

Among the many nano-objects, nanowires are currently attracting great interest for their properties induced by their one-dimensional structure. They are interesting for basic as well as applied research to the development at the industrial scale. Kinetic Monte Carlo (kMC) simulations were developed to describe all the kinetic processes occurring during epitaxial growth on vicinal surfaces and to interpret the formation of one-dimensional structures for different chemical species [1]. Moreover, we know that whatever the considered mechanism, it allows the attachment of deposited atoms in the step edge of the substrate surface. Among these mechanisms that can be studied as adjustable parameters by kMC, are the Ehrlich-Schwoebel (ES) barrier, the KESE [1] and the exchange mechanisms, have been considered in this work and shown to play a key role in the formation of perfect nanowires on Cu(100) substrate.In particular, depending on the deposited ad-atom, we found different temperature ranges for perfect mono-atomic wires to be formed (between 200K and 500K for Ag/Cu, but from only 425K to 525K in the case of Co/Cu). The ES barrier was varied between 0 and 1 eV to study the variation of the filling ratio of Co and Ag nanowires at the bottom of Cu surface-steps. An ES barrier between 0.15eV and 0.20eV is found to be realistic in a good agreement with the observation of Gambardella et al. [2,3]on Pt(997) vicinal surfaces. We also assessed the effect of the deposition flux and the terrace width on the morphology of nanowires. This work provides experimentalists with optimum growth parameters and basic mechanisms governing the creation of a uniform distribution of wires on vicinal surfaces.

[1] A. BH. Hamouda, R. Sathiyanarayanan, A. Pimpinelli, and T. L. Einstein, Phys. Rev. B 83 (2011) 035423.
[2] P. Gambardella, M. Blanc, L. Burgi, K. Kuhnke, K. Kern, Surf. Sci., 449 (2000) 93-103.
[3] Essolaani Wafa, Fabien Picaud, Christophe Ramseyer, Pietro Gambardella, Moncef Said, Daniel Spanjaard, Marie-Catherine Desjonquères, Surf. Sci. 605 (2011) 917-922.

P2.076 Surface structure of Ag-In-RE (Gd,Tb,Yb) 1/1 approximants

S S Hars[1], T P Yadav[1], H R Sharma[1], J A Smerdon[1], R Tamura[2], M Shimoda[3], A P Tsai[4] and R McGrath[1]

[1]University of Liverpool, UK, [2]Tokyo University of Science, Japan, [3]National Institute for Materials Science, Japan, [4]Tohoku University, Japan

Quasicrystals are orientationally-ordered alloys with classically forbidden rotation symmetries (5,10 fold axes) which are incompatible with the periodic translational ordering and the discovery has completely changed the understanding of crystallography[1]. The surface properties of quasicrystalline alloys differ from those of conventional crystalline metallic materials. Surface studies can provide insight into the influence of quasiperiodic ordering on the physical properties and potential applications of these materials. The i-Ag-In-Yb quasicrystal provides the first non-Al-based aperiodic system that is suitable for study using conventional surface science ultra-high vacuum techniques. The surface of icosahedral i-Ag-In-Yb quasicrystal has been studied in detail using scanning tunneling microscopy, low-energy electron diffraction and reaction high-energy electron diraction [2-3].

Approximants are crystalline materials with chemical composition similar to quasicrystals. Although they are periodic materials, they have large unit cells and a cluster-based structure similar to quasicrystals. In the present investigation, the clean surface of the Ag-In-Gd 1/1 approximant has been characterized with LEED and STM. The surface structure of the Ag-In-Gd 1/1 approximant will be compared with the bulk structure model and with the i-Ag-In-Yb quasicrystal surface.

[1] The Nobel Prize 2011: D.Shechtman et al. Phys.Rev. Lett.53,1951 (1984).
[2] H.R.Sharma, et al. Phys. Rev. B 80, 121401 (2009).
[3] P.J.Nugent et al. Phil. Mag. 91, 2862 (2011).

P2.077 Effect of surface preparation on the bond strength of Aluminum alloy 2024

M Khabiri, M G Nejad, M Abbasi and A Movafagh

Malek-Ashtar University of Technology, Iran

Adhesion is a surface phenomenon that controlled by the condition of the surface of the adherent. Specific adhesion of metals like aluminum and it's alloys are significantly affected by surface preparation. Aluminum surface treatment used to improve the adhesion in industry. Anodizing method by chromic acid is one of the best known techniques for aluminum alloys pretreatment. When there is an attention to both adhesion and conditional protection, the sealing should be considered after anodisation to establish adherent surface. To find the optimum adhesion on the sealed aluminum, the size of the pores was measured by FE-SEM technique. The pores size should be controlled in a way that is not closed by sealing. In the present study the aluminum alloy (AL2024) were anodized and sealed in different concentration of the chromic acid. Next, the size of the pores was determined by FE-SEM. In this way we were able to find the concentration that creates smallest pores size with a proper adhesion. However increasing the concentration will close the pores and reduce the strength of adhesion. Therefore, we are able to determine the proper adhesion with adequate protection.

P2.078 Investigation of ultrathin Fe films on Ag(001) by multi-photon photoemission

T R F Peixoto[1], M Pazgan[1], F Bisio[2], A Winkelmann[1], M Dabrowski[1], M Przybylski[1] and J Kirschner[1]

[1]Max Planck Institute of Microstructure Physics, Germany, [2]CNR-SPIN, Italy

Investigations of iron films grown on silver surfaces have shown an intriguing thickness-dependent oscillatory magnetic anisotropy [1,2]. This behaviour was explained by the appearance of quantum well states (QWS) in the Fe film. In order to access the relevant electronic states, we investigated ultrathin Fe/Ag(001) films by angle- and spin-resolved one-photon (1PPE, $h\nu$ = 6.2 eV) and multi-photon photoemission (2PPE, 3PPE, $h\nu$ = 3.1 eV) at 150 K. Consistent with the literature on QWS in Fe/Ag(001) [1,2], we report periodic thickness- and energy-dependent intensity variations of electronic transitions in 1PPE and 2PPE spectra. Using different incident light polarizations, we identify the presence of specific unoccupied states in 2PPE. The Fe films show an average spin-polarization up to 25% near E_F in 2PPE and 10% in 1PPE. This difference is attributed to the influence of unoccupied states. By means of angle-dependent 3PPE, the n=1 image-potential state of Fe/Ag(001) is identified, with an estimated electron effective mass of $m_{eff} = 0.75 m_e$ and a binding energy of E_B = 0.77 eV with respect to the vacuum level.

[1] U. Bauer and M. Przybylski, Phys. Rev. B 81, 134428 (2010).
[2] J. Li et al., IEEE Trans. Magn. 47, 1603 (2011).

P2.079 Influence elements (V and Nb) on the microstructure and corrosion behaviour of a stainless steel type 309

A Himour, A Gharbi, S Abderrahmane and K Maddouri

University Badji Mokhtar, Algeria

The austenitic stainless steels such as the AISI 309 have very important industrial applications to high temperature in corrosive conditions. However, the chromium carbides ($Cr_{23}C_6$) cause under these conditions an embrittlement and an intergranular corrosion. To improve the mechanical properties and behaviour with corrosion of this steel, the elements, Vanadium and Niobium, were added to percentages of: V ≤ 1.5%, Nb ≤ 0.14%. The characterization of alloys obtained was carried out, front and after heat treatments, by metallographic observations, mechanical tests and electrochemical measurements in stationary and transitory mode. The results showed that the addition of V and of Nb, improves the mechanical properties of steel, front and after heat treatment, following the reduction in the intergranular precipitation of chromium carbides in favour of an intragranular precipitation of carbides of V and Nb (VC, V_4C_3, NbC).The tests of corrosion carried out on these alloys in a solution with 0.1M HCl show an improvement of behaviour to corrosion: ennoblement of the potential of corrosion in correlation with the increase in the resistance of polarization.

[1] Z.Z. Yuana, , Q.X. Daia, Q. Zhanga,b, X.N. Chenga, K.M. Materials Characterization 59, 18(2008).
[2] S. M Abbasi, A Shokuhfar,Iron and steel research, international, 14,74(2007).
[3] A. F. Padilha, I. F. Machado, R. L Materials Processing Technology 170, 89 (2005).
[4] H. Yan, H. Bib, X.Lib, Z.Xua,Microstructure and Materials Characterization 5 9, 1741 (2008).
[5] M.G. Pujar, N. Parvathavarthini ,R.K. Dayal, S. Thirunavukkarasu, Corr. Sci. 51, 1707 (2009).

P2.080 Optical properties of the Cu, β-Sn and In nanoscale films on glass substrates

A A Wronkowska, G Czerniak, Ł Skowroński and A Wronkowski

University of Technology and Life Sciences, Poland

The key phenomenon connected with optoelectronic properties of metal nanostructures in a dielectric surrounding is exciting of surface plasmons by the incident electromagnetic radiation. We will present the optical response dependence on a thickness of the Cu, β-Sn and In ultrathin films (mass thickness ranges from d=2 nm to 40 nm) evaporated onto glass substrate. All metal films were grown with a rate 0.05 nm/s at a base pressure 10^{-4} Pa. Scanning electron micrographs exhibited a granular structure of the produced nanolayers as result of the Volmer-Weber mechanism of their growth. Spectroscopic ellipsometry (SE) and transmittance (T) spectra were measured in the photon energy E range 0.6 – 6.5 eV to derive the complex dielectric function $\varepsilon(E) = \varepsilon_1(E) + \varepsilon_2(E)$ of the films. A classical Drude-Lorentz dispersion formula was used for a quantitative description of features in ε(E) related to the electron intra- and interband transitions and plasmonic effects. For the Cu thin films above the percolation threshold (d ≥ 10 nm) we have found a coexistence of the free-electron Drude term, developing with increasing film thickness, and becoming weaker plasmon mode in the near infrared. In case of β-Sn, the Drude absorption shoulder appears for the thicker films (d ≥ 20 nm) than for Cu layers. In contrast, the optical spectra of the In films are dominated by absorption bands of the Lorentzian type, which progressively shift to lower energies with increasing film thickness and suppress the free-electron contribution to ε(E).

P2.081 Proprieties of Ti-C-N coating deposited by magnetron sputterings

S Nadia[1], S Sanjiv[2], E Rudolph[2] and C J Darrell[2]

[1]Centre for the Development of Advanced Technologies (CDTA), Algeria, [2]University of the Witwatersrand, South Africa

In recent years, significant attention of the researchers is given to multicomponent interstitial compounds of titanium (carbonitrides, carboxides, and oxynitrides). This is explained by the fact that their physicomechanical properties are better than the properties of binary compounds [1]. Titanium carbonitride (TiCN) coatings are very interesting coatings that combine the high hardness and low friction coefficient of the TiC phases and the high toughness of the TiN phases [2-7]. These unique properties make TiCN coatings a good solution for the applications requiring high abrasion and wear resistance.

The deposition of TiCN coatings by sputtering has important specific advantages such as low levels of impurities and easy control of deposition rate. This method also enables the production of thin coatings of various morphology and crystallographic structure.

When a sputtering technique is used for depositing TiCN coatings, the coatings properties are widely changed by the variation of the sputtering conditions, such as reactive gas pressure, total pressure, and substrate bias voltage. Therefore, it is interesting to study the effects of the deposition parameters on TiCN coatings.

In this work, Ti(C,N) coating have been deposited by RF reactive magnetron sputtering (13.56 MHz). We've been studied the effect of the nitrogen partial pressure and the substrate bias voltage on the properties of titanium carbonitride coatings prepared by RF reactive magnetron sputtering. The deposited coatings were characterized by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and micro-indentation.

P2.082 Oxidation state analysis of Cr in the oxide layer between stainless steel and metallic tin by AES

S Fukushima, T Kimura, H Iwai and A Tanaka

National Institute for Materials Science, Japan

Auger electron spectroscopy (AES) is widely used as one of the method in micro-beam surface analysis. However,there is not so much practical application to the chemical state analysis in small area. In this report, the basic investigation about the oxidation state analysis of Cr by AES measurement with theoretical calculation (cluster calculation without consideration of spin-orbit and spin-spin interaction), and its application to the identification of the existence of Cr oxide in the surface oxide layer of stainless steel will be presented. This oxide layer was prepared by heating (350 °C in the air, 1000 hours) with melting tin drop, for the purpose of the preliminary investigation about the corrosion process of the stainless steel surface by melting tin.

From the measurement results of Cr LMM spectra of metal and Cr_2O_3 as the standard of Cr(III) state, the peaks of Cr_2O_3 showed about 4 ~ 8 eV sift from metal. From the cluster calculation by DV-Xα method using large cluster models (constructed with more than 100 atoms), the tendency of the peak sifts were reproduced well, and it was confirmed that the measurement results reflected the change of chemical state correctly.

Using above results,the analysis of the oxide layer on the stainless steel surface which contacted directly with melting tin during the heating process was executed. From the measurement, it was revealed that the oxide layer was consist of two layers either Cr was contained or not. And, it was presumed that Cr in this layer took metallic state.

P2.083 Surface diffusion involved intermixing of ultrathin In and Ag layers and formation of AgxIn1-x surface alloys on the tungsten surface

K Okulewicz, A Bukaluk and M Trzcinski

University of Technology and Life Sciences in Bydgoszcz, Poland

Indium layers of 2.0 to 6.0 ML thickness were deposited on the less than one half area of the polycrystalline tungsten sample of 12 mm diameter, and the same amount of silver was evaporated on the opposite side of the tungsten surface. In and Ag layer thickness was monitored by measurement of work function changes, ratios of intensities of In4d and W2p, as well as Ag4d and W2p intensities of XPS spectra compared with UPS spectra of the same levels. Consecutive heating of the sample to the temperature of 600 K caused surface diffusion of indium and silver atoms and their intermixing in the central part of the surface area. After cooling the sample to the room temperature we observed UPS spectra of In4d and Ag4d lines involved by HeI and HeII monochromatized radiation. We found that diffusion of In and Ag and their intermixing in the centre of the tungsten substrate resulted in drastic change of the shape of Ag4d line and the change of the binding energy of both Ag4$d_{3/2}$ and Ag4$d_{5/2}$ lines. Annealing and intermixing also caused decrease of the width In4d doublet of about 20%. These effects was previously observed during heating of the layered structures of In/Ag/W and Ag/In/W, which caused formation of surface Ag_xIn_{1-x} alloys. Therefore we were of the opinion that effective intermixing of In and Ag layers caused by surface diffusion of both constituents resulted in formation of Ag_xIn_{1-x} surface alloy.

P2.084 Self-organization of magnetic nanostructures embedded into Cu(100) surface

S Kolesnikov, A Klavsyuk and A Saletsky

Lomonosov Moscow State University, Russia

Recent years have brought significant advances in experimental and theoretical studies of small magnetic clusters. The small magnetic clusters are current focus of intensive research due to both their importance in fundamental low-dimensional physics and the potential applications in nanoscale materials and devices.

The main goal of our work is to investigate the evolution of magnetic nanostructures embedded into a Cu(100) surface at the atomic scale. The present calculations using the Self Learning kinetic Monte Carlo method [1] with energy barriers of all relevant events calculated by means of the molecular-dynamics method with ab initio based interatomic potentials are performed. The atomic processes responsible for the linear and angular chain formations are identified. We demonstrate the key role of substrate vacancies in the motion of embedded impurity atoms and investigate the self-organization of impurity atoms in different conditions.

The interplay between structure and magnetic properties of small magnetic clusters (linear and angular chains) embedded in a Cu(001) surface is studied performing ab initio calculations in a fully relaxed geometry. We reveal that the strain relaxations at the interface between the nanostructures and the substrate have a profound effect on their structure. We show that the atomic relaxations strongly reduce the magnetic anisotropy energy (MAE) and the orbital magnetic moments of embedded clusters. The largest MAE is found for a single impurity atom in the Cu(001) surface. A strong enhancement of the spin magnetic moments in embedded clusters as compared to a single impurity atom incorporated in the Cu(001) surface is found.

[1] O. Trushin, A. Kara, T.S. Rahman, Phys. Rev. B 72, 115401 (2005).

P2.085 Stress relief by trenches on nitrogen-adsorbed Cu(001) surfaces at near-saturation coverage

M Yamada, Y Iwasaki, K Yagyu, S-Y Ohno, K Nakatsuji and F Komori

University of Tokyo, Japan

Nitrogen adsorption on Cu(001) has been attracting a lot of attention since various nanometer-scale patterns develop on the surfaces. The best-known is a grid-like pattern formed at N coverage of ~0.3, where square N-adsorbed islands of the size, 5nmx5nm, are aligned along [100] directions. The driving force to the self-ordering is compressive stress induced by N-adsorption. We have proposed models for boundaries (bright lines in STM) between N-islands and discussed the stress relief in the grid pattern [1]. When N coverage increases further, trenches of monolayer deep appear, which run along [110] directions. In this paper, we present a model for the trench and explain effective relief of N-induced compressive stress.

Adsorbed N atoms are arranged in c(2x2) on Cu(001). Therefore, there exist two domains, which are equivalent energetically and out-of-phase to each other. We noticed that, when trenches coexist with a grid, they always begin at crossings of the grid, and that one of the two boundaries entering the crossing is wide, which indicates that N-adsorbed domains are out-of-phase across the trench. Trenches are amazingly straight, rarely exhibiting kinks. Based on these findings, we propose the anisotropic expansion of the topmost N-adsorbed layer, which relieves the compressive stress while keeping the topmost layer commensurate with the substrate along the trench. When the grid disappeared completely at the saturation, we observed “dark curves” extending from trench ends. We ascribe them to antiphase domain boundaries where continuous connection of two antiphase domains produces top-layer Cu atoms sitting on bridge sites.

[1] M. Yamada et al., Surf. Sci. 604 (2010) 1961.

P2.086 H_2O adsorption on Cu{100}-c(2x2)-Cl surface

M Puisto[1], K Pussi[1], M Alatalo[1], D Hesp[2] and V Dhanak[2]

[1]Lappeenranta University of Technology, Finland, [2]University of Liverpool, UK

The importance of aqueous interfaces in many key technological systems has spurred experimental and theoretical efforts to understand the water-solid interaction and particularly how water bonds to and wets metal surfaces. The wetting behavior directly influences both molecular properties, such as nucleation, diffusion, and transport, as well as nanoscale properties, such as friction, and even macroscopic flow of ice past a solid. Determining the structure of water at the solid interface is the key to understanding wetting, but the weak interaction between water and solid surfaces, combined with the critical role of hydrogen bonding in stabilizing adsorption, makes these systems extremely challenging to study.

A possible way to stabilize an ordered commensurate ice layer is to form a suitable template by modifying the surface so that different adsorption sites are chemically distinct. Here we study the coadsorption of H_2O and Cl on Cu{100} surface. After Cl adsorption, centered (2×2) periodicity is formed, with Cl atoms sitting at hollow sites. Because the desired O-O distance in hexagonal ice is 2.75 Å, more than one water molecule per unit cell is needed. In our calculations, we have used the coverage of two water molecules per unit cell. We have found that the water-water interaction dominates the system, and the interaction between the water layer and the surface is noted to be weak. We also discovered that the H2O molecules form chains in (100)-direction.

P2.087 DFT study of Pentacene adsorption on aperiodic copper film

M Lahti[1], K Pussi[1], K Young[2], H R Sharma2 and R McGrath[2]

[1]Lappeenranta University of Technology, Finland, [2]The University of Liverpool, UK

The interaction of organic molecules with solid surfaces is of central importance for various issues in science and technology. These include, for example, surface chemistry and catalysis, basic steps during organic semiconductor layer growth, and the concept of molecular electronics which aims at utilizing single molecules as functional building blocks with defined switching, sensing, or conduction properties. Pentacene $C_{22}H_{14}$ is a linear polycyclic hydrocarbon and has recently gained ample attention due to its promising bulk properties as an organic semiconductor.[1]

We have used density functional theory (DFT) to analyse the detailed adsorption geometry and orientation of the molecule on aperiodic copper thin film grown on AlPdMn quasicrystal. The crystal includes two different kinds of steps: shorter and longer. Hence, there are plenty of possible adsorption sites on the surface. However, benzene rings take up positions with the geometry of the surface quite well. Because of the size of pentacene, and restriction of computational resource, we modeled pentacene molecule with naphtalene and anthracene molecules. Because of the symmetry of the surface the chosen molecules relate well trends of adsorption of the pentacene. However, the most significant discovery of this study is that the molecule at the good adsorption sites has an influence on the geometry of the surface.For the DFT calculations we used Vienna ab inition simulation package (VASP) [2][3].

[1] Physical Review B 70, 245415 (2004).
[2] Physical Review B 47, 558 (1993).
[3] Computational Material Science 6, 15 (1996).

P2.088 The surface electronic and magnetic structures of the oxidized ultrathin iron film on the Ir(001) surface

F Maca[1], J Kudrnovsky[1] and J Redinger[2]

[1]Institute of Physics of the Academy of Sciences, Czech Republic, [2]Institut für Allgemeine Physik, Austria

We present detailed ab initio study of the electronic structure of the Fe monolayer on the Ir(001) surface covered with adsorbed oxygen. The system of clean Fe/Ir(001) has been intensively studied recently [1-3], a strong tendency to antiferromagnetic order and a complex magnetic structure were indicated. The present study concentrates on the influence of two adsorbate species, namely oxygen and hydrogen, the electronic and magnetic ground state. We show that the adsorption of oxygen (contrary to hydrogen) modifies the sample geometrical structure and lowers the stability of the antiferromagnetic phase leading to the ferromagnetic ground state. We have found a well-defined iron surface state whose energy position varies with adsorbate coverage. On the other hand, the influence of hydrogen on the geometrical as well as electronic structure is very weak and cannot be responsible for observed magnetic signal disappearance for ultrathin iron films. A comparison with recent experimental data will be also given.

[1] V. Martin at al., Phys. Rev. B 76, 205418 (2007).
[2] J. Kudrnovsky, F. Maca, I. Turek, and J. Redinger, Phys. Rev. B 80, 064405 (2009).
[3] A. Deak, L. Szunyogh, B. Ujfalussy, Phys. Rev. B 84, 224414 (2011).

P2.089 Structure and magnetic properties of Fe/W(110)

I Zasada[1], K Freindl[2], J Korecki[2,3], N Spiridis[2], and M Rybicki[1],

[1]University of Lodz, Poland, [2]Polish Academy of Sciences, Poland, [3]AGH University of Science and Technology, Poland

The magnetic properties of a thin iron films on a tungsten substrate have been studied in the past experimentally by using the nuclear resonant scattering of synchrotron radiation [1]. It was found that the observed in-plane spin reorientation transition originates at the Fe/W(110) interface and proceeds via noncollinear magnetization structure towards the surface with increasing film thickness.

In the present work we focus first on the structure of the thin Fe film on the W(110) surface using LEED technique and DFT calculations. IV spectra collected at normal incidence from Fe/W(110) were subsequently analyzed by dynamical tensor LEED [2]. The structural results of LEED were confirmed by the calculation within the density functional generalized gradient approximation approach implemented in the VASP program [3]. Furthermore, we discuss an in-plane spin reorientation transition in thin Fe films on W(110) in terms of thermodynamics of inhomogeneous low-dimensional systems based on a Néel sublattices concept while using a spin 1 Heisenberg hamiltonian. The model allows us to investigate straightforward the layer dependent phenomena. Using the structural results, we propose a model of noncollinear magnetization structure based on the appropriate distribution of the anisotropy parameters inside the thin Fe films on W(110).

[1] T. Slezak, et al. Phys. Rev. Lett., 105, 027206 (2010).
[2] V. Blum, K. Heinz, Comput. Phys. Commun. 134, 392 (2001).
[3] G. Kresse, J. Furthmüller, Phys. Rev. B 54, 11169 (1996).

P2.090 Stress evolution during polycrystalline thin film growth studied in-situ by video-rate STM

A Saedi, J Frenken and M Rost

Leiden University, The Netherlands

It is well-known that Volmer-Weber type growth of polycrystalline thin films involves three stages of intrinsic stress, compressive-tensile-compressive (CTC), at sufficiently high homologues temperatures. In addition, experiments have shown that the films experience a fully reversible stress jump upon growth interruption and resumption (in tensile and compressive directions respectively). This implies the existence of a reversible structural change of the polycrystalline film. Even though several models have been proposed to explain these phenomena, there is no direct experimental evidence to identify the origin of the observed effects. We have performed direct, in-situ measurements, with a specially designed video-rate STM, in order to unravel the atomic mechanisms responsible for stress evolution during the growth of thin silver films and stress jumps upon interruptions.

P2.091 Structure and formation of PdIn surface alloys

G McGuirk[1], J Ledieu[1], E Gaudry[1], V Fournée[1] and M Armbrüster[2]

[1]Institut Jean Lamour, France, [2]Max-Planck-Institut für Chemische Physik fester Stoffe, Germany

The catalytic properties of Pd-based nanoclusters on oxide-supports are of current interest to hydrogen-based alternative energy industrial applications, primarily in methanol steam reformation (MSR). The high catalytic activity towards MSR of Pd/ZnO, Pd/In_2O_3 and Pd/Ga_2O_3 has been ascribed to the formation of PdZn, PdIn and PdGa alloys by reduction of the powder catalyst at high temperature. Therefore numerous studies have been focusing on the formation and properties of such bimetallic alloys, most of them concerning PdZn.

Ultrathin surface alloys can be formed by annealing Zn multilayers deposited on Pd(111) to ~ 500 K. This results in multilayer PdZn surface alloys with composition close to 1:1. Further annealing leads to diffusion of Zn atoms from subsurface layers into the bulk while the surface layer remains mainly unaltered except for a change in corrugation that correlates with a modification of its catalytic properties. Therefore a detailed knowledge of structure and formation of these model systems is crucial to allow a microscopic understanding of the mechanism involved in the MSR reaction.

While the formation of PdZn alloys is well documented, little is known about PdIn, which is the topic of our current work. We will report on our first investigations of the growth of In ultrathin films (up to 2 ML) deposited on Pd(111) by STM, LEED and XPS. Evidences for intermixing are already noted after room temperature deposition, associated with the formation of a (2x2) and a (√3xr√3)R30° mixed phase. Upon annealing, a (1x1) phase is observed with composition close to 1:1.

P2.092 Photon scanning tunneling microscopy of alloyed gold surfaces

O Gürlü, M S Tamer, M Sertkol, R Yılmaz and D Yıldız

Istanbul Technical University, Turkey

As most of the surface/interface phenomena, the observation of photon emission from tunnel junctions due to inelastically tunneling electrons dates back to pre-scanning tunneling microscope (STM) era. After its implementation, attempts to observe photon emission from tunnel junction of an STM were quite immediate. The idea of detecting local photon emission from the surfaces, simultaneously with the surface topography was applied on various surface systems. Several types of photon detection mechanisms were developed. Regardless of the surfaces under consideration or the set up used, it is well known that the photon emission spectrum and intensity heavily depends on both the tip material and the tip geometry. We modified a commercial STM and implemented our photon collection setup; also a modified tip preparation procedure was employed. Using this setup we studied the photons emitted from different gold surfaces with various surface morphologies. Contrary to common knowledge, the intensity of the photon emission from similar regions of a rough Au surface was observed to be different. The local surface morphology was correlated to the photon emission intensity, as well as to the spectrum of the emitted photons. We studied natural and artificial defects on Au surfaces through the emitted photons due to inelastic plasmon-electron scattering in an attempt to understand their effect on the localization of the surface plasmons. Here we suggest the possible dependence of the intensity and spectra of the emitted photons on the local alloying of the gold surfaces.

P2.093 X ray-induced reversible switching of dimetacyano azobenzene on Bi(111)

A Krüger, M Bernien, C Felix Hermanns and W Kuch

Freie Universität Berlin, Germany

The adsorption of the photoswitch dimetacyano-azobenzene (DMC) evaporated onto Bi(111) at 110 K was studied for different coverages in order to determine the influence of substrate and intermolecular interactions on the switching probability. Angle-dependent NEXAFS spectroscopy was used to resolve the adsorption geometry of the molecules. For the adsorption of one monolayer of molecules we find the molecules physisorbed in a nearly planar conformation parallel to the surface. By illumination with X-ray photons corresponding to the azo N 1s → LUMO transition energy of 399 eV, the angle dependences of the π* resonances in NEXAFS spectra of the N-K as well as the C-K edge change significantly. We interpret this effect as switching from thetransto thecisconformation, where at least 20% of molecules are switched. After waiting for 1 h in darkness at 110 K, the NEXAFS spectra of the N- and C-K edges become identical to the spectra before the illumination with X rays. This indicates a thermally induced back reaction. By using off-resonant X rays with a photon energy of 270 eV for illumination, no modification of the

NEXAFS spectra is observed. A multilayer of DMC on Bi(111) shows comparable effects upon illumination with X rays, with an even higher percentage of switching molecules. This work has been supported by the DFG (Sfb 658).

P2.094 Exploiting resonance effects on Bi(111)

P Kraus, A Tamtögl and M Mayrhofer-Reinhartshuber

Technical University Graz, Austria

The Surfaces of Bismuth exhibit unexpected electronic and vibrational properties. Being a semimetal with metallic surface-behavior, the strong corrugation found by Tamtögl et al. [1] was rather unexpected but enabled the investigation of elastic surface resonances and thus the measurement of the He-Bi(111) interaction potential. Using the signal enhancement and suppression caused by the bound-state- and threshold-resonance effects, phonon states located in the bulk can be identified that would otherwise be unaccessible by helium atom scattering.

On the other hand, the enhancement of previously identified surface-phonon modes can improve the accuracy of the information about the bound-state energy in the interaction potential and thus enable far more detailed insights into the interaction potential between the probe atom and the surface under investigation.

Therefore, several elastic and inelastic helium atom scattering measurements were performed on the Bi(111) surface. Besides the usual angular distribution and time-of-flight measurements, also the temperature-dependence of the elastic specular peak intensity was measured and compared to predictions for the resonant energies.

[1] A. Tamtögl, JPCM 22, (2010) 304019.

P2.095 Investigation of Au(100) film epitaxial growth on Ir(100) surface

O Fedchenko[1], D Kutnyakhov[2], H Gollisch[3], R Feder[3], S Protsenko[4], S Nepijko[2] and G Schönhense[2]

[1]Sumy State University, Ukraine, [2]University of Mainz, Germany, [3]University of Duisburg-Essen, Germany

The performance of the novel imaging spinfilter [1, 2] on the basis of specular reflection from single-crystal surfaces depends on several criteria. Besides the figure of merit S^2I/I_0 (S - Sherman function, I/I_0 – reflectivity) the number of resolvable image points behind the spinfilter is an important quantity. Third, the lifetime of the analyzer crystal surface is an important parameter in practical use. The purpose of this work was the investigation of Au/Ir(100) as promising spin filter in all three aspects.

The Ir(100) detector crystal for the spin analyzer was prepared at $7\cdot10^{-11}$ mbar. For hot oxygen treatment the crystal was heated up to 1100 – 1150 K under O_2 partial pressure of $8\cdot10^{-8}$ mbar during 5 – 7 cycles for 5 minutes. Subsequently at short (~20 s) high temperature (~1600 K) oxide-flash was carried out at $3\cdot10^{-10}$ mbar. Then the Ir(100) surface shows the well-known 5x1 reconstruction [3]. The crystal surface was covered by Au with a deposition rate of 0.1 nm/min and was annealed to 1000 – 1050 K (3 times for 5 seconds). On each stage a series of LEED pictures were taken for kinetic energy values in the range of 10 – 120 eV. On their basis IV intensity profiles were determined for the 00, 10 and 11spots.

For comparison we measured the IV-curves for Ir (1x1), Ir (5x1), and for different Au thicknesses. Thicker layers show a complicated superstructure. Measured intensity profiles showed that after gold deposition and anneal the reflex intensities increase. Good agreement of experimental data with theory was found. Epitaxially grown Au(100) overlayer on Ir(100) stayed intact for several days at 10^{-10} mbar. Spinpolarisation measurements are under way.

[1] M. Kolbe et al., PRL 107, 207601 (2011).
[2] C. Tusche et al., APL 99, 032505 (2011).

[3] R. Koch et al., PRL 64, 3416 (1991).

P2.096 An STM/XPS study of the oxychlorination of Cu(111) and Cu(110) surfaces.

H Altass[1], P Davies[2] and A A F Carley[2]

[1]Cardiff University, UK, [2]Cardiff Catalysis Institute, UK

The reaction of chlorine containing molecules with copper is relevant to a number of industrially important reactions including the Deacon process, an important route by which HCl from waste streams can be converted into chlorine gas. The Deacon process is catalysed by a copper chloride/copper oxide catalyst but the mechanism remains controversial at least partly because of our incomplete understanding of the behaviour of copper chloride surface phases. Similarly, polychlorinated dibenzo-p-dioxins (PCDD), and polychlorinated dibenzo-furans (PCDF) (referred to collectively as PCDD/F's) are known to be generated during combustion processes and over copper surfaces on carbon fly ash particles. PCDD/F's are environmentally harmful compounds and there is considerable debate on the mechanism and the nature of the copper phases involved.

We are investigating the role of surface oxygen in determining the chloride phases formed at copper single crystals. On Cu(110) a new short lived Cu(II) surface phase was identified which may account for some aspects of the unusual catalytic behaviour of the copper chlorides. The present poster discusses the chloride phases formed on Cu(111) surfaces and compares reactivity and stability to those observed on Cu(110).

P2.097 Protection against corrosion: thermally oxidized stainless steel studied by atomic force microscopy and scanning kelvin probe force microscopy

C Pirri[1], J-L Bubendorff[2], B Maachi[3], F Mechehoud[3], A Mehdaoui[4], N-E Hakiki[3]

[1]University of Mulhouse, France, [2]IS2M, France, [3]University of Oran, Algeria

The presence of passive oxide layers on the surface of metals like stainless steels plays an important role in corrosion processes in various corrosive environments. The oxide film electronic structure could be assimilated to a p-n heterojunction constituted by the outer n-type Fe_2O_3 iron oxide and the inner p-type Cr_2O_3 chromium oxide. The space charge regions developed by the two oxides limit the electronic and ionic transfer and hence increase the effective protection against corrosion. A localized disappearance of one of the two layers and thus of the junction makes corrosion possible.Thermally oxidized AISI304 and AISI316 stainless steels are studied by Atomic Force Microscopy, Scanning Kelvin Probe Force Microscopy (SKPFM) as a function of their growth temperature[1]. We discuss the growth mode of the oxide layers in term of scaling laws analysis using topographic images as input. We show that SKPFM is a power-full tool to map the Volta potential of our samples and to localize the features present on the surface and may be responsible of the corrosion. In particularity, an efficient protection against corrosion is obtained at a higher oxide thickness (oxidation temperature) for AISI304 stainless steel than for AISI316. Magneto-Optical Kerr effect measurements demonstrate that the iron oxide layer contain a magnetite phase (Fe_3O_4) and that the coercitive magnetic field is three time higher in the case of AISI316 samples. Our results open the way to a better understanding of protection against corrosion at the nanoscale range.

[1] B. Maachi et al, Corrosion Science 53 (2011) 984-99.

P2.098 Anomalous hall effect in ferromagnetic metals: role of phonons at finite temperature

A Shitade[1] and N Nagaosa[2]

[1]Kyoto University, Japan, [2]University of Tokyo, Japan

Anomalous Hall effect (AHE) is a phenomenon where the transverse conductivity arises owing to the spin-orbit interaction and spontaneous magnetization. Its mechanisms can be classified into the extrinsic mechanisms by disorder and the intrinsic mechanism by the anomalous velocity or Berry curvature. Recently, these different mechanisms have been unified at zero temperature by using the perturbation theory with respect to disorder, but the effects of inelastic scattering at finite temperature remain to be studied.

In this work, the AHE in a multiband tight-binding model is numerically studied taking into account both elastic scattering by disorder and inelastic scattering by the electron-phonon interaction [1]. The Hall conductivity is obtained as a function of temperature, inelastic scattering rate, chemical potential, and impurity concentration. We find that the new scaling law holds over a wide range of these parameters, which says that the extrinsic mechanisms are rapidly suppressed by inelastic scattering while the intrinsic mechanism is robust. Next, the frequency dependence in the self-energy is seriously taken into account and the condition of this scaling law is examined. Also, it is found that the intrinsic mechanism depends on temperature under a resonance condition. These results are consistent with the recent experimental observations on ferromagnetic Fe and Ni films [2,3].

[1] A. Shitade and N. Nagaosa, to be published in J. Phys. Soc. Jpn.
[2] Y. Tian, L. Ye, and X. Jin, Phys. Rev. Lett. 103, 087206 (2009).
[3] L. Ye, Y. Tian, X. Jin, and D. Xiao, Phys. Rev. B 85, 220403(R) (2012).

P2.099 AC magnetic susceptibility measurements at high pressure in uranium intermetallics

M Kepa, C O'Neill and A Huxley

The University of Edinburgh, UK

We discuss the development of a diamond anvil cell AC-susceptometer set-up, comparing the performance of two co-axial coil susceptometer designs. In the first, a pick-up micro coil is placed within the pressure region of a diamond anvil cell surrounding the sample [1]. The second technique makes use of designer diamonds which encapsulate a thin-film micro-coil [2-3]. An external excitation coil is used in both cases to apply a high frequency magnetic field. A ruby fluorescence system for our cryogen free closed cycle refrigerator allows us to determine pressure at low temperature making use of optical fibres. The apparatus can be used to make accurate measurements of pressure, temperature and magnetic transitions to reveal new details in the phase diagrams of uranium intermetallics and other compounds. These compounds exhibit a host of exciting physical effects including quantum criticality that can be reached with pressure as a tuning parameter.

[1] P.L. Alizera, S.R. Julian Rev. Sci. Instrum. 74, 4728 (2003).
[2] S.T. Weir et al Appl. Phys. Lett. 77, 21 (2000).
[3] D.D. Jackson et al Rev. Sci. Instrum. 74, 2467 (2003).

P2.100 NISXW study of Si adsorbed on an Al-Co-Ni quasicrystal

R Diehl[1], A Chaudhuri[2], J Ledieu[3], H Li[1], S Su[1], A Mayer[1], N Stanisha[1], K Lovelock[4], R Jones[4], L Wearing[5], R McGrath[5] and D P Woodruff[2]

[1]Penn State University, USA, [2]University of Warwick, UK, [3]Institut Jean Lamour, CNRS, France, [4]University of Nottingham, UK, [5]University of Liverpool, UK

The normal incidence standing x-ray wavefield (NISXW) technique has never before been applied to the determination of adsorption structures on quasicrystals, even though it is quite clear that, under the right conditions, x-ray standing waves do exist in quasicrystals. This omission may be due to a misconception that the relationship between the phase of the standing waves and the atoms at a quasicrystal surface is arbitrary.

We have performed a NISXW experiment for the adsorption of Si atoms on the nominally 10-fold surface of the decagonal Al-Co-Ni quasicrystal. NISXW spectra were obtained for a Si coverage of about 0.3, for two different angles of incidence: normal to the 10-fold surface, and at an angle of about 60° from the surface normal. These angles correspond to two strong x-ray reflections of the quasicrystal. The intensity of the Si 1s photoemission signal was measured in order to determine the location of the Si atoms.

In order to accurately model the 5-fold symmetry of the surface, our analysis employed a 200 Å x 200 Å x 8 Å structure model for the quasicrystal. The results indicate that the Si atoms have an average height of 1.80 Å above the surface, and are arranged in 6-atom pentagonal clusters centered at points of 5-fold symmetry. This study demonstrates the feasibility for using NISXW as a structural tool for adsorbed atoms or molecules on quasicrystal surfaces.

P2.101 Studying the nanostructure of the copper surface after ion bombardment

T E Amos, G J Ackland and R J Cole

University of Edinburgh, UK

The study of metallic surfaces after ion bombardment is of importance to determine operating lifetime of materials in nuclear reactors, spacecraft, and artificial satellites, all of which undergo constant irradiation. Using results from Molecular Dynamics simulations it is possible to accurately model the behaviour of defects on the Cu(110) surface after ion bombardment at 144 K using Monte Carlo methods.

The developed model successfully recreates the surface topology after approximately 30 minutes of diffusion, as seen in collected STM images of the irradiated surface [1], and also gives further validation of surface energy barriers and surface topology nano-seconds after bombardment, as calculated by Lane *et al.* using Molecular Dynamic simulations [2]. It has also been possible to reconstruct Reflection Anisotropy Spectroscopy (RAS) signals (an optical probe used to measure the directional anisotropy of surface electron states) of the Cu(110) surface at 144K during ion bombardment using the Poelsema-Comsa method, where surface electrons are scattered by defects, destroying the surface electron states local to the defect .

[1] G. E. Isted, P. D. Lane, R. J. Cole, M. Caffio, and R. Schaub. Estimating the range of influence of point defects on Cu (110) surface states. *Physical Review B*, 83(15):155403, April 2011.
[2] P. D. Lane, G. J. Galloway, R. J. Cole, M. Caffio, R. Schaub, and G. J. Ackland. Validating molecular dynamics with direct imaging of radiation damage debris. *Physical Review B*, 85(9), March 2012.

Novel methods: instrumentation, facilities and computation

P2.102 Inverse simulation technique for the determination of amorphous structures

J Los and T Kuehne

Johannes Gutenberg University, Germany

Finding the structure of amorphous phases is a major challenge in material science, both experimentally and theoretically, due to the absence of lattice periodicity. Theoretically, it is to some extent also an ill-defined problem, since a characteristic of an amorphous material is that there is no unique structure, nor does the structure correspond to an absolute minimum of the Gibbs free energy.

In current state-of-the-art Molecular Dynamics simulation methods, based on empirical or ab-initio (within DFT) total energy descriptions, candidate amorphous structures can be generated by cooling down from the liquid phase at a certain speed which can be varied but which is mostly much higher than typical experimental cooling speeds due to computational limitations. Subsequently, the properties of the obtained, amorphous structure can be compared with experimental data, with variable succes depending on the case.

In order to ilucidate the amorphous structure more efficiently and accurately, we developed an inverse hybrid Monte Carlo simulation technique based on the NVE ensemble, which aims at minimizing a funtional that not only includes total energy but also available experimental data, such as the structure factor, HOMO-LUMO band gap to name a few. So far we have applied the method to amorphous carbon for which some results and analysis are presented.

P2.103 XAFS on thin films and surfaces at SAMBA, the general purpose hard X-ray beamline of SOLEIL

E Fonda[1], L Barthe[1], B Domenichini[2], P Paufert[2] and H Magnan[3]

[1]Synchrotron SOLEIL, France [2]Université de Bourgogne, France, [3]CEA-Saclay, DSM/IRAMIS/SPCSI, France

X-ray Absorption Fine Structure spectroscopy gives access to the local structure or chemical environment of an element. The method can be applied in the solid, liquid or gas phases and it can be employed as well to study elements at surfaces and interfaces [1].

The SAMBA beamline operates since 2008 on a bending magnet source of Synchrotron SOLEIL, the French national synchrotron source, it provides the community with a large panel of sample environments to perform x-ray absorption in the 4-40keV range, thus covering most K and L edges of the elements [2]. The beamline has been equipped with a dedicated setup for surface science, where it is possible to study the local structure of atoms down to a 0.1 layer coverage. Examples on absorbed molecules and bimetallic clusters will be given [3].

Close to grazing angle XAS measurements enhance the sensitivity and recent ex-situ results in air will be illustrated pointing out the importance of combining grazing incidence and polarization dependent measurements. Current developments for in-situ measurement in the surface EXAFS setup will be described [4].

[1] S. Pizzini, F. Baudelet, A. Fontaine, D. Chandesris, H. Magnan, A. Fert and C. Marlière, Appl. Surf. Science 69 (1993) 7-11.

[2] Briois,V.,Fonda,E.,Belin,S.,Barthe,L.,LaFontaine,C.,Langlois,F.,Ribbens,M.,&Villain,F.(2011). “UVX2010-10^{e}ColloquesurlesSourcesCohérentesetIncohérentesUV,VUVetX;ApplicationsetDéveloppementsRécents”.EDP-Sciences,41-47.http://dx.doi.org/10.1051/uvx/2011006.

[3] Campiglio P., Moreau, N., Repain, V., Chacon, C., Girard, Y., Klein, J., Lagoute, J. and Rousset, S., Bulou, H., Scheurer, F. Goyhenex, C., Ohresser, P., Fonda, E., Magnan, H., Phys. Rev. B 84, 235443 (2011).

[4] Tougerti, A., Llorens, I., D'Acapito, F., Fonda, E., Hazemann, J. L., Joly, Y., Thiaudiere, D., Che, M., & Carrier, X. Angewandte Chemie International Edition, 2012, (on-line first).

P2.104 Bulk Molybdenum tip for scanning tunneling microscopy

P Carrozzo, C Spartaco Casari, M Passoni, A Li Bassi and C Enrico Bottani

Politecnico di Milano, Italy

Scanning Tunneling Microscopy and Spectroscopy (STM-STS) has proven to be a very powerful tool to investigate the morphological, structural and electronic properties of surfaces and nanostructures at the atomic scale. STM-STS measurements in ultra high vacuum (UHV) are usually performed with chemically etched tungsten tips [1]. Recently we produced a bulk Cr tip for Spin-polarized STM [2].

In this work, we present a method for the preparation of bulk Molybdenum tips and we show their potentialities in performing high-quality and high-resolution STM-STS.

Tips are produced by electrochemical etching of 99.99% Mo wire in a 3.0 M NaOH solution. Mo tips are characterized by a regular shape at the micron scale and a shorp tip apex with a radius of curvature of about 50 nm, as shown by scanning electron microscopy images.

We tested Mo tips by performing atomically resolved STM measurements of single crystal surfaces in UHV. Mo tips showed very high quality images of the superstructure of Au(111) and STS measurements showed the Shockley peak at 0.5 eV. Atomic resolution of the Si(111)-7×7 surface was also achieved, showing in particular rest atoms of the Si(111)-7×7 reconstruction at negative bias (below -1.5 V), contraty to what happens with conventional W tip[3].

[1] C. Bai, "Scanning Tunneling Microscopy and its application", Springer Verlag (2000).
[2] Li Bassi et al., Applied Physics Letters 91, 173120 (2007).
[3] Y. L. Wang et al., Phys. Rev. B 70, 073312 (2004).

P2.105 Scanning capacitance microscopic studies on the stability of the electrical junction width formed by microwave annealing

M-N Chang[1], C-W Hu[1], T-H Chou[2] and Y-J Lee[2]

[1]National Chung Hsing University, Taiwan, [2]National Nano Device Laboratories, Taiwan

Scanning capacitance microscopy (SCM) with high spatial resolution has been a powerful tool imaging charge distribution and electrical junctions. Since typical SCM may suffer from photoperturbations, a dark-mode SCM (DM-SCM) can acquire carrier concentration profiles without photoperturbation problems, providing an opportunity to deeply study the stability of electrical junctions formed by ion implantation and thermal annealing. For boron-implanted silicon, annealing processes such as rapid thermal annealing (RTA) and spike annealing (SA) are generally performed at high temperature in order to electrically activate boron atoms. With post-SA furnace annealing (FA), prior works have revealed that the junction widths formed by SA are instable due to the residual point defects after SA a low-thermal-budget process. Microwave annealing (MA) a low-temperature process can electrically activate boron atoms with insignificant boron diffusion. For studying the stability of the junction widths formed by MA, we for the first time employed a DM-SCM with a solid-Pt tip to examine the junction regions before and after post-MA FA. Patterned p-type regions carried out from BF_2^+ implantation and MA were prepared on n-type silicon wafers. All the DM-SCM images were acquired at room temperature using a BrukerD3100 scanning probe microscope at a modulation bias of 0.3 V. In comparison with post-SA FA, the change in the junction widths after post-MA FA is insignificant, implying that the junction width formed by MA is stable. Our experimental results further indicated that the stability of the junction widths is due to charge balance by the junction region after the FA treatment. In addition, the physical mechanism of a high-sensitivity DM-SCM will also be discussed in this work.

P2.106 Alignment apparatus for magnetic resonance force microscopy

S Won

Korea Institute of Materials Science, Korea

Magnetic resonance force microscopy (MRFM) was proposed as a means to improve detection sensitivity to the single-proton level. We adopt a charge coupled device (CCD) unit in MRFM apparatus. In MRFM experiment, the fiber-to-cantilever alignment is one of the most crucial things because the oscillation of cantilever is detected using fiber-optic displacement sensor.The sensor is based on the optical interference occurring in the micron-sized distance between the cleaved optical fiber and the cantilever. Typically fiber-to-cantilever spacing is less than 10mm in our case. But it is difficult to sustain a high-accuracy fiber-to-cantilever alignmentduring long-time experiments. Besides, this sensing module is positioned in a vacuum chamber in order to achieve good force sensitivity. Therefore micromanipulating 10mm is a time consuming task, and is likely to result in breaking the cantilever. Here we describe a system capable of correction for fiber-to-cantilever alignment. Easy alignment system utilizes a commercially available CCD unit. MRFM spectra in a diphenyl-picryl-hydrazyl particle demonstrate the potential of MRFM alignment system in low temperature MRFM experiments.

P2.107 Photoluminescence imaging of high temperature aluminide coatings for turbine engine applications

S Greenwell[1], J Day[1] and J Kell[2]

[1]University of Bristol, UK, [2]Rolls-Royce, UK

Protective coatings are an essential addition to turbine blades and nozzle guide vanes, without them they would rapidly oxidise and corrode in the high temperature environment experienced in a turbine aero-engine.

The most common protective coatings are the aluminides; a layer of aluminium deposited onto a component by chemical vapour deposition and diffused into the superalloy substrate to provide an aluminium reservoir for the formation of a protective alumina layer.

The aluminide coatings become depleted of aluminium during service and as such are periodically stripped and re-deposited to ensure the components are continuously protected from environmental degradation.

It is essential that all traces of the depleted aluminide coating are removed from the substrate prior to re-coating; remnants of old coating prevent successful re-deposition by preventing adequate adhesion to the substrate, leading to premature coating failure. This is currently confirmed with a heat-tint inspection, a method that monitors the tinting of coatings and substrates when oxidised at high temperatures. The heat-tint inspection of turbine components is a time and labour intensive process.

We propose a novel imaging instrument, developed between the Interface Analysis Centre, University of Bristol and Rolls-Royce, which improves upon the current method. By stimulating fluorescence from aluminium oxides on remnant coating, their presence can be identified with minimal surface preparation. The proposed method is technically simple, fast and objective. Here we demonstrate the instrument is capable of detecting remnant aluminide and overlay coatings on a range of components.

P2.108 Miniaturized pattern formation at soft interfaces

J Sarkar and H Annepu

Indian Institute of Technology Delhi, India

A single incompressible soft elastic film in contact proximity with an external contactor, with van der Waals interactions active between the film and the contactor, leads to formation of inhomogeneous instabilities with a definite length scale of $\sim 3h$ (where h is the thickness of the film). For the further miniaturization of length scales, we explore two different routes - soft elastic bilayers instead of a single elastic film and using a patterned substrate instead of a flat substrate with a single elastic film cast on top. Through a linear stability analysis we show that using soft elastic bilayers, with a special configuration in which the bottom layer is made to be very thin (in the wetting limit with thickness <100 *nm*), the bilayer is forced to deform in a "squeezing mode'' and yields myriads of instability length scales. Length scales ranging from $<<3h$ to $>>3h$ can be obtained by simply tuning the properties like shear modulii ratio, surface tension and thickness ratios of both the layers. The instability length scales formed as well as the strength of interactions required decrease when the top film compliance is made to increase by increasing its thickness or by decreasing its shear modulus. Such squeezing instabilities are shown to be accompanied by excessive delamination of the film-film interface by varicose instabilties when the top layer is made to be very thin and stiff compared to the bottom layer. When periodically patterned substrates are used instead with the single elastic films, the variation of the film thickness along the length of the film make the zones of small local thickness to offer stronger elastic stiffness compared to the zones of larger local thickness. This increases the effective elastic stiffness of this film compared to a film cast on a flat substrate and results in the film surface undulating at length scales less than $3h$. The stronger the difference between these two elastic stiffnesses i.e. the higher the substrate pattern amplitude, the smaller will be the length scales obtained (as small as $0.3h$) and these are found to be nearly independant of the substrate pattern lengthscales.

P2.109 Border Search Method - potential energy surface mapping technique alternative to metadynamics

P Hapala and P Jelinek

Institute of Physics of Czech Academy of Science, Czech Republic

Mapping of Potential Energy Surface (PES), searching for local and global minima of atomistic systems or paths with minimal energy barrier between these local minima is a long term goal of computational material science. One of the most pronounced methods for this purpose is so called Metadynamics [1].

Metadynamics provides map of PES around each local minimum, which is useful for an estimation of the Free energy. In this method, a walker in the configuration space is repelled from a current local minimum increasing potential energy by addition of Gaussian function to PES at his current configuration.

Here, we introduce a new method inspired by Metadynamics keeping its advantages, while improving it in some aspects. Our method samples PES in discrete steps of given spatial grid. Simultaneously it keeps track of already sampled area. Using this information all new trial steps are done just on the border of the sampled area at the proximity of lowest energy point of this contour. This strategy significantly reduces time needed to explore configuration space of given system.

Typical the Metadynamics algorithm needs to evaluate PES many times close to local minimum in order to gradually increase the potential energy. After certain time, the potential energy exceeds the energy barrier permitting inspection of another PES valley. However, in our method, each position is visited only once, which strongly limits both computational time and memory requirements. Second, in our method forces are not required, which reduces not only computer time but it also simplifies significantly algorithm of force projection to constrain parameters (angle, bond length). Finally, we will provide several benchmarks, where the efficiency of our new method will be demonstrated.

[1] B. Ensing, M. De Vivo, Z. Liu, P. Moore, M. L. Klein, "Metadynamics as a Tool for Exploring Free Energy Landscapes of Chemical Reactions", Acc. Chem. Res., 39, 73-81, (2006).

Oxide surfaces

P2.110 Theoretical insights into the Ag doping in monolayer and bilayer ZnO armchair nanoribbons: Edge effect and position-dependent properties

Y Li[1], X Zhao[2] and W Fan[2]

[1]University of Paderborn, Germany, [2]Shandong University, China

Generally, the optoelectronic behaviors of semiconductors are dominated by the defects and impurities. Zinc oxide (ZnO) is known as one of the most important optoelectronic functional material, but its acceptor doping with low resistivity and high mobility has proved highly challenging. It is well known that the reduced dimensionality and size of nanostructures can facilitate more efficient carrier transport, and the active sites can distribute on the surface uniformly due to the high-surface-volume ratio. In particular, one-dimensional nanoribbons, whose thickness is smaller than width, exhibit special confinement and edge effects far from uniform in the cross section. Therefore, research of p-type doping in ZnO nanoribbons would be an opportunity to improve the p-type properties of ZnO and further find out some new phenomenon for its nanoelectronic and optoelectronic applications.

We present first-principles calculations on the structures and electronic properties of Ag-doped monolayer and bilayer ZnO armchair nanoribbons. The aim is to address how the dopant locations and edges of nanoribbons affect the electronic properties of ZnO. On this basis, we propose some suggestions on achieving effective p-type conduction in ZnOANR system. As the monolayer ZnO(0001) nanosheets have been synthesized recently, on the basis of our research, we expect that effective p-type could be obtained via controlling Ag incorporating positions in monolayer ZnO nanoribbons experimentally.

P2.111 Self-limited growth of ZnO films on Ag(111)

B-H Liu[1], M E McBriarty[1,2], I M N Groot[1], S Shaikhutdinov[1] and H-J Freund[1]

[1]Fritz Haber Institute, Germany, [2]Northwestern University, USA

Cu and ZnO supported on Al_2O_3 is the industrial catalyst for methanol synthesis. Several experiments in the literature suggest that the active phase may include Cu particles, which are partially or totally encapsulated by a thin ZnO film. In order to explore this model as well as to study the elementary processes of the methanol synthesis reaction, we intend to build planar model catalysts based on well-ordered ZnO thin films.

The films were grown using PVD of Zn in ambient oxygen and annealing. It is found that the preparation of crystalline ZnO films on Cu(111) suffers from the formation of CuO_x sub-oxides. Therefore, we focus on growth of ZnO films on Ag(111), since the Ag/ZnO system shares very similar catalytic activity with Cu/ZnO. According to STM and LEED results, the films are highly ordered and show several different coincident lattice structures with respect to Ag(111), with film coverage around 90%. The film growth slows dramatically after the first monolayer has been deposited, presumably due to the decreasing sticking coefficient of Zn atoms during deposition. The results may shed light on the encapsulation mechanism of metal particles by ZnO. The reactivity of the model catalyst under technically relevant conditions is under investigation.

P2.112 Resistive switching in TiO_2 crystals

M Rogala[1], Z Klusek[1] and K Szot[2]

[1]University of Lodz, Poland, [2]Peter Grünberg Institut & JARA-FIT, Germany

Resistive switching based on redox processes in metal oxides seems now to be one of the most promising methods of dense information storage in future memory devices. This efficient, fast and non volatile process, leading to modification of local resistivity, was observed in a variety of materials. Despite the fact that large effort was put in the past years to describe the switching processes and that prototype memristive devices have been already produced, the satisfying knowledge of the origin of the switching phenomena is still incomplete. To overlap this gap we analyze the single crystals of TiO_2, which is a model material for resistive switching and which has a long history of investigations of its electronic and crystallographic structure under the impact of reduction and oxidation processes.

We demonstrate the nanoscale investigations of resistivity of the surface layer of TiO_2, which show high in-plane heterogeneity. This can be connected to the presence of extended structural defects, which in our opinion are responsible for oxygen ion migration and resistivity modifications during resistive switching processes. Additionally the local conductivity atomic force microscopy (LC-AFM) allowed us to perform local resistive switching and follow the electronic and structural changes, which correspond to that process [1].

[1] K. Szot, M. Rogala,W. Speier, Z. Klusek, A. Besmehn, R. Waser, Nanotechnology 22 254001 (2011).

P2.113 Electronic structure and optical properties of tin monoxide bulk and its (001) surface

S Küfner[1], S André[2] and F Bechstedt[1]

[1]Friedrich-Schiller-Universität Jena, Germany, [2]Lawrence Livermore National Laboratory, USA

Tin dioxide (SnO_2) is an oxide semiconductor that is used as a transparent conductor for many ptoelectronic applications and that has large future technological potential. It is produced by the oxidation of tin, a process which often leads to the coexistence of both SnO2 as well as tin monoxide (SnO) in the same crystal, due to the two possible oxidation states of tin, i.e., Sn_{2+} and Sn_{4+}. While SnO_2 and its low-index surfaces have widely been investigated in the literature, little is known about SnO.

In order to predict the stability of the two oxides for various preparation conditions, we use density functional theory along with a local approximation for exchange and correlation to calculate the free energies of SnO in the litharge structure as well as the rutile polymorph of SnO_2 as a function of the oxygen chemical potential. These results allow us to construct a phase diagram which we use to discuss the different stability ranges.

For a parameter-free calculation of the electronic structures of bulk SnO and its (001) surface, we take the spin-orbit interaction into account and we use a more sophisticated approximation of exchange and correlation based on hybrid functionals. Furthermore, we investigate the optical properties of both systems within the independent-particle approximation. Results such as band structures, densities of states, and dielectric functions are presented and discussed with respect to the sparse experimental data available.

P2.114 Adhesion forces at zinc/ α-Al_2O_3 (0001) interface

R Cavallotti[1], J Goniakowski[1], R Lazzari[1], J Jupille[1], A Koltsov[2] and D Loison[2]

[1]University of Pittsburgh Medical Center (UPMC), USA, [2]ArcelorMittal, UK

Understanding microscopic mechanism determining the properties of metal/oxide interfaces is of a key importance in various domains of applicative research, ranging from microelectronic to corrosion. In the field of iron industry, new steels known as “High Yield Strength”areenrichedinadditional elementslikealuminum. During annealing whichprecedesgalvanization,somealloyelementsoxidizeandformparticlesorfilmson steel surface, what may reduce or even prevent adhesion of zinccoating.In order to identify factors behind the adhesion strength at such oxide/zinc interfaces, and to help developing and optimizing efficient anticorrosive coatings, we have studied model Zn/α-Al_2O_3(0001) interfaces using both surface science experimental techniques and ab initio numerical modeling.

Experimentally, zinc deposition was followed by SDR to determine contact angle and aggregates’ geometry on alumina. Zinc layers were deposited on substrate by variation of oxygen partial pressure (10^{-9} mbar – 10^{-6} mbar) and temperature (T°C ambient to 450°C). XPS and LEED characterizations are also investigated.

In parallel, with an ab initio approach based on DFT (LDA and GGA) we have studied the adhesion properties at Zn/α-Al_2O_3(0001) interfaces. Three alumina (0001) surface terminations (single Al layer, double Al layer and O termination) have been considered, under vacuum (bare) or in presence of water vapor (fully hydrogenated). While in vacuum the most stable surface is terminated by a single Al monolayer (non polar termination), hydrogenation strongly stabilizes the O-terminated surface (polar termination). Zinc (both ad-atoms and constitute deposits) adsorb the best on bare polar terminations. However, surface hydrogenation does efficiently block the metal-oxide interaction.

P2.115 Distinct physicochemical properties of the first ceria monolayer on Cu(111)

O Stetsovych[1], L Szabová[1], F Dvořák[1], M Camellone[2], S Fabris[2], J Mysliveček[1] and V Matolín[1]

[1]Charles University, Czech Republic, [2]Scuola Internazionale Superiore di Studi Avanzati (SISSA), Italy

Discontinuous ceria layers on Cu(111) represent heterogeneous catalysts with notable activities in water–gas shift and CO oxidation reactions. Ultrathin ceria islands in these catalysts are composed of monolayers of ceria exhibiting CeO_2(111) surface ordering and bulklike vertical stacking (O–Ce–O) down to a single ceria monolayer representing the oxide-metal interface. Scanning tunneling microscopy (STM) reveals marked differences in strain buildup and the structure of oxygen vacancies in this first ceria monolayer compared to thicker ceria layers on Cu(111). Ab-initio calculations allow us to trace back the distinct properties of the first ceria monolayer to pronounced finite size effects when the limiting thickness of the oxide monolayer and the proximity of metal substrate cause significant rearrangement of charges and oxygen vacancies compared to thicker and/or bulk ceria.

P2.116 Oxide layers on the surface of polycrystalline gold foil produced by RF discharge in oxygen: XPS and TPD study

A Stadnichenko, S Koscheev and A Boronin

Boreskov Institute of Catalysis, Russia

Now it is established reliably that nanosized gold particles supported on the reducible metal oxides possess high activity in many catalytic reactions, including the oxidation reactions. The pathways in the oxidation reactions are determined to a great extent by oxygen species, so their nature is a key factor in the understanding of the reaction mechanisms. Unfortunately, the state and reactivity of oxygen are not clearly established because of certain difficulties in the application of the surface analysis methods (XPS, UPS, AES etc.) in the investigation of oxygen species on the surface of the supported gold catalysts. In our work the investigation of the oxygen species on the gold surface was performed on the surface of massive samples using RF discharge in O_2 atmosphere.

The experiments were carried out using electron spectrometer VG ESCALAB equipped with XPS and TPD methods. The oxidized gold surface was characterized by means of XPS (Au4f and O1s spectra) and TPD, the reaction probability of oxygen was tested using step by step exposure by gas flow of CO. It was found that interaction of gold surface with RF-activated oxygen produces three-dimensional gold oxide films by thickness 5-10nm. TPD experiments showed that decomposition of gold oxide phase occurred at ~ 530 K with E_a(des) ≈ 100 kJ/mol. O1s spectra analysis allowed to reveal some additional oxygen species in the range of BE(O1s) from 529,3 eV to 535,5 eV. The maximal reactivity of adsorbed oxygen towards CO at room temperature was found to be $c \sim 5\times10^{-4}$. For the first time the dissolved oxygen in bulk gold was registered, its desorption was observed at temperature around 680 K.

P2.117 Morphology and thermal stability of thin AlF_3 films on Cu(100)

J J de Miguel[1], G Ruano[2], J C Moreno-López[2], M C G Passeggi, Jr.[2], R Vidal[2], J Ferrón[3], M Á Niño[4] and R Miranda[1]

[1]Universidad Autónoma de Madrid, Spain, [2]Instituto de Desarrollo Tecnológico para la Industria Química (INTEC, CONICET-UNL), Argentina, [3]Universidad Nacional del Litoral, Argentina, [4]IMDEA-Nanociencia, Campus UAM, Spain

The growth and thermal stability of thin AlF_3 films grown on Cu(100) have been studied by a combination of surface science techniques. AlF_3 is an interesting material for many applications; it is a wide band-gap insulator (10.8 eV), transparent in the visible range and chemically inert, what makes it a good passivating agent. Furthermore, it can be easily decomposed by electron irradiation leaving deposits of metallic Al, which can be taken advantage of for e-beam nanopatterning purposes.

STM measurements show that the growth of AlF_3 on Cu at room temperature starts with the decoration of the substrate atomic steps followed by the formation of 2-dimensional dendritic islands that coalesce to form porous layers. STM and thermal energy atom scattering (TEAS) also reveal that films with thicknesses below 2 ML are morphologically unstable upon thermal treatments: when heated up to 430 K these layers de-wet the substrate and form three-dimensional islands. On the contrary, thicker films are stable up to 730 K, where desorption in molecular form starts taking place.

The effect of electron irradiation has also been characterized by means of surface spectroscopies. It is shown that even very small doses of electrons are enough to provoke the decomposition of the aluminum fluoride and the release of molecular fluorine.

[1] G. Ruano et al., Surf. Sci. 606, 573 (2012).

P2.118 HR-EELS studies on oxide nanoparticles

S Frey, M Kroll and U Köhler

Ruhr-Universität Bochum, Germany

High resolution electron energy loss spectroscopy is a useful tool in heterogeneous catalysis as it provides information about vibrational states of adsorbates. With this, not only the adsorbed species can be identified, but also their orientation can be determined. While HR-EELS on single crystals has found wide spread and nowadays serves as a sophisticated tool to obtain adsorbate information, most studies on oxide nanoparticles rely on infrared spectroscopy (FTIRS, [1]) as EELS requires a reflecting sample with high conductivity. In the field of heterogeneous catalysis this causes a material gap between idealized single crystalline model systems (analyzed with HR-EELS) on the one hand and real catalysts based on nanoparticles (looked up with FTIRS) on the other hand.

Enabling HR-EEL Spectroscopy on nanoparticles opens up a new approach to get closer insight into the behavior of real oxide materials that are used in heterogeneous catalysis. We studied ZnO and TiO_2 nanoparticles and their corresponding metal loads Cu and Au, which are used for methanol synthesis and CO oxidation. Our experience shows that a thoroughly sample preparation and pretreatment is vital in order to obtain reasonable results of a nanoparticle sample in the EELS. The nanoparticle layer has to be smooth and closed to produce adequate reflection intensity. Moreover sufficient conductivity is required to prevent surface charging. Both requirements can be met by sedimenting oxide powder on a gold plate as SEM images and loss spectra show. In the case of ZnO a clear phonon spectrum emerges which is comparable to Fuchs-Kliewer phonons present on a single crystalline surface.

P2.119 DFT+U study of adsorption of small molecules on model CeO_2/Cu(111) catalysts

L Szabova[1], V Matolin[1] and S Fabris[2]

[1]Charles University in Prague, Czech Republic, [2]CNR-IOM DEMOCRITOS Simulation Center and SISSA, Italy

Ceria based materials are important heterogeneous catalysts for example in fuel cell application. Their catalytic activity is directly related to their ability to store and release oxygen via formation of oxygen vacancies, which are acompanied by reversible valency change Ce^{4+}<->Ce^{3+}. The catalytic activity of ceria can be increased by metal doping. The interaction of metal with oxide is substantial for the effectivity of the catalyst. Copper was reported to promote various reactions as CO oxidation or NO reduction [1,2].

In the present work we study the adsorption properties of small molecules on model catalytic CeO_2/Cu(111) systems described in [3]. This system contains different types of active centers in ceria (such as oxygen vacancies and/or Ce^{3+} ions) due to the interaction with copper depending on the thickness of the layer [3,4]. This provides an opportunity to compare the activity of ceria in perfect stoichiometry to defective or reduced ceria and better understand and identify the chemical and electronic effects arising from the interaction at the copper/ceria interface and leading to the improved catalytic properties of these systems.

[1] W. Liu, M. Flytzani-Stephanopoulos, J. Catal. 153 (1995).
[2] P. Bera, S. T. Aruna, K.C. Patil, M.S. Hegde, J. Catal. 186, 36 (1999).
[3] L. Szabova, O. Stetsovych, F. Dvorak, M. Farnesi Camellone, S. Fabris, J. Myslivecek, V. Matolin, J. Phys. Chem. C 116, 6677-6684 (2012).
[4] F. Dvorak, O. Stetsovych, M. Steger, E. Cherradi, I. Matolinova, N. Tsud, M. Skoda, T. Skala, J. Myslivecek, V. Matolin, J. Phys. Chem. C 115, 7496–7503 (2011).

P2.120 STM and LEED studies on reduced TiO_2 (001) surface

A Busiakiewicz and I Zasada

University of Lodz, Poland

Although the reduced (001) surface of rutile TiO_2 is considered as a base for catalysis, the information about its structure and properties is still limited. In the present work we have combined scanning tunnelling microscopy and spectroscopy (STM and STS) with low-energy electron diffraction (LEED) to explore the behaviour of reduced TiO_2(001) surface in ultra-high vacuum at elevated temperatures. It is shown that reduced (001) surface undergoes a structural change above 1173 K leading to domain-like ordering along [110] and [-110] directions [1]. Inside the domains periodic rows are observed and they are spaced by 2.6 nm which is twice the distance of {114} facets which are known high-temperature phase on $TiO_2(001)$ [2]. LEED measurements have been performed on stechiometric, lightly- and heavily-reduced $TiO_2(001)$ surfaces which presents the evolution of surface ordering as a function of reduction and temperature. It is shown that the growth of domains increases the long-range order which is confirmed by LEED patters. To establish the structure of $TiO_2(001)$ at different stages the intensities of selected LEED spots have been also measured as a function of electron energy I(E) and analysed by theoretical calculations.

[1] A. Busiakiewicz, Z. Klusek, M. Rogala, P. Dabrowski, P. J. Kowalczyk and P K Datta, J. Phys.: Condens. Matter 22, 395501 (2010).
[2] L. E. Firment, Surf. Sci. 116, 205 (1982).

P2.121 Preventing fouling with silicon carboxides films synthesized by DBD-APCVD

J Guillot[1], E Lecoq[1], D Duday[1], J-B Chemin[1], M Riihimäki[2], E Puhakka[3] and P Choquet[1]

[1]CRP-Gabriel Lippmann, Luxzembourg, [2]University of Oulu, Finland, [3]Technical Research Centre of Finland (VTT), Finland

Limiting fouling is one of the growing research areas in process heat transfer and heat exchanger technology. A way to achieve this goal is the development of new surface materials with controlled surface energy and morphology. The silicon carboxides films developed in this study are synthesized in a dielectric barrier discharge chemical vapour deposition process working at atmospheric pressure (DBD-APCVD), using metacrylic acid (MA) and vinyltrimethoxysilane (VTMOS) polymer precursors in an argon discharge. The copolymerised films are characterized by mean scanning electron spectroscopy (SEM) for the surface morphology, X-ray photoelectron spectrometry (XPS) and Fourier transformed infra-red spectrometry (FTIR) for the surface and bulk composition respectively. The anti-fouling properties of the films are tested with surface crystallisation of $CaCO_3$ in a home-made laboratory scale set-up of a flat heat exchanger.

The control of the duty cycle of the electrical pulsed excitation during the DBD plasma discharge allows the tuning of the morphology and the chemistry of the silicon carboxides coatings. The roughness of the films varies from rather smooth to grain shaped surfaces (S_z ranging from 35 nm to 650 nm respectively). The variation of the main negatively charged chemical groups' concentration at the surface modifies the total surface charge state. The antifouling properties (induction time and fouling rate) have been determined for every sample and are linked with zeta potential and surface energy measurements in order to improve the antifouling properties of the coatings.

P2.122 Growth of thick ceria films on Cu(111)

F Dvorak, O Stetsovych, J Myslivecek and V Matolin

Charles University in Prague, Czech Republic

Cerium oxide (CeO_2, ceria) is widely used in applications in heterogeneous catalysis [1]. CeO_2 layers grown on Cu(111) represent useful model systems for research in heterogeneous catalysis [2-4].

We present a STM study of evolution of morphology of thick (5 - 40 ML) ceria layers on Cu(111). Using constant temperature during growth, the ceria multilayer grows in a form of three-dimensional ceria pyramids stacked of monolayer-high steps ("wedding cakes" [5]) resulting in growth of a rough and discontinuous ceria multilayer. A different temperature treatment during the growth cause reorganization of the ceria accompanied with creation of screw dislocations [5]. Introducing of the screw dislocations into the film results in a growth of continuous ceria films with a greatly suppressed roughness. That represent, in combination with sufficient thickness, almost ideal mimic of bulk $CeO_2(111)$ surface.

[1] Catalysis by ceria and related materials, ed. A. Trovarelli, Imperial College Press (2002) London

[2] F. Šutara, et al., Thin Solid Films 516 (2008) 6120.
[3] J. A. Rodriguez, et al., Angew. Chem. Int. Ed. 48 (2009) 8047.
[4] F. Dvořák, et al., J. Phys. Chem. C 115 (2011) 7496.
[5] A. Redinger, et al., Phys. Rev. Lett., 100 (2008) 035506.

P2.123 Oxidation of iron

J Weissenrieder and M Soldemo

Royal Institute of Technology, Sweden

With applications in such diverse fields as heterogeneous catalysis, information technology, and of course construction materials, the importance of iron and its oxides can hardly be overestimated. Corrosion and initial oxidation of iron single crystals have been studies for decades, but the exact atomic structure of its surface oxides remains to be determined. Lately, ultrathin iron oxide films supported on platinum has been subject for great interest as it possesses high activity for low temperature CO oxidation. With the intention to determine the structure of these initial oxides and to potentially use them as catalytic model support, we have studied the oxidation of the low index surfaces Fe(110) and Fe(100) using low energy electron diffraction (LEED), scanning tunneling microscopy (STM), high resolution core level photoelectron (PES), and near edge X-ray absorption fine structure spectroscopy (NEXAFS).

STM and LEED reveal a rich phase diagram of surface oxides for the two iron surfaces. For Fe(110) the first structure formed upon oxidation is a FeO(111) film, not very unlike what is formed by a monolayer FeO on Pt(111). With its hexagonal structure on the substrate's rectangular, the film gives rise to Moiré patterns in LEED and STM. The FeO(111) film is assumed to be bound by an oxygen layer to the Fe(110) substrate. This assumption is supported by PES data from the O 1s and Fe 2p core levels. At higher oxygen coverage bulk oxide formation commences.

On Fe(100), oxide formation proceed epitaxially. By tuning the oxidation pressure and temperature several closely related structures can be formed (e.g. 2x2 and c(4x4) as shown by LEED and STM). Chemical state of the different films was determined by PES and NEXAFS. These oxides seem promising as catalytic support as they grow with less strain than the oxides on Fe(110). CO was used as probe molecule to investigate termination and bonding at some surfaces.

P2.124 Surface evolution of (100) magnetite during oxidation

J de la Figuera[1], E Loginova[2], L Vergara[2], M Monti[1], J F Marco[1], N C Bartelt[2] and K F McCarty[2]

[1]Instituto de Química-Física "Rocasolano", Spain, [2]Sandia National Laboratories, USA

Magnetite is a ferrimagnetic semimetal. Although the oldest magnetic material known to mankind, recently it has been discovered to be multiferroic and a half-metal, suggesting applications in spintronics [1]. But its use in magnetic spin-valves and magnetoresistance devices has been dissapointing. This is presumably because the interface and the surface of magnetite can differ strongly from the bulk material. Magnetite has a inverse spinel structure that can accomodate a wide range of stoichimetries, and even of cationic order. Furthermore, oxidation of magnetite eventually produces maghemite and hematite. How these transformations occur and the role of surfaces are unclear.

Here we study the morphology and evolution of magnetite (100) single crystal surface by low-energy electron microscopy, x-ray photoemission microscopy and scanning tunneling microscopy. We find an intricate relationship between oxygen pressure, temperature and the evolution of surface morphology. We show that this evolution gives insight into the kinetic mechanisms that govern surface stoichiometry.

[1] M. Bibes, J. E. Villegas, and A. Barthelemy, "Ultrathin oxide films and interfaces for electronics and spintronics", Adv. Phys. 60, 5 (2011).

P2.125 Ab initio study of low-coordinated sites on the MgO(001)-surface using hybrid functionals

P Auburger[1], M Kolb[2] and M Bockstedte[1]

[1]Universitaet Erlangen-Nuernberg, Germany, [2]Leiden University, The Netherlands

In catalysis metal oxides play an important role. Low-coordinated surface sites, such as surface oxygen vacancies, step edges, and reverse corners represent the reactive centers for example at the MgO(001) surface. To unravel the role of particular centers in chemical reactions, it is pivotal to understand their properties, in particular their localized electronic states. Density functional theory together with the local density or generalized gradient approximation for the exchange-correlation functional, however, underestimates the band gap of metal oxides by a large margin and often even fails to describe the bonding correctly. Employing hybrid functionals like the HSE06, which include a fraction of screened Hartree-Fock exchange, are known [1] to improve the description of metal oxides considerably.

Here we investigate surface color centers at the MgO (001) surface including the surface oxygen vacancy, step edges, and vacancies at step edges using the DFT-HSE06 approach and a slab model. This enables a proper description of localized and extended states, e.g. the dispersion of shallow surface states at the step edge. For the relevant surface and localized states within the band gap we find large corrections to the DFT-LSDA. In addition, the calculations reveal a negative electron-affinity in agreement with recent calculations within in the many body perturbation theory [2]. Our results show a considerable dispersion of step-induced states. Yet, oxygen vacancies at steps or kink sites consitute electron traps well below these states. Their unoccupied levels, however, are resonances within the step induced states. Optical excitation can thus inject electrons into the step state continuum triggering chemical interaction with adsorbates at step edges.or on the terrace. Our findings are in good agreement with recent STS-experiments on vacancy centers at step edges of MgO-films [3].

[1] A. Krukau, *et al.* J. Chem. Phys. 125, 224106 (2006); G. Pacchioni, J. Chem. Phys.128, 182505 (2008).
[2] M. Rohlfing , et al, Phys. Rev. Lett. 91, 2568021 (2003).
[3] M Sterrer et al, J Phys. Chem.B 110, 46-49 (2006).

P2.126 Interaction of atomic and molecular hydrogen with ZnO

C M Kim and P Roy

Kyungpook National University, South Korea

Zinc oxide (ZnO) has attracted a significant amount of attention because of its potential applications as catalysts, gas sensors, wide band gap semiconductors and other microelectronic devices. Undoped ZnO normally exhibits n-type conductivity. It has been suggested that interstitial hydrogen, which might be incorporated during crystal growth or in the ambient condition, is responsible for the n-type conductivity. There is some debate about the role of hydrogen in the n-type conductivity of as-grown ZnO. However, it is generally observed that ZnO shows an increase in free carrier concentration and electrical conductivity under high pressure of hydrogen.

In the surface science studies of the interaction between hydrogen and ZnO, atomic hydrogen is generally used because molecular hydrogen is not dissociated on the ZnO surface in the UHV condition. We have been studying the initial adsorption of atomic hydrogen on ZnO single crystal surfaces and subsequent diffusion into the bulk by using TPD and XPS. In this talk, we will present the adsorption of atomic hydrogen on three different ZnO single crystal surfaces; ZnO(0001), ZnO(000-1), and ZnO(10-10). We will report the identification of surface and bulk hydrogen atoms and the activation energy for the bulk diffusion of the surface hydrogen atoms. The interaction of molecular hydrogen and ZnO was also investigated by utilizing ambient-pressure XPS. We will present the real-time observation of the dissociation of H_2 on ZnO surfaces in the pressure range of 1 to 150 mTorr.

P2.127 XPS quantification of ZnO(000-1) polar surfaces irradiated with 0.5-5 keV Ar ions

M Krawczyk, W Lisowski, J W Sobczak and A Jablonski

Polish Academy of Sciences, Poland

We performed X-ray photoelectron spectroscopy (XPS) studies to determine atomic zinc and oxygen content of single-crystalline ZnO with polar (000-1) surfaces bombarded with Ar ions of energy 0.5-5 keV at the incidence angle of 55° with respect to the surface normal. XPS spectra were recorded on the PHI 5000 VersaProbe^{TM} scanning ESCA Microprobe using monochromatic Al K_a radiation. The atomic concentration of zinc and oxygen were evaluated using the multiline program [1]. The polar surfaces were preliminary sputter-cleaned (0.5 keV Ar^+, 5 min). As result, 8 nm in depth of the material was removed, revealing the non-stoichiometric surface enriched in zinc. The O/Zn at. concentration ratio was found to be 0.666±0.012, as a result of ion-beam induced loss of oxygen from the surface. Further surface sputtering involved four 5 min cycles of argon ion-bombardment at a constant ion energy, and each cycle was followed by XPS analysis. The same sputtering procedure was realized for various Ar-ion energy from 0.5 keV up to 5 keV. Under these conditions, the O-terminated face of ZnO was found to be stable, and only negligible effect on the O/Zn value was observed. In conclusion, our studies on low/medium energy Ar-ion irradiated ZnO(000-1) crystals would be beneficial to use these highly resistive materials under appropriate conditions.

This research was partially supported by the European Union within European Regional Development Fund, through grant Innovative Economy (POIG.01.01.02-00-008/08), and by the grant no. 2011/01/B/ST4/00959 of the National Science Center of Poland.

[1] A. Jablonski, Anal. Sci. 26 (2010) 155.

P2.128 Study of fractal properties of MnO_2 pyrolytic films

L Skatkov[1] and V Gomozov[2]

[1]Argo Printed Circuit Board (PCB), Israel, [2]National Technical University "KhPI", Ukraine

The theory of scattering by a porous solid was developed by Wong [1], and the theory main formula is as follows: $I(q) \sim$ constant x q^{-D} (1) Here D is the surface fractal dimension that shows fractal behavior.

The relationship shows the fractal behaviour. Indeed, on the graph, the coefficient of the curved part slope, which can be closely approximated by line $\alpha = -d\lg I(q)/d\lg q = 2.87$

Comparison result (2) with the formula (1) gives (for $\alpha = D$) the value of D=2.87.

Obtained D value coincides with the previously [1] found value of surface fractal dimensionality in a sintered niobium powder pellet (Nb) with high accuracy, $D_{(Nb)} = 2{,}81$.

So far, the authors are at a loss and cannot say whether it is a mere coincidence or the result of some specific generation features of the capacitor MDS structure. But it as was noted earlier , in case of sintered niobium the scattering is stipulated by the sample surface.

[1] Po-zen Wong, Phys.Rev B 32 (1985) 7417.

P2.129 Tuning the morphology of carbon substrates by oxygen plasma treatment

I Khalakhan, M Vorokhta, M Chundak, M Dubau, S Haviar and V Matolin

Charles University in Prague, Czech Republic

Different carbon substrates (glassy carbon, carbon foil, carbon nanotubes) were treated by the oxygen plasma for different time. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) study showed the dramatic influence of oxygen plasma on the morphology of carbon substrates. It leads to the formation of nanostructured surface which consist of well separated vertical nanostructures. The surface roughness was found to increase with increasing the treatment time.

By using magnetron sputtering of platinum and cerium oxide we can prepare oxide layers continuously doped with Pt atoms during the growth. This technique provides etching of the carbon substrate and the deposit growth simultaneously. This leads to the formation of high surface area catalyst which makes this method promising for production of the catalysts for PEMFC, CO oxidation etc.

Semiconductor surfaces

P2.130 Atomic-scale wires on Si(553)-Au: observation of current-dependent periodicity

S Polei[1], I Barke[1], P C Snijders[2] and K-H Meiwes-Broer[1]

[1]Universität Rostock, Germany, [2]Materials Science & Technology Division, USA

Quasi one-dimensional metallic chains on silicon have received considerable attention recently, particularly due to various unusual electronic properties [1]. Recently, a magnetic ground state has been predicted for the Au-induced reconstruction of the Si(553) surface [2]. We present STM and STS studies to investigate the nature of the phase transition to a reconstructed Si step edge at low temperatures and the possible development of non-zero Si spin-polarization. Different periodicities are observed at the Si step-edge chains depending on the tunneling current. When the current is increased the reconstruction along the chains changes gradually from 1x3 to 1x2. As a result, the STM topography has a 1x6 periodicity in the transition regime. The findings are discussed in the context of a possible magnetic state [2].

[1] J. N. Crain et al., PRB 69, 125401 (2004); P. C. Snijders et al., PRL 96, 076801 (2006); I. Barke et al., PRL 97, 226405 (2006) [2] S. C. Erwin, F. J. Himpsel, Nat. Commun. 1, 58 (2010).

P2.131 Depth profiling of melting and metallization in Si(111) and Si(001) surfaces

R Gunnella[1], A Di Cicco[1], M Ali[2], M Abbas[3], E Principi[4] and F D'Amico[4]

[1]University of Camerino, Italy, [2]COMSATS Institute of Information Technology Pakistan, [3]Laboratoire IMS, France, [4]Synchrotron ELETTRA, Italy

Surface melting has been studied for a long time in view of the importance of this phenomenon in understanding basic questions related to first-order phase transitions in solids (see [1,2] and references therein). An original approach for measuring the depth rofile of melting and metallization of the Si(111) and Si(001) surfaces is proposed and applied[3]. The different probing depths of the Auger electron and electron energy loss (EELS) spectroscopies are exploited to study the number of molten and metallic layers within 5-30 Angs from the surface up to about 1650 K. Melting is limited to 3 atomic layers in Si(001) in the range 1400-1650 K while the number of molten layers grows much faster (5 layers at about 1500 K) in Si(111) as also indicated by the L3 -edge shift observed by EELS. The relationship between melting and metallization is briefly discussed.

[1] U. Tartaglino, T. Zykova-Timan, F. Ercolessi, and E. Tosatti, Phys. Rep. 411, 291 (2005).
[2] A. Trayanov and E. Tosatti, Phys. Rev. Lett. 59, 2207 (1987).
[3] R. Gunnella, M. Ali, M. Abbas, F. D'Amico, E. Principi and A. Di Cicco, Phys. Rev. Lett. 107, 166103 (2011).

P2.132 Faceting transitions in polysilicon films

T Rodionova, N Nakhodkin and N Kulish

Kiev National Taras Shevchenko University, Ukraine

Polysilicon films are widely used in integrated circuit technology, as a material for solar cells and other applications. As is known, the film structure determines significantly their mechanical, optical, and electrical properties. In particular, the characteristics of the electronic devices that are fabricated from polycrystalline silicon are directly connected with the structural properties of their internal interfaces (grain boundaries (GB), twin boundaries in the interior of grains). Some GB in polysilicon films are faceted. Faceted GB have a low trap density [1]. Thus, the presence of the faceted GB is favorable for polycrystalline electronic devices, such as thin transistors and solar cells. Faceting of GB under post-deposition annealing often strongly influences both the structure and the properties of polycrystalline and especially nanocrystalline materials where GB range up to 50% of the film volume. In particular, GB faceting leads to drastic changes in GB energy, diffusion mobility, impurity segregation, etc. [2].

In this work the faceting of GB under annealing in phosphorus-doped polysilicon films, produced by low-pressure chemical vapor deposition, has been investigated by transmission electron microscopy.

It has been shown that the facet types and number of facet depend on annealing temperature. The stability diagram for the different facet types was constructed. It has been shown that there are two kinds of GB transition that take place in polysilicon films. In particular: 1 - transition when the original GB dissociates onto flat segments whose energy is less than that of original surface or GB; 2 - transition, when a smooth facet is replaced by another; 3 - the transformation of curved GB into a GB facet with increasing temperature. This transition was observed for the first time for silicon.

[1] S. B. Lee, J. Moon, C.-H. Chung, Yo.-H. Kim, J. H. Lee, and D.-K. Choi, J. Vac. Sci. Technol. B 24, 2322.
[2] S. B. Lee, Mater. Lett. 57, 3779 (2003). (2006).

P2.133 Surface preparation and polarity determination of GaN(0001) and InN(0001)

M Walker, L Fishwick, J Mudd, D Park, M Misra, E Davis, A Marsden and C McConville

University of Warwick, UK

Tuning the composition and hence the band gap of InGaN films opens the door to potentially highly efficient solar cells which can utilise light across the entire visible range of the electromagnetic spectrum [1]. On the road to industrial application, it is of key importance to understand both the electronic and atomic structure of InN and GaN, the materials at the extremes of this compositional range. In this study we have used a range of modern surface science techniques to study the cleaning of III-N surfaces using low energy nitrogen ion bombardment and annealing. After cleaning (1 x 1) low energy electron diffraction (LEED) patterns were observed from both surfaces. X-ray photoemission spectroscopy (XPS) using a monochromated Al k_α source showed the surfaces to be virtually free from contamination, with the shape of the valence band spectrum indicating the polarity of the films. Co-axial impact collision ion scattering spectroscopy (CAICISS) [2,3] was used to determine the surface atomic structures and to verify the XPS polarity determination. In the case of InN(0001), evidence of metallic In crystallite formation was observed in all of the experimental data, so further SEM and STM studies were conducted to investigate the coverage of the droplets.

[1] J. Wu, W. Walukiewicz et al., J. Appl. Phys. 94, 6477 (2003).
[2] M. Walker, M.G. Brown et al., Phys. Rev. B 83, 085424 (2011).
[3] C.R. Parkinson, M. Walker et al., Surf. Sci. 545, 19 (2003).

P2.134 Desorption-induced structural changes of metal/Si(111) surfaces – kinetic Monte Carlo simulations

P Kocan, P Sobotik, P Matvija and I Ostadal

Charles University in Prague, Czech Republic

Deposition of metals on the Si(111) surface together with thermal activation results in variety of reconstructions. A special class can be reserved for the structures formed during desorption of material from the surface. For example, in the case of In/Si(111) surface, structural changes $4\times1 \rightarrow \sqrt{31}\times\sqrt{31} \rightarrow \sqrt{3}\times\sqrt{3} \rightarrow 7\times7$ were observed during desorption [1]. Importantly, some structures are formed only by means of desorption, i.e. deposition of corresponding amount of metal and thermal treatment without desorption results in formation of different structures. Even though significant amount of experimental data (TDS, electron diffractions, STM) has been gathered on the topic during last decades, many questions remain open – e.g. no reasonable explanation is available for surprisingly zeroth-order desorption reported in several cases [1,2].

We have developed a kinetic Monte Carlo model (kMC) which allows studying relation between processes (in the model represented by their rates) and observable quantities like desorption rates (TDS) or changes of morphology (STM). On two examples of Pb [2] and Tl [3] on Si(111) surface we demonstrate capabilities of the model to reproduce experimentally obtained quantities. We will show that zeroth-like-order desorption can be modeled by means of first-order processes when considering enhanced desorption from domain boundaries. In addition to evaluation of desorption parameters, the model is used to fit diffusion rates and stabilities of structures formed during desorption.

[1] N. Minami et al., Surf. Sci. 542 (2003) 199-205.
[2] J. A. Carlise et al., Phys. Rev. B 45 (1992) 3400.
[3] P. Kocán et al., Surf. Sci., DOI: 10.1016/j.bbr.2011.03.031.

P2.135 Probing the Diffusion and Structure of Te and CdTe on Cu(111)

M King, C Jack, D MacLaren and M Kadodwala

University of Glasgow, UK

We combine photoemission spectroscopy, electron diffraction, scanning tunnelling microscopy and transmission electron microscopy to provide a comprehensive description of the growth of Te and CdTe on Cu(111): systems that are prototypical of photovoltaic cells' back-contacts. Alloying of Te with Cu(111) is found to activate above 275 K and rapidly develops an unusual, non-stoichiometric $Cu_{3-x}Te_2$ phase. A multiplicity of Cu vacancy sites appears to promote rapid and extensive alloying, even for thick Te films. In the case of CdTe deposition, alloying is again observed to occur, with Te diffusing into the bulk and Cu diffusing into the overlayer. Curiously, Cu diffusion into the CdTe is substantially enhanced if an interfacial Cu_3Te_2 alloyisformed first, contrary to the expectation of forming a barrier layer. Developing a deeper understanding of the growth, interdiffusion and alloying of CdTe/ Cu films will be essential to optimisation of the efficiency of CdTe photovoltaics.

P2.136 Structural study of the Si(111)-$\sqrt{3}$x$\sqrt{3}$-Pd by transmission X-ray diffraction

H Tajiri[1], H Toyokawa[1] and O Sakata[2]

[1]Japan Synchrotron Radiation Research Institute, Japan, [2]National Institute for Materials Science, Japan

In the initial stage of Pd growth on a Si(111) substrate at around 570 K, a well-ordered superstructure with the ($\sqrt{3}$x$\sqrt{3}$)R30° periodicity is formed by depositing Pd to one monolayer thickness. This Pd/Si(111) surface has the twin-domain structure and its structure model has been proposed by transmission electron microscope and diffraction analyses [1].

It is noted that the structure model of the Pd/Si(111) surface resembles that of the Ag/Si(111)-$\sqrt{3}$x$\sqrt{3}$ surface revealed by first-principles calculations and scanning tunneling microscopy, which is known as the inequivalent triangle model [2], in the twisted structures of metal triangles characteristic of the models. Pd triangles also tilt from the symmetric position in the p31m space group by ca. 6° in the model proposed previously. However, detailed atomic arrangements of the Pd/Si(111) surface have not yet been reported especially in the depth direction.
In this presentation, we show the results of the structure analysis of the Si(111)-$\sqrt{3}$x$\sqrt{3}$-Pd, in both the in-plane and depth directions, by transmission X-ray diffraction [3]. The synchrotron X-ray experiments were done at the beamline BL13XU for surface and interface structure analysis at SPring-8.

[1] K. Akiyama, K. Takayanagi, and Y. Tanishiro, Surf. Sci., 205 (1988) 177-186.
[2] H. Aizawa, M. Tsukada, N. Sato, and S. Hasegawa, Surf. Sci., 429 (1999) L509-L514.
[3] H. Tajiri, O. Sakata, and T. Takahashi, Appl. Surf. Sci., 234 (2004) 403-408.

P2.137 Adsorption of Al on the Si(100) surface studied by STM and KMC simulations

M Kučera, M Sevtín, P Sobotík, P Kocán and IOšťádal

Charles University in Prague, Czech Republic

For low coverages, aluminium grows on Si(100) 2×1 surface in form of single-atom wide chains consisting of dimers. Therefor it is a suitable model system for investigating 1-D objects. We study growth characteristics of these chains by means of STM for coverages from 0.02 ML to 0.09 ML and substrate temperatures up to 420 K. For all investigated coverages and temperatures chain length distribution is scalable and has a monomodal character. It is in contrast with behaviour of two other group III metals (In and Ga) [1, 2], for which the distribution is monotonically decreasing. In order to understand this dicrepancy a growth model for Al, based on experimental data, was proposed and tested using kinetic Monte Carlo simulations. The model takes into account anisotropy of hopping barriers, dimer structure of aluminium chains and their morphology. Using computed values of bonding energies of adatoms, we tuned and eventually found values of the hopping barriers for the best agreement between experimental and simulated growth characteristics.

[1] M. A. Albao, M. M. R. Evans, J. Nogami, D. Zorn, M. S. Gordon and J.W. Evans: Phys. Rev. B , 72 (2005) 035426-1
[2] Kocán P., Sobotík P., Ošťádal I., Javorský J., Setvín M.: Surf. Sci. 601 (2007) 4506

P2.138 Isolated silicon dangling bonds (IDBs) on water saturate Si (001)-2 x 1 surface

D Pierucci[1], A Naitabdi[2], A Khaliq[2], H Tissot[1], J Jacques Gallet[2], F Bournel[2], F Rochet[2], M Silly[3] and F Sirotti[3]

[1]LCPMR/Synchrotron Soleil, France, [2]Laboratoire de Chimie Physique-Matière et Rayonnement (LCPMR), France, [3]Synchrotron Soleil, France

On clean Si (001)-2 x 1, water dissociates into H and OH fragments that decorate the silicon dangling bonds left by surface dimerization. In fact two reaction channels, the intrarow and the on-dimer, are opened with equal probability[1]. The competition between these two channels explains why, at surface saturation, isolated dangling bonds (IDBs) in $^{\cdot}$Si-SiOH or $^{\cdot}$Si-SiH units, are observed by STM as bright features in occupied state images, contrasting with the lower "density-of-state" imprint of the silicon atoms capped with OH or H [2,6]. An isolated dangling bond is born by a trivalent Silicon[3] (similar, but not identical, to the P_b defects at the Si(111)/SiO_2 interface). It presents three charge states, denoted D^+, D^0, D^- (corresponding to zero, one or two electrons in the dangling-bond orbital), related to the position of the Fermi energy with respect to the charge-transition levels, and a positive Anderson Correlation Energy U (lattice relaxation energy less than electron-electron repulsion)[4]. The magnitude and the sign of the charge of the defect are determined by the substrate doping[5].In this work we performed a combined XPS and STM/STS study in order to examine the role of substrate doping and water vapour pressure on the adsorption kinetics. Time-resolved XPS at TEMPO beamline (Synchrotron Soleil) was used to monitor the electronic structure (core-level peak position and intensity, measurement of secondary electron cut-offs) while dosing the surface with water. Details in the positioning of the surface Fermi level within the gap and the charge state of isolated dangling bonds (IDBs) left at saturation coverage were studied as a function of doping.

[1] Lee, J.-Y. et al., Journal of Physical Chemistry B 2006, 110, 18455-18458.
[2] Andersohn, L. et al., Surface Science 1993, 284, 77-90.
[3] Lenahan P. M. et al., Journal of Applied Physics 1983, 54, 1457-1460.
[4] Broqvist, P. et al., Physical Review B 2008, 78,075203.
[5] Liu L. et al., Nanoptterning–From Ultralarge-Scale Integration to Biotechnology, MRS Symposia Proceedings 705 (Materials Research Society, Pittsburgh 2002), Y6.6.1.
[6] Bournel , F. et al., Journal of Physical Chemistry C 2011, 115, 7686–7693.

P2.139 Ethylene adsorption on silicon surfaces modified by group III and IV metals studied by STM

P Zimmermann[1], M Setvín[2], P Sobotík[1], I Ošťádal[1] and P Kocán[1]

[1]Charles University, Czech Republic, [2]The Academy of Sciences of the Czech Republic, Czech Republic

Modifying silicon surfaces by one-atomic layer of group III (In) and IV (Sn) atoms is used as a novel approach to studying interactions of organic molecules with silicon substrates. Adsorption of conjugated organic molecules onto bare silicon surfaces proceeds by breaking up the molecular π–bonds followed by covalent rebonding with the silicon dangling bonds. In contrast to a free molecule, the adsorbed molecule is often distorted, having its interesting properties removed.

On the strongly anisotropic Si(100)–2×1 surface, tin and indium atoms passivate the dangling bonds by bonding to the underlying silicon dimers while self-assembling into linear dimer chains. At the 0.5 monolayer coverage, a complete passivation of the silicon dangling bonds is achieved. Alternatively, the Si(111)–4x1–In surface consists of long quasi-1D conductive chains.

The simplest organic molecule with a double bond — ethylene — serves as our model molecule to gain insight into the interaction of larger conjugated molecules with the modified silicon surfaces. The adsorption of ethylene on the Si(001)–4×3–In, Si(001)–2×2–Sn and Si(111)–4×1–In substrates is studied by STM, furthermore STS is employed to trace ethylene induced changes in the local electronic structure.

P2.140 Strain induced intermixing of Ge into Si epitaxial layer

Y Shigeta[1], A Tosaka[1], I Mochizuki[2] and R Negishi[3]

[1]Yokohama City University, Japan, [2]Japan Atomic Energy Agency, Japan, [3]Osaka University, Japan

The growth mechanism of thin film has been widely investigated because of its importance for development of nanotechnology. There are three famous growth modes such as the layer-by-layer growth (F-V) mode, the island growth (V-W) mode and the islands growth following the layer-by-layer growth (S-K) mode. The main factor to influence the growth mode is a balance between the surface energies of the thin film and the substrate and lattice parameters between them. In addition to the balance between surface energies, a strain in the thin film is also important parameter deciding the growth mode of the thin film. The third growth mode, S-K mode, is observed when the strain in the film is too large to keep the layer structure.

In this paper, we will show an additional influence of strain in the thin film growth of Si on Ge(111), especially the influence on the intermixing. We measure the strain with an indirect method through a change of effective mass with the strain, because the effective mass in the metallic layer on the Si/Ge(111) is sensitive to the strain[1,2]. The intermixing of Si layer on Ge(111) which is induced the strain of layer has been investigated by scanning tunnelling microscopy and angle resolved ultraviolet photoelectron spectroscopy (ARUPS). It has been shown that there is a critical thickness occurring the intermixing in the hetero-epitaxial growth. By the results of Ge-3d core level photoelectron spectra from Si on Ge(111) and ARUPS results of $\sqrt{3}\times\sqrt{3}$-Ag structure on the Si(111) layer on Ge, the effect of strain and the intermixing between Si and Ge is discussed.

[1] I. Mochizuki, R. Negishi, and Y. Shigeta, J. Appl. Phys. 106, 013709 (2009).
[2] I. Mochizuki, R. Negishi, and Y. Shigeta, J. Appl. Phys. 107, 084317 (2010).

P2.141 Effect of electron-optical phonon interaction on resonant tunneling in wurtzite GaN/InxGa1-xN double barrier structures

S Ban and J Zhu

Inner Mongolia University, China

Quantum well structures based on nitrides of III-V groups have attracted great interest for their novel properties in applications of optoelectronic devices, in which the precise control of vertical transport plays an important role. Many experimental and theoretical workshave been contributed to probe the vertical transport in these kinds of structures. The existing experiments have proved that these structures with large conduction band offsets can be suitable candidates for resonant tunneling diodes since these exist high peak to valley ratios.However, the investigations about phonon-assisted tunneling (PAT) are rarely on wurtzite III-V semiconductor heterostructures because their lower symmetry and strong spontaneous and piezoelectric polarizations give rise to complex phonon dynamics and electron-phonon interactions.

In this paper, the dispersion relations of optical phonon modes in a double barrier structure of $\mathrm{GaN/In_xGa_{1-x}N}$ are given in detail within the framework of the dielectric continuum model. Furthermore, based on the calculation of the spatial distribution of electronic wave functions, the interaction between an electron and optical phonons as well as its ternary mixed crystal effect in these structures are investigated. Then, the optical PAT currents are studied by using the Fermi golden rule. Our result shows that the contributions to the PAT from interface phonon modes are more important than that from the longitudinal, confined and propagating optical phonon modes.

P2.142 Transport and mechanical properties of molecular junctions formed by acetophenone deposited on Si (100) surface

O Krejčí, M Setvín, Z Majzik, P Hapala, P Mutombo and P Jelínek

Institute of Physics of Czech Academy of Science, Czech Republic

One of the main challenges of Molecular electronics is to understand and control charge transfer through a reproducible single molecule contact between electrodes. Most investigations of electron transport through molecules have been performed in “blind” junction experiments, where the molecular conformation and contact geometry cannot be probed. Therefore large gaps in our knowledge remains since in molecular electronics the atomic-scale structure of the entire junction including the leads is important for its conductance properties.

Our goal is to study electrical transport through well-defined molecular junction on semiconductor surfaces. Formation of molecular junctions using organic molecules on semiconductor surfaces might lead to interesting phenomena. For example, the presence of the band gap in electrodes can lead to the negative differential resistance observed in transport through molecules bonded to dangling-bond sites [1]

In this contribution, we investigate formation of molecular junction consisting of a single acetophenone molecule deposited on Si (100) surface in upright position by means of simultaneous AFM/STM measurements and DFT calculations. We used a modified UHV VT STM/AFM Omicron machine allowing simultaneous acquisition of the current and forces with atomic resolution using a tuning fork sensor [2]. The simultaneous acquisition of the tunneling current and force during tip approach allows precise control of contact formation and its consequence on the charge transport through molecular junction [3]. On other hand, DFT simulations provide more insight into interaction mechanism between probe and molecule. It also helps to understand induced structural and electronic relaxations during tip approach.

[1] T. Rakshit et al. Nanoletters 4, 1803−1807 (2004).
[2] Z. Majzik et al, Beilstein J. Of Nanotech. 3, 249 (2012).
[3] N. Fournier et al Phys. Rev. B 84, 035435 (2011).

P2.143 A combined STM and SXRD investigation into the ZnO(0001) polar surface

L Deacon[1], R Bennett[1], S Cavill[2] and C Nicklin[2]

[1]University of Reading, UK, [2]Diamond Light Source Ltd., UK

Zinc Oxide, a wide band-gap semiconductor (~3.2eV) with many industrial applications, has great potential in next generation opto-electronic and spintronic devices. The {0001} surfaces are polar and are unstable due to diverging dipole moment running perpendicular to these surfaces, which necessitates a mechanism to correct this[1,2].The polar Zn-terminated (0001) surface has therefore been investigated in UHV using a combination of surface science techniques, including scanning tunneling microscopy (STM) to study surface morphology, low energy electron diffraction (LEED) and surface x-ray diffraction (SXRD) to determine the crystal structure. We find that the Zn-terminated surface reconstructs to form many triangular pits and islands of various sizes, in agreement with the work of others[3–5]. Further to this, SXRD measurements were taken to determine the structure near to and at the surface.Our results give further scientific insight into how the Zn-terminated surface reconstructs and stabilizes, demonstrating that the stabilization occurs via a geometric change, and is neither electronic nor adsorbate induced.

[1] P W Tasker, Journal of Physics C: Solid State Physics 12, 4977–4984 (1979)
[2] Claudine Noguera, Journal of Physics: Condensed Matter 12, R367–R410 (2000)
[3] Georg Kresse, Olga Dulub, and Ulrike Diebold, Phys. Rev. B 68, 245409 (2003)
[4] Frank Ostendorf, Stefan Torbrügge, and Michael Reichling, Phys. Rev. B 77, (2008)

[5] H. Meskine and P. A. Mulheran, Phys. Rev. B 84, 165430 (2011)

P2.144 Ultrasoud influence on the Si-SiO$_2$ interface properties

D Kropman[1], T Laas[2] and E Dauksta[3]

[1]Tallinn University of Technology, Estonia, [2]Tallinn University, Estonia, [3]Riga Technical University, Latvia

The effect of ultrasonic treatment (UST) on the defect structure of the Si–SiO$_2$ system by means of electron spin resonance (ESR), metallography, MOS capacitance technique and secondary ions mass-spectroscopy (SIMS) is presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and structure and may be caused by vibrational energy dissipation which are a function of defect centers type. The influence of the UST on the Si–SiO$_2$ interface properties depends on the oxide thickness and crystallographic orientation.The density of point defects and absorbed impurities at the Si–SiO$_2$ interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation conditions.

Surface dynamics: space/time/energy-resolved

P2.145 Adsorption of cyclooctyne on clean and hydrogen precovered Si(001) surfaces

G Mette, M Dürr, R Bartholomäus, U Koert and U Höfer

Philipps-Universität Marburg, Germany

The adsorption of organic molecules on semiconductor surfaces is of special interest with respect to surface functionalisation and its use in molecular electronics. Whereas several alkenes and alkynes form well-ordered monolayers on Si(001), second- and multilayer attachment is still a central challenge towards successful functionalisation [1].

In this context, the adsorption of cyclooctyne on clean and hydrogen precovered Si(001) surfaces was studied by means of scanning tunneling microscopy. Cyclooctyne's high ringstrain due to its stiff triple bond should make it a good candidate for chemoselective cycloadditions in more complex multifunctional compounds.

In our real-space studies, we observe one predominant adsorption geometry at low coverage and very similar adsorption behavior at surface temperatures of 50 K and 300 K. The latter observation indicates a direct adsorption channel of cyclooctyne on Si(001) in contrast to systems like C_2H_4/Si which adsorb via a mobile precursor state.

This conclusion is backed by experiments on hydrogen precovered surfaces for which no change in the adsorption behavior was found at distorted dangling-bond configurations. At high surface coverage, cyclooctyne forms a well-ordered first layer on Si(001). This observation of highly ordered surface structures in combination with a direct adsorption channel is of interest for the generation of organic/semiconductor interfaces when implemented in multifunctional adsorbates.

[1] M. A. Filler and S. F. Bent, Progr. Surf. Sci. 73, 1 (2003)

P2.146 Molecular orientation in monolayer H_2 on ionic surfaces

D Jack, B Kootnekoff and C Makins

Univeristy of British Columbia, Canada

The development of intermolecular H_2-H_2 and H_2-ionic surface potentials for rotating molecules are presented. These rotationally averaged potentials are based on a previously developed quantum mechanically based potential [1] and are characterized by the distance between molecules as well as the orientation of the rotational axis of quantization. The interaction potentials were subsequently used in a Monte Carlo computer simulation of a monolayer of H_2 molecules adsorbed on the (001) face of an ionic (MgO) crystal. These results were compared with previous simulations based on classical interactions [2]. Molecules adsorbed over cation sites had an orientation where the rotational axis was on average vertical to the surface, i.e. the ortho-helicoptering (J=1, m=1) mode. Molecules not directly on the cation sites had a more complex distribution. The simulations predict that these molecules will prefer to adsorb in an ortho-cartwheeling (J=1, m=0) mode. In all cases, ortho (J=1) state molecules bind more strongly than para (J=0) molecules.

[1] P. Diep and J. K. Johnson, J. Chem. Phys. 112, 4465 (2000).
[2] J. N. Dawoud and D. B. Jack, Appl. Surf. Sci. 256, 1443 (2009).

P2.147 H_2 diffraction from a strained pseudomorphic monolayer of Cu deposited on Ru(0001)

C Díaz[1], F Madrid[1], G-J Kroes[2], M Minniti[1], D Farías[1] and R Miranda[1]

[1]Universidad Autónoma de Madrid, Spain, [3]University of Leiden, Poland

Diffraction of atoms (H, He) and light molecules (H_2, D_2) from surfaces has been proposed as a very useful tool to characterize the potential energy surface (PES) of these systems [1], because diffracted atoms and molecules are very sensitive to the PES characteristics [2]. Here, we have studied diffraction of H2 from a strained pseudomorphic monolayer of Cu deposited on Ru(0001) (H_2/Cu/Ru(0001)), both experimentally and theoretically. Our experimental measurements show a remarkable diffraction probability, both in-plane and out-of-plane. In particular, we observe for the first time third-order diffraction peaks. These striking experimental results have been analyzed by performing theoretical simulations, using both quantum and quasi-classical dynamics methods. Taking into account the relationship between diffraction (quantum phenomenon) and reflection (classical observable), we have performed a classical analysis on a meaningful set of classical trajectories. This analysis reveals that for H_2/Cu/Ru(0001), diffracted molecules practically explore the whole PES, thus favoring high order diffraction. We have also compared H_2/Cu/Ru(0001) diffraction results with those obtained for H_2/Cu(111) [3] and H_2/Ru(0001) [4]. This comparison have allowed us to investigate the possible relationship between diffraction and dissociative adsorption.

[1] D. Farías and R. Miranda, Prog. Surf. Sci. 86, 222 (2011).
[2] D. Halstead and S. Holloway, J. Chem. Phys. 88, 7197 (1988).
[3] C. Díaz et al J. Phys. Chem. C 114, 11192 (2010).
[4] P. Nieto, et al, Phys. Chem. Chem. Phys. 13, 8583 (2011).

P2.148 Incommensurate sliding of graphene flakes on graphite: effect of pressure, substrate and distortions

M van Wijk and A Fasolino

Radboud University Nijmegen, The Netherlands

The interest in the study of friction has very much increased in recent years due to the improved experimental probes and the possible applications for nanotechnology. However, the dynamics of friction and the related energy dissipation at the atomic scale are not yet well understood. Graphene flakes on graphite are a prototype model system to study friction, since graphene is both a simple material and an excellent lubricant. The friction of graphene flakes on graphite strongly depends on the orientation of the flake with respect to the substrate. Incommensurate orientations are expected to have very low friction. Graphene flakes in Friction Force Microscope experiments have shown this 'superlubric' behaviour. Rotations can however bring the flake in commensurate contact with a drastic increase of friction. In the superlubric regime, also a sudden, reversible increase of friction with load has been observed [1] that cannot be attributed to rotations. This reversible phenomenon cannot be explained by models where the flake and substrate are considered rigid. By accurate Molecular Dynamics simulations using a combination of the AIREBO and Kolmogorov-Crespi potentials we investigate the role of internal distortions of the flake and substrate on this behaviour.

[1] Dienwiebel, M. (2003). Atomic-scale friction and superlubricity studied using High-Resolution Frictional Force Microscopy. Ph.D. Thesis. Leiden University, The Netherlands.

P2.149 Beyond the oxidation of ferritic stainless steel surfaces: Initial oxidation stages of CrC and CrN enriched Fe-17Cr(100)

M Ahonen, K Lahtonen, M Hirsimäki and M Valden

Tampere University of Technology, Finland

The oxidation of ferritic stainless steel surfaces is a very interesting, and of course, an extremely important process to understand in both technological and fundamental point of view. Unfortunately, the lack of atomic level information upon the initial oxidation process may lead to non-optimized process conditions and thus major losses in controllability of oxide nanostructures may arise. [1-3]

In order to gain further insight into the origins of the initial oxidation stages of CrC and CrN enriched Fe-17Cr(100) surface we have utilized the modern methods of surface science approach. For example, Supersonic Molecular Beam Surface Scattering (SS-MBSS) experiments have been conducted on structurally modified Fe-17Cr(100) surface in order to study adsorption mechanisms of molecular oxygen (O_2) at different surface temperatures. Surface characterizations have been done by X-ray Photoelectron Spectroscopy (XPS), Scanning Tunneling Microscopy (STM), Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED).

First we show how O_2 dissociation (e.g. adsorption dynamics and kinetics) on CrC and CrN enriched Fe-17Cr(100) surface can be explained via steering mediated adsorption process if the low translational energy (E_T) adsorption channel is under consideration ($E_T < 200$ meV). By combining the results gained from the SS-MBSS and XPS studies the high translational energy regime ($200 < E_T < 600$ meV) can be interpreted by direct dissociation mechanism.

[1] M.P. Ryan, D.E. Williams, R.J. Chater, B.M. Hutton and D.S. McPhail 2002 Nature 415 770.
[2] H. Over and A.P. Seitsonen 2002 Science 297 2003.
[3] C. Uebing, V. Scheuch, M. Kiskinova and H.P. Bonzel 1994 Surface Science 321 89.

P2.150 Dynamics and condensation in alkali metal films on Ni(100)

S Paterson, A Jardine, J Ellis and W Allison

Univerisity of Cambridge, UK

At low coverages, the dynamical behaviour of alkali metal atoms is well understood[1]. Adatoms form a lattice-gas with interactions dominated by repulsive dipole forces[2]. At higher coverage, solid phases develop with corresponding changes to the bonding and electronic structure[3]. Little is known of the region of intermediate coverage where condensation begins.

We present quantitative Helium Spin-Echo (HeSE) measurements of the dynamics of alkali metals on the Ni(100) surface, identifying translational diffusion and confined motion. Our results reveal the complex nature of these seemingly simple metallic adsorbates.

HeSE spectroscopy allows measurement of adsorbate dynamics on the picosecond time scale and angstrom length scale, inaccessible by other means[4]. We focus on the Na/Ni(100) system, where a change in the rate and mechanism of motion are observed with increasing coverage. This change coincides with the onset of condensation into islands of ordered structures.

Langevin Molecular Dynamics simulations are employed to probe the Na/Ni(100) potential energy surface and nanoscale friction as well as investigating the nature of interadsorbate interactions. We compare the behaviour of sodium with that of lithium on Ni(100) and discuss these observations in the context of the more widely studied alkali metal/Cu(100) systems.

[1] G. Alexandrowicz et al, Phys. Rev. Lett., 97, 156103, (2006).
[2] J. Topping, Proceedings of the Royal Society of London: Series A, 114, 766, 67, (1927).
[3] C. Huang et al, Phys. Rev. B., 82, 8, 081413(R), (2010).
[4] A. P. Jardine et al, Prog Surf. Sci., 84, 11-12, 323, (2009).

P2.151 Two dimensional C_{60} vapour on graphite(0001)

R Houchin and M Hunt

Durham University, UK

Submonolayer films of C_{60} adsorbed on the basal plane of graphite have been studied by scanning tunnelling microscopy as a function of temperature. Features observed between close packed islands have been identified as corresponding to fullerene molecules in the vapour phase. By comparing the experimentally determined variation of vapour density as a function of substrate temperature with the results of Monte-Carlo simulation and classical thermodynamics we determine that the energy required to sublime a single C_{60} molecule from the edge of a two-dimensional island into the vapour phase is between 0.19 and 0.28 eV, close to literature values for the van der Waals binding energy between two isolated fullerene molecules [1].

[1] Girifalco, L.A., Journal of Physical Chemistry, 96 (1992) 858-861.

P2.152 A new type of detector for dynamic XPS measurements

K Winkler, P Baumann, B Krömker, G Prümper, C Williams and A Feltz

Omicron NanoTechnology GmbH, Germany

Real time observation of fast processes occurring in a time window of a few milliseconds to a few minutes have been always difficult to observe by x-ray excited photoemission (XPS) studies under laboratory conditions. However the demand to understand the chemistry of surface processes e.g. during heating processes, electro migration and diffusion is of high relevance in various research fields.

In this contribution we will report on first results of a new multi-anode detector concept with 128 individual anodes, preamplifiers and counters. It has the capability to allow of quantitative XPS studies on fast time scales with good signal to noise ratio excited with a monochromated Al Ka laboratory source. The detector can be operated in snapshot XPS mode. This mode allows recording an energy window in the spectrum versus time with high repetition-rates and good energy resolution, e.g. a 15 eV detectable energy window with an approximate energy resolution of 0.5 eV.

As an early application we report on results of removing an in-situ grown SiO_2 layer on a Si substrate. The measurement was made during a sample temperature ramp from room temperature to 900° Celsius within a time frame of one hour. The target of the experiment was to analyze the time window in which the oxide was removed.

Snapshot spectra have been recorded with an acquisition time of 0.5 seconds per spectrum to follow the evolution of the subcomponents Si4^{+} to Si^{0}during the heating process of the Silicon. The snapshot series with >5000 spectra shows the evolution of the peak versus time. The complete removal of the oxide occurred at a very small temperature window around 850°C. A closer look into the data revealed that the removal of the oxide from the silicon took place in about 2.5 minutes. Within this transition time 300 spectra have been recorded.

P2.153 Deposition of alkane fragments on aluminium studied by numerical simulations

C Turgut[1], L Mether[2], K Nordlund[2], P Philipp[1] and M Belmahi[3]

[1]CRP Gabriel Lippmann, Luxembourg, [2]University of Helsinki, Finland, [3]Université de Lorraine, France

The deposition and sticking of molecules and molecular fragments in the sub-monolayer range is of great importance in plasma surface treatments, as this monolayer defines the adhesion properties in the context of reversible adhesion between metal and polymer surfaces. In this work, molecular dynamics (MD) simulations and density functional theory (DFT) calculations are used to get insight into the molecule-surface interactions during the deposition process.

In this presentation, a simple hexane molecule as well as its fragments are chosen in order to facilitate the MD simulations. The deposition parameters (deposition energy and incidence angle) are varied systematically for whole molecules and fragments. Deposition on silicon is modelled using the bond-order potential by Beardmore and Smith[1]. Simulations on aluminium oxide have been carried out using the reactive force field developed by the group of John Kieffer at the University of Michigan[2-4]. Simulation results show no adhesion for the intact molecules on Si while sticking was frequent for the fragments. For incidence angles between 0° and 30° with respect to the surface normal, about 905 of the fragments are sticking. For angles above 70§, this value is decreasing rapidly. For deposition on aluminium with its native oxide layer, the situation is different and an increased adhesion of intact molecules is observed. Both groups of numerical results will be discussed in detail. The discussion includes the differences between the force fields and the system properties.

[1] Beardmore, K.; Smith, R. Philos. Mag. A 1996, 74, 1439-66.
[2] Huang, L. P.; Kieffer, J. J.Chem.Phys. 2003,118, 1487-98.

[3] Huang, L. P.; Kieffer, J. Phys.Rev.B 2006, 74, 224107.
[4] Zhou, J. H.; Kieffer, J. J.Phys.Chem.C 2008, 112, 3473-81.

P2.154 Sputter deposition of Polystyrene (PS) molecular fragments on silver (Ag)

C Turgut[1], L Mether[2], K Nordlund[2], P Philipp[1] and M Belmahi[3]

[1]CRP Gabriel Lippmann, Luxembourg, [2]University of Helsinki, Finland, [3]Université de Lorraine, France

Plasma surface treatments present nowadays an efficient and ecological tool for surface functionalisation. For this application, the deposition and sticking of molecules in the sub-monolayer range is of great importance, as this monolayer defines the surface properties in general, and the adhesion properties in the context of reversible adhesion between metal and polymer surfaces. In this presentation, in order to study the sticking and adhesion of molecules in the sub-monolayer range, experimental techniques (sputter deposition) and numerical methods (MD simulations, DFT calculations) are employed.

Fragments of Polystyrene (PS) molecules are sputter deposited on a silver substrate by the Storing Matter (StoMat) prototype[1-3] and the deposit are analyzed in a static time-of-flight secondary ion mass spectrometer (ToF-SIMS). ToF-SIMS mass spectra show successful adhesion of PS fragments after double fragmentation of PS. This is proven by a stage scan of the collectors with the PS deposit and a corresponding Gaussian distribution of the deposit. Sputter deposition parameters (impact energy of ions during sputter deposition, thickness of deposit) are studied in order to investigate their effect on sticking behaviour of molecular fragments. The results obtained will be discussed in detail and compared to numerical simulations.

[1] T. Wirtz and H. N. Migeon, Appl. Surf. Sci. 255, 1498 (2008).
[2] C. Mansilla and T. Wirtz, Journal of Vacuum Science & Technology B 28, C1C71-C1C76 (2010).
[3] N. Becker, T. Wirtz, and H. N. Migeon, Surf. Interface Anal. 43, 413 (2011).

P2.155 Computational simulation of time-dependent porosity in micro-porous molecular materials

M Lewis, A Trewin and J Jordanovic

University of Liverpool, UK

Materials with molecular-scale porosity are important in a wide range of applications such as gas storage, molecular separation, and heterogeneous catalysis. Discrete molecules tend to pack efficiently in the solid state resulting in minimal void volume, hence very few molecular materials exhibit permanent porosity. [1] Molecular porous materials are able to respond locally to the presence of a guest leading to the potential for diffusion of molecules that would not be expected by analysis of the static crystalline structure alone.

For example, although experimentally porous to N_2, molecular crystal Cage 3 [1,2] displays disconnected voids in the calculated solvent accessible surface area of the structure obtained from single crystal data suggesting a formally non-porous system. It is only when the time averaged calculated surface area for a molecular dynamic simulation is considered that the structure appears to exhibit connected porosity. Understanding the time dependence of pore connectivity can give essential information about the structural properties of a material and its gas uptake mechanisms.

We have developed a novel methodology for investigating the time-dependent relationship between structure and pore connectivity, and hence we are able to investigate co-operative diffusion mechanisms. By considering Dianin's molecule as a test case we investigate the fluctuations of solvent accessible surface area through an entire molecular dynamics run.The technique yields maximum and minimum surfaces, surface change over time, and, the potential to identify periods in time or specific structural volumes in which dynamic porosity mechanisms are evident.

[1] J. R. Holst, A. Trewin, A. Cooper, Nature Chem., 2010, 2, 915-920.
[2] T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner & A. I. Cooper, Nature Materials, 2009, 8, 973 – 978.

P2.156 Organic nanofibers as waveguides and emitters of surface plasmon polaritons

T Leissner[1], S Jauernik[1], J Fiutowski[2], C Lemke[1], K Thilsing-Hansen[2], A Klick[1], J Kjelstrup-Hansen[2], M Bauer[1] and H-G Rubahn[2]

[1]Christian-Albrechts-Universität zu Kiel, Germany, [3]University of Southern Denmark, Denmark

Surface plasmon polariton (SPP) excitation and propagation at gold films as governed by the presence of organic nanofibers composed of self-assembled para-Hexaphenylene (p6P) molecules is studied using interferometric time-resolved photoemission electron microscopy (ITR-PEEM). Two different SPP modes are identified in the experiment: a) the nanofibers act as superior sources for the emission of SPPs at the gold-vacuum interface [1]; b) along the interface between nanofiber and goldfilm we observe 1-d SPP waveguiding as recently also reported by Radko et al. [2]. A quantitative analysis of the data enables us to determine critical SPP propagation parameters such as damping length and group velocity. The results are compared with model simulations based on Hugyens principle and the effective index method [3].

[1] T. Leißner et al., Plasmonics, accepted.
[2] Radko et al., Opt. Ex. 19, 16 (2011).
[3] Holmgaard and Bozhevolnyi, Phys. Rev. B 75, 245405 (2007).

P2.157 Diffusion of Hydrogen on the Ni(111) surface Studied with Helium Spin Echo

J Zhu, P Kole, E McIntosh, A Jardine, W Allison and J Ellis

University of Cambridge, UK

First principle calculations of potential energy landscapes for hydrogen adsorbed on surfaces can readily be calculated using density functional theory, yet commonly only the crudest of approximations are used in calculating the rate of diffusion from these landscapes: typically an energy barrier is calculated and the classical expression for the pre-exponential factor (kT/h) used. We show how a much more accurate prediction of the pre-exponential factor can be produced by calculating the bandstructure of the actual hydrogen states in the 3D hydrogen-surface potential. Helium Spin Echo (HeSE) measures surface diffusion on atomic length (Angstrom) and time (ps-ns) scales - and as such can be used to determine the pre-expontential factor with great accuracy [1]. We present HeSE data on the diffusion of hydrogen and deuterium on Ni(111) and demonstrate the greater accuracy in prediction of the pre-exponential factor achieved using the bandstructure method.

[1] A.P. Jardine, H. Hedgeland, G. Alexandrowicz, W. Allison and J. Ellis, Progress in Surface Science 84, 323 (2009).

P2.158 Monte Carlo study of quasi-orthorhombic acetylene thin films on KCl (001)

A Sallabi and H Aldrwish

Misurata University, Libya

Monolayer and multilayers of C_2H_2 molecules adsorbed on the (001) surface of KCl are examined using Monte Carlo simulations based on a semi-empirical potential. It is found that the monolayer forms an ordered $(\sqrt{2}\times\sqrt{2})R45°$ (T-shaped) geometry containing two molecules per unit cell; bilayers adopt the same geometry of the monolayer with lateral orientation of the molecules in subsequent layers is not characteristic for the orthorhombic phase. These simulations confirm the predicts in a previous study [Jochen Vogt, Phys. Rev. B 73, 085418 (2006)], the adsorbed films containing misoriented acetylene layers are stable and energetically more favorable.

P2.159 Electron stimulated processes of astrophysically relevant molecules at solid surfaces

D Marchione, M Collings, M R S McCoustra and A Abdulgalil

Heriot-Watt University, UK

In the Interstellar Medium (ISM), icy mantles accreted on dust grains are a reservoir of simple chemical species (e.g. H_2O, CO, CO_2, etc). These ices are processed by photons and cosmic rays (radiolysis), leading to the formation of the complex molecules that are ultimately observed in the gas phase. Reflection-absorption infrared spectroscopy (RAIRS) and mass spectrometry are powerful tools for studying dynamic processes at solid interfaces of astrophysical relevance. Both can be used to obtain information on the structure and bonding of adsorbed molecules. Both also allow us to investigate the effect of secondary electrons generated by cosmic rays on molecules adsorbed on interstellar icy mimics in the laboratory and to determine the cross section for electron-promoted processes. Applications for organic species, such as benzene and acetonitrile, are presented.

[1] J. D. Thrower, M. P. Collings, F. J. M. Rutten, M. R. S. McCoustra, Chem. Phys. Lett. 505 (2011) 106.

[2] A. G. M. Abdulgalil, D. Marchione, A. Rosu-Finsen, M. P. Collings, M. R. S. McCoustra: J. Vac. Sci. Technol. A 30 (2012) 0415051.

Surface reactions, kinetics and catalysts

P2.160 Temperature induced reaction of Maleic anhydride on Pt (111) surface

G Sinha, V Viitanen and J Lahtinen

Aalto University, Finland

Maleic anhydride (MA) is a versatile material that has potential in both fundamental and technological research. MA anchor group has been used for dye adsorption in oxide surface based solar cells and also in pharmaceutical productions. Hydrogenation of MA can produce constituents important for the production of different polymers, plastic and additives. Here we report sub-monolayer and multilayer adsorption of MA on Pt (111) single crystal surface at low temperature (170K). We have studied the behavior of distinct carbon and oxygen species of MA (i.e., carbonyl and olefin carbon species and carbonyl and anhydride oxygen species) with temperature using XPS. We also verified desorption pattern of MA with Temperature programmed desorption (TPD), which indicates three desorption sites. At 250K, we observed molecular desorption of nearly 70% of the total MA molecules on the surface. However, small fraction of molecules undergoes decomposition and desorbs C_2H_2, CO and CO_2 at higher temperature (550K).

P2.161 Design and commisioning of a new, highly integrated UHV surface science system

E Galloway

AWE Plc, UK

Presented in this poster is the design and preliminary experimental studies of a new multi-million pound surface science instrument developed by VG Scienta and AWE that is intended to study the corrosion and aging of inorganic materials that are used in the UK's nuclear industries.

The instrument is of modular design comprising of loading, beam-forming, scattering and analysis chambers. The loading chamber is equipped with techniques to allow for inert sample transfer from a glovebox (with cut & micron finish polishing capability) or *in-situ* synthesis using Ar-sputtering, electron beam evapouration, gas atomising and moisture dosing.

The scattering chamber houses a LEED assembly and an angular resolved mass spectrometer for analysis of modulated molecular beam experiments, with the supersonic molecular beam incident from the beam forming chamber.

The analysis chamber houses a number of analytical instruments for sample characterisation, namely: XPS, UPS, Auger electron spectroscopy, EDX, SEM and SIMS.

Due to the complexity of the instrument, semi-automated control for user safety, equipment protection, and ease of operation of the equipment is satisfied by a Profibus and PID control interface.

P2.162 Hydrogenation of unsaturated hydrocarbons over Fe_3O_4 supported Pd nanoparticles: activation and reactivity of the pro-chiral molecule isophorone

C O'Brien, K-H Dostert, S Schauermann and H-J Freund

Fritz-Haber-Institut, Germany

Recent progress in understanding the micro-kinetics and the reaction mechanism of the hydrogenation of simple unsaturated compounds on oxide-supported Pd nanoparticles opened up opportunities to investigate more complex systems. The aim of the long term project is to study the mechanism and the kinetics of heterogeneous enantioselective hydrogenation over Palladium on a prototypical compound.

Currently we focus on the selective hydrogenation of the pro-chiral molecule Isophorone, which contains conjugated C=O and C=C bonds. In the first step we studied the adsorption properties of Isophorone on Pd(111), Fe_3O_4, and Fe_3O_4-supported Pd nanoparticles by different techniques: IRAS measurement and Temperature Programmed Desorption (TPD) in a UHV molecular beam setup was combined with Synchrotron NEXAFS experiments. The experimental results reveal a partially dehydrogenation of Isophorone on Pd at low temperature and a mostly flat adsorption geometry. These results get strongly supported by theoretical calculations.

Additionally, we present first results on the selective hydrogenation of Isophorone over Pd(111). We show that predominant hydrogenation of the C=C entity occurs and nearly no hydrogenation of the C=O functional group is detected.

P2.163 Catalyzed oxidation of aniline to form nitrobenzene, obtained from a graphene oxide layer

H Lee

Sookmyung Women's University, South Korea

The new insight of catalyzed oxidation reaction from aniline to nitrobenzene using a graphene oxide (GO) was investigated using core-level photoemission spectroscopy (CLPES), Atomic force microscope (AFM), and RAMAN. Oxygen carriers present on the graphene oxide layer were found to act as a heterogeneous catalyst, which facilitated the oxidation reaction. Increasing the annealing temperature up to 550 K accelerated the oxidation process, and the amount of nitrobenzene produced varied according to the annealing conditions, as monitored by the binding energies of the N 1s and O 1s core level spectra. The work function is dramatically changed indicating that the exposed aniline on the graphene oxide layers conveyed n-type doping characteristics. The annealing conditions could be used to adjust the p-type doping character via the quantity of nitrobenzene formed on the graphene oxide surface. We also confirmed the morphological change of graphene oxide surface during oxidative reaction of aniline as we monitored it using AFM.

P2.164 Adsorption and polymerization of TCPQ molecules on Cu(100) surfaces

Y Wang[1], M Alcamí[1], F Madrtín[1], C Urban[2], J R Fernández[1], R García[2], M. Á Herranz[2], N Martín[2], J M Gallego[3], R Otero[1] and R Miranda[3]

[1]Universidad Autonoma de Madrid, Spain, [2]Universidad Complutense de Madrid, Spain, [3]Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nano), Spain

This presentation reports first-principles studies on the adsorption and (oligo) polymerization of 15,15,16,16-tetracyano-6,13-pentacene-p-quinodimethane (TCPQ) on Cu(100) surfaces discovered by recent scanning tunneling microscope (STM) and X-ray photoelectron spectroscopy (XPS) experiments [1]. As a derivative of the well-known tetracyano-p-quinodimethane (TCNQ) [2], TCPQ molecules are deposited on Cu(100) surfaces characterized by two bright lobes for each molecule in the STM images. After annealing to 190 °C, the molecules are grouped to one another forming chains of up to twenty molecules long. In order to elucidate these intriguing findings, density functional theory computations are performed. Contrary to the conformation in gas phase, the geometry optimizations show a significantly distorted structure of the isolated molecule on surface. The polycyclic backbone is almost planar, with two cyano-groups bonded to the surface and the other two cyano-groups pointing upwards into the vacuum. This conformation modified by the surface excellently dictates the STM patterns in experiments and gives charge transfers consistent with the XPS observations. As far as the polymerization of TCPQ on surface is concerned, several possible products and the corresponding intermediates have been proposed and then simulated. By comparing with XPS measurements and STM images, the most plausible mechanism of the polymerization is determined. The first step of the reaction is the formation of TCPQ radicals after losing the “upper” cyano-groups by heating, which is facilitated by efficient charge transfer from surface to molecule. Then the molecular chains are formed and grown when these radicals meeting one another over the surface. These surface-induced reactions clearly exemplify an unprecedented way in the role that metal surfaces may play on organic and/or polymer reactions.

[1] C. Urban, Y. Wang, J. R. Fernández, R.García, M. A. Herranz, M. Alcamí, N. Martín, F. Martín, J. M. Gallego, R. Oter, R. Miranda, submitted.

[2] T. C. Tseng, C. Urban, Y. Wang, R. Otero, S. L. Tait, M. Alcamí, D. Ecija, M. Trelka, J. M. Gallego, N. Lin, M. Konuma, U. Starke, A. Nefedov, A. Langner, C. Woll, M. A. Herranz, F. Martín, N. Martín, K. Kern, R. Miranda, Nature Chemistry, (2010), 2, 374.

P2.165 Diffusion of particles over heterogeneous surface: A case of patchwise bivariate lattice.

A Tarasenko[1] and L Jastrabik[2]

[1]Institute of Physics of the Academy of Science, Czech Republic, [2]Palacky University, Czech Republic

The diffusion of particles adsorbed on a patchwise surface with two nonequivalent sites is investigated in the framework of the lattice-gas model. The coverage dependencies of the tracer, center-of-mass and Fickian diffusion coefficients are calculated for some representative values of the lateral interactions. Using simple ideas about particle diffusion we propose analytical expressions for the diffusion coefficients.

The theoretical dependencies we compare with the numerical data obtained by the kinetic Monte Carlo simulations. The good coincidence of the data obtained by two quite different methods strongly supports the approach used to describe the particle migration on such complex, heterogeneous lattices.

P2.166 XPS and HRTEM study of nanosized CuO oxides active in CO oxidation at low temperatures

D Svintsitskiy[1], A Chupakhin[1], E Slavinskaya[2], O Stonkus[2], A Stadnichenko[1] and A Boronin[1]

[1]Novosibirsk State University, Russia, [2]Boreskov Insitute of Catalysis, Russia

The study of surface processes using model catalytic systems is very important and powerful tool for investigations of real catalysts. In the present work different model nanosized CuO catalysts (nanopowders, nanostructured film, isolated nanoparticles) were studied in CO oxidation at low temperatures. The nanostructured film (particle size 20-40 nm) was prepared during copper foil oxidation by activated in RF-discharge oxygen. Two oxygen species were observed by XPS. The initial high reaction probability at 80 °C ($\sim 5\cdot 10^{-5}$) was attributed to additional oxygen form (BE=530.9 eV). Isolated copper clusters (2-5 nm) were characterized by absence of additional oxygen and the reaction probability of CuO lattice oxygen (BE=529.4 eV) was very low ($\sim 5\cdot 10^{-9}$). The CuO nanopowders prepared by precipitation were active in the low-temperature CO oxidation ($T_{50}\sim 100$ °C). After removal of the adsorbed species H_2O/OH^-, CO_3^{2-}/HCO_3^- it was also observed additional oxygen state with BE=531.3 eV at the surface. Thin epitaxial Cu_2O layer was found by HRTEM at the CuO surface after exposure of reaction mixture $CO+O_2$. The CuO nanopowders surface was found to be very defective in contrast to surface of bulk CuO. Thus, the high LT activity of nanosized CuO was probably provided by the epitaxial Cu_2O/CuO surface structures, which stabilize active oxygen species.

P2.167 Thermally-assisted electron-induced atomic manipulation in the STM

S Sakulsermsuk[1], T Pan[1], L Tang[1], K Rusimova[1], P Sloan[2] and R Palmer[1]

[1]University of Birmingham, UK, [2]University of Bath, UK

Atomic manipulation in the scanning tunnelling microscopy (STM), provides at least in principle, a mean to create and control nanoscale architectures. A thorough knowledge of the manipulation in mechanism at play is essential to realizing the potential. Here we investigated the thermally-assisted bond-specific dissociation and (non-local) desorption of chlorobenzene molecules on the Si(111)-7x7 surface [1-5] at different temperatures.

In the case of the C-Cl dissociation, we found that besides the previously proposed two-electron induced process [1], a thermally-activated one-electron process can also be observed [2]. By plotting the dissociation rate at different temperatures in an Arrhenius plot, an activation energy of around 0.8 eV is obtained. This energy is far smaller than the C-Cl wag mode (60 meV), but is the same as the energy barrier between the chemisorption state and the physisorption state of chlorobenzene / Si(111)-7x7. Thus the molecule is first excited from the chemisorbed to the physisorbed state thermally and then undergoes a one-electron dissociation process, similar to that in the gas phase.

In the case of non-local chlorobenzene desorption, previously identified as a one-electron process [3], we found that, as the temperature decreased, the range of the non-local effect was reduced from several hundred ångströms down to several tens of ångströms, while the integrated desorption yield also decreased significantly. The difference in yield, at between 323 K and 77 K can be as much as one order of magnitude. In this case the Arrhenius plot gives an activation energy of only around 25 meV. Thus the one-electron desorption process is also thermally-assisted, most likely due to the excitation of a low energy molecule-substrate vibrational mode or even a pure surface phonon. Theoretical treatment of the new process would be very welcome!

[1] P. A. Sloan, R. E. Palmer, Nature 434, 367 (2005).
[2] S. Sakulsermsuk et al., ACS Nano 4, 7344 (2010).
[3] P. A. Sloan et al. Nano Lett. 5, 835 (2005).
[4] P. A. Sloan et al., Phys. Rev. Lett. 105, 048301(2010).
[5] S. Sakulsermsuk et al., J. Phys.: Condens. Matter 22, 084002 (2010).

P2.168 XPS study of strongly oxidized palladium nanoparticles

L Kibis[1], A Stadnichenko[2], S Koscheev[1], V Zaykovskii[1] and A Boronin[2]

[1]Boreskov Institute of Catalysis, Russia, [2]Novosibirsk State University, Russia

Palladium based catalysts show high activity in various oxidation reactions. Nevertheless in many catalytic processes the nature of active palladium sites and the mechanism of their action have not been fully established yet. For instance, there is a lively discussion concerning the palladium state with binding energy E_b(Pd3d) around 338 eV observed in Pd/CeO_2 catalytic systems. Many authors assign this species to Pd^{4+} in PdO_2 oxide. However the synthesis and the precise spectroscopic characterization of PdO_2 nanoparticles (NPs) have not been performed. In this work we managed to prepare PdO_x ($x \sim 1.3$) NPs directly in the chambers of the photoelectron spectrometer and investigate their electronic properties, thermal stability and reaction probability in CO oxidation reaction.

Oxidized palladium NPs were deposited on a tantalum foil by the RF-sputtering of the Pd electrode under an oxygen atmosphere followed by XPS and TEM investigation. The RF-sputtering leads to the formation of the NPs with average size 3 nm. The Pd3d spectra are characterized by two well-resolved peaks with E_b typical for Pd^{2+} (336.5 eV) and Pd^{4+} (338.6 eV) species. It can be proposed that Pd^{4+} state is stabilized in anhydrous form by the PdO oxide. The Pd^{4+} species show rather high thermal stability ~425-450K and extremely high reaction probability in CO oxidation reaction. The reaction probability of the Pd^{2+} state (PdO) turned out to be ten times less than one for strongly oxidized palladium species (PdO_2).

P2.169 TPD and STM investigations on novel p(3×1)Sn_xPt (110) and p(6×1)Sn_xPt (110) surface alloys

J Zheng, S Agnoli, F Sedona, L Artiglia, M Di Marino, M Sambi and G Granozzi

Padova University, Italy

In this contribution, two novel Pt based surface alloys are reported. i.e. p(3×1)-Sn_xPt(110) and p(6×1)-Sn_xPt(110). The two surface alloys can be prepared by evaporating the same amount of tin (about 3ML), while the post-annealing temperature for the p(6×1) is higher than for the p(3×1). STM results show that the two surfaces have different topography. Modeling of the two structures has been carried out following the guidelines reported in [1]. The chemical properties have been tested by TPD experiments similar to literature ones [2, 3]. CO TPD reveals that two distinct desorption peaks are present for the p(3×1) surface, while three peaks are observed for the p(6×1) surface. All the desorption peak temperatures are lower than from clean Pt(110). Rather interestingly, it is also well evident that evolution of CO_2 takes placefrom both surfaces, implying that they can break C-O bonds. Methanol TPD results indicate that both surfaces catalyze the decomposition of methanol into CO, H_2, formaldehyde and some other minority species, but the catalytic activity is rather weak. Different possible mechanisms for methanol oxidation on the two different surfaces have been hypothesized. As a general outcome, the two surface alloys can represent as possible candidates for high CO poison resistant catalysts for PEMFC.

[1] Agnoli S, Barcaro G, Barolo A, Fortunelli A, Sambi M, Sedona F, Di Marino M, Skala T and Granozzi G 2011 Interplay between Layer-Resolved Chemical Composition and Electronic Structure in a Sn/Pt(110) Surface AlloyJ Phys Chem C115 14264-9.

[2] von Schenck H, Janin E, Tjernberg O, Svensson M and Gothelid M 2003 CO bonding on tin modified Pt(110)-(1 x 2)Surf Sci526 184-92.

[3] Wang J and Masel R I 1990 Methanol Adsorption and Decomposition on (1 X 1)Pt(110) and (2 X1)Pt(110) - Identification of the Active-Site for Carbon-Oxygen Bond Scission during Alcohol Decomposition on PlatinumJ Catal126 519-31.

P2.170 XPS and HRTEM study of self-sustained oscillations in the reaction of CO oxidation using Pd/Al_2O_3 catalysts

A I Boronin [1], E M Slavinskaya, O A Stonkus[1], R V Gulyaev[1], A S Ivanova[1] and V I Zaikovskii[1,2]

[1]Boreskov Institute of Catalysis, Russia, [2]Novosibirsk State University, Russia

Pd/Al_2O_3 catalysts were studied in the reaction of CO oxidation by both catalytic and physicochemical methods, including HRTEM and XPS. We observed self-sustained oscillations phenomena in the reaction of CO oxidation when the catalysts were cooled in the $CO+O_2$ medium. It was established that the effect of the $CO+O_2$ mixture in the oscillatory regime of the CO oxidation provides significant changes in the structure and chemical state of the supported palladium. For catalyst Pd/Al_2O_3 calcined at 1000°C, after prolonged self-sustained oscillations at the isothermal regime the surface of large PdO particles exhibited the formation of small metallic palladium clusters. The effect of the reaction mixture during the prolonged self-sustained oscillations at varied CO concentrations resulted in the formation of core-shell structures, where the core was a PdO particle and the shell was formed by small Pd^0 clusters. In this case, small Pd^0 clusters were ordered along one direction due the Pd^0-PdO epitaxy. For catalyst Pd/Al_2O_3 calcined at 1200°C, in the oscillatory regime under isothermal conditions the surface of the metal palladium particles underwent destruction and formation of core-shell structures in which the core consisted of Pd^0 and the shell consisted of PdO.

Thus, a well-known "redox" mechanism of self-sustained oscillations in the reaction of CO oxidation on Pd catalysts should be supplemented by the formation of core-shell structures metal/oxide.

P2.171 Thermal desorption spectroscopy of astrophysically relevant molecules on Olivine and single crystal Forsterite

T Suhasaria, N Heming, R Frigge, B Siemer and H Zacharias

University of Muenster, Germany

Over the years, it has been known that gas-grain chemistry is responsible for molecule formation in the interstellar medium [1]. These dust grains are thought to be silicates or carbonaceous materials. More than 140 different gases have been reported in the dense regions of interstellar space till date [2]. At low temperatures (~ 10 K) in the ISM the icy grain mantles undergo processing and are forming molecules due to exposure to ultraviolet, x-ray, cosmic radiation and heat. Temperature programmed desorption (TPD) is the most widely used characterization technique to investigate these primary effects and provide binding energies and reaction orders .We have performed TPD measurements on several molecules like D_2, CO, CH_4,CO_2 etc. adsorbed on single crystal forsterite (MgSiO4) and olivine ($Mg_x Fe_{1-x} SiO_4$) surfaces. These crystals are analogues to silicates found in the interstellar medium. Averaging over several measurements, it is seen that both surfaces, olivine and forsterite, show the same energy for D_2, CO, CH_4,CO_2 molecules in the range between 2 kJ/mol (D_2) and 26 kJ/mol (CO_2).

[1] D. A. Williams, E. Herbst, Surf. Sci. 500, 823, (2002).
[2] D. J. Burkew, W. A. Brown, Phys. Chem. Chem. Phys. 12, 5947-5969, (2010).

P2.172 Surface-bulk phase transitions as a driving force of the active sites formation in Pd/CeO_2 catalysts of low-temperature CO oxidation

R Gulyaev, O Stonkus, E Slavinskaya, A Ivanova and A Boronin

Boreskov Institute of Catalysis, Russia

Investigation of catalytic phases, localized on the surface or in bulk/subsurface layers of the catalysts, is essential for understanding of heterogeneous catalytic reactions. In this work the formation of the surface and bulk palladium/ceria phases was established. It was shown that phase transition between these phases occurred in the case of Pd/CeO_2 catalysts of low temperature CO oxidation (LTO CO). The investigation of Pd/CeO_2 catalysts by XPS showed that palladium exists in two states which are characterized by Pd3d doublets with $E_b(Pd3d_{5/2})$ = 336.0 and 338.0 eV. Comparison with HRTEM and XRD data showed that first state can be attributed to the oxidized clusters PdO_x on the surface, while the second Pd state is the solid solution $Pd_xCe_{1-x}O_2$ located in bulk (and on the surface) of CeO_2. High activity in LTO CO reaction could be achieved only when the both palladium states are presented in the catalyst. Variety of the solid solutions $Pd_xCe_{1-x}O_2$ with different palladium content was synthesized in this work. XPS data showed that phase equilibrium PdO_x(s)<->$Pd_xCe_{1-x}O_2$(b) was realized in the catalyst structure. Formation of both PdO_x(s) clusters and $Pd_xCe_{1-x}O_2$(b) strongly depends on the calcination temperature. Detailed analysis of XPS data allowed to estimate the palladium distribution in ceria surface/subsurface layers.

P2.173 Methanol decomposition on Pt nanoclusters on a thin film of Al_2O_3/NiAl(100)

M-F Luo and C Chao

National Central University, Taiwan

Methanol decomposition on Pt nanoclusters supported on an ordered Al_2O_3/NiAl(100) thin film was studied with a variety of surface probe techniques. The Pt clusters, grown from vapor deposition, had a mean diameter near 2.2 nm and height near 0.4 nm before cluster coalescence, and were structural ordered – they had a fcc phase and grew with their facets either (111) or (001) parallel to the θ-Al_2O_3(100) surface, depending on the growth temperature. More than 50 % of adsorbed methanol on the Pt clusters decomposed and two channels were revealed: dehydrogenation to CO is dominant and C-O bond scission proceeds at higher temperatures. In the channel of dehydrogenation, adsorbed methanol were dehydrogenated to CO first at low-coordinated Pt sites, at 150 K on Pt(001) clusters and 200 K on Pt(111) clusters, whereas both terrace and low-coordinated Pt sites were reactive toward the dehydrogenation, despite of the cluster size. The produced CO, reflecting the dehydrogenated methanol, per surface Pt on the clusters are 2 – 6 times more than those on the single crystal counterparts. In addition, the co-adsorbed atomic hydrogen from dehydrogenated methanol can prevent CO from dissociating further to elemental carbon. In the alternative reaction path, the C-O bond scission began about 250 K; the intermediate methyl form methane by combining the atomic hydrogen above 250 K, rather than dehydrogenating to other hydrocarbons. The C-O bond scission exhibited an evident cluster size effect – the probability of C-O bond breaking declined when the cluster size was increased by coalescence. The CO pre-adsorbed on atop Pt sites failed to inhibit this reaction channel; the C-O bond scission still occurred on the unblocked sites, the bridge or hollow sites, but gave methane desorption at higher temperatures, 400 ~ 600 K.

P2.174 Density Functional Theory-based Analysis on O_2 Molecular Interaction with the Doped and Un-doped Tri-s-triazine-based graphitic Carbon Nitride

S Aspera and H Kasai

Osaka University, Japan

Interest in carbon and carbon-based materials as a promising candidate catalyst for many surface science applications has been gaining importance in the field of alternative energy development. O_2 molecule interaction with surfaces can be an intermediate step in different catalytic processes such as H_2O splitting for the production of H_2 and O_2, and oxygen reduction reaction (ORR) process as occurring in the cathode side of the fuel cell. Analysis of the interaction of O_2 molecule with these materials for varied surface reactions is an important step to evaluate the plausibility of using these materials for specific reactions and exploit materials design to functionalize these materials towards a specific usage. With this, we used first principles calculation through density functional theory (DFT) to determine the structural and electronic properties of O_2 molecular adsorption on the Tri-s-triazine-based graphitic carbon nitride (g-C_3N_4) surface [1]. We found that the O_2 molecule is merely physisorbed on the surface of g-C_3N_4 through the interaction of its lowest unoccupied molecular orbital (LUMO) with the orbitals of the 2-coordinated nitrogen atoms of the surface and that the O_2 molecule gains very small amount of electron charges from the surface. As compared with O_2 interaction on pure graphene, these may attribute to a more effective oxygen reduction reaction (ORR) catalyst at the cathode electrode of proton exchange membrane fuel cell (PEMFC). Materials design through doping (e.g. boron atoms) provides a way to functionalize this material through altering surface electronic properties and consequently, how O_2 molecule interacts with the surface.

[1] S. M. Aspera, H. Kasai, H. Kawai, Surf. Sci. 606 (2012) 892-901.

P2.175 $Mo(CO)_6$ monolayer growth and decomposition on copper (111) and (100) surfaces

M Petukhov, X Wan, P Krüger, B Domenichini and S Bourgeois

Université de Bourgogne, France

Molybdenum hexacarbonyl has been deposited on copper substrates at low temperature (160K) and studied by scanning tunneling microscopy (STM), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy and extensive density functional theory (DFT) calculations. The physisorbed molecules form a dense hexagonal monolayer with lattice constant 6.7 Å on both Cu(111) and Cu(100) surfaces. The molecules arrangment and orientation on the surface is confirmed by DFT calculations including Van-der-Waals interaction.

The adsorbed molecules can be easily decomposed, either thermally at slightly elevated temperatures or as an effect of the electron beam irradiation or STM tip scanning. The decomposition products chimisorb on the substrate surface and generate well-defined monolayers. A dense 1x2 superstructure with particular domain orientation is observed on both Cu(111) and Cu(100) and is analyzed on the basis of the experimental and theretical results, indicating that the monolayers are formed by Mo(CO)x (x=2;3;4) fragments, where the number of CO groups depends on the substrate temperature.

P2.176 Ultrathin phases of ceria on Cu(111)

V Stetsovych[1], O Stetsovych[1], F Pagliuca[2], F Dvořák[1], J Beran[1], K Mašek[1], J Mysliveček[1] and V Matolín[1]

[1]Charles University, Czech Republic, [2]Università di Modena e Reggio Emilia, Italy

Oriented ceria thin films on copper are important model systems in the research of catalysis over ceria [1,2]. Decreasing the thickness of ceria films below 1ML results in the so called ceria-based inverse model catalyst with exceptional activity in technologically relevant reactions such as water–gas shift (WGS) [3, 4] and CO oxidation [5,6].

Traditionally, thin films with bulk like CeO2(111) termination are prepared by reactive Ce deposition in oxygen background. Locally, this preparation results in growth of different ultrathin surface phases of ceria: 1 ML CeO_2(111) [7], "precursor" to 1 ML CeO_2(111) [8], and 1 ML CeO_2(100) [9].

In this study we discuss alternative ways to prepare above-mentioned ultrathin phases of ceria. In contrast to traditional method of preparation single-phase samples are formed. This allows us to discuss the structure and electronic properties of different ultrathin phases of ceria and obtain well defined inverse model catalyst for further catalytic studies.

[1] Trovarelli, A. Catalysis by Ceria and Related Materials; Imperial College Press: London, 2002.
[2] Mullins, D. R.; Radulovic, P. V.; Overbury, S. H. Surf. Sci. 1999, 429, 186.
[3] Rodriguez, J. A.; Ma, S.; Liu, P.; Hrbek, J.; Evans, J.; Perez, M. Science 2007, 318, 1757.
[4] Rodriguez, J. A.; Graciani, J.; Evans, J.; Park, J. B.; Yang, F.; Stacchiola, D.; Senanayake, S. D.; Ma,S.; Perez, M.; Liu, P.; Sanz, J. F.; Hrbek, J. Angew. Chem., Int. Ed. 2009, 48, 8047.
[5] Eck, S.; Castellarin-Cudia, C.; Surnev, S.; Prince, K. C.; Ramsey, M. G.; Netzer, F. P. Surf. Sci. 2003,536,166.
[6] Wrobel, R.; Suchorski, Y.; Becker, S.; Weiss, H. Surf. Sci. 2008,602, 436.
[7] Szabová, L; Stetsovych, O; Dvořák, F; Camellone, M. F.; Fabris, S; Mysliveček, J; Matolín, V. J. Phys. Chem C, 2012, 116 (11), pp 6677–6684.
[8] Dvořák, F.; Stetsovych, O.; Steger, M.; Cherradi, E.; Matolínová, I.; Tsud, N.; Škoda, M.;Skála, T.; Mysliveček, J.; Matolín, V. J.Phys. Chem. C 2011, 115, 7496.
[9] Yang, F.; Choi, Y.; Agnoli, S.; Liu, P.; Stacchiola, DJ.; Hrbek, J.; Rodriguez J. A. J. Phys. Chem. C, 2011, 115 (46), pp 23062–23066.

P2.177 Adsorption and dissociation of hydrogen sulfide on metal surfaces: a first-principles calculation

D Matsunaka, J Seo and Y Shibutani

Osaka University, Japan

Sulfur contaminants such as H_2S, which is a common impurity in fossil derived fuels and chemical feedstocks, have highly poisonous effects on metal-based catalysts encountered in many chemical reactions in the petrochemical industry. The interaction of H_2S with metal surfaces is of considerable interest as a model system to understand the poisoning of metals by sulfur compounds.

In this study, we carry out first-principles calculations of adsorption and dissociation of H_2S on Pd(111), V(110) and Pd/V(110). The adsorption energies of H_2S, SH, S and H on each surface are estimated respectively. H_2S molecules are physically-adsorbed, preferably at the top sites of Pd(111) and Pd/V(110), and at the bridge site of V(110). SH prefers to be adsorbed at the bridge site of Pd(111), and the hollow sites of V(110) and Pd/V(110). S and H atoms are adsorbed at the hollow sites. On the other hand, the reaction path of the H_2S decomposition into S and H adatoms is evaluated by the NEB method. The activation energy barrier for the H_2S decomposition is higher and the reaction energy gain is lower on Pd/V(110), implying favorable resistance property for the sulfur poisoning.

P2.178 Functional groups on carbon surfaces: how do they influence the deposition of gold?

R Davies, P Davies and R Howarth

Cardiff University, UK

We show how functional groups influence the stability and nature of gold deposited on carbon substrates. The effectiveness of gold supported on carbon as a catalyst for the hydrochlorination of ethyne was predicted by Hutchings in 1985 on the basis of the highly positive standard electrode potential of Au(III),[1] and later proved experimentally. In contrast to the Au/oxide catalysts used in CO oxidation, gold supported on carbon (Au/C) has received little attention from the surface science community. Gold evaporated onto graphite supports has been investigated in UHV but Au/C hydrochlorination catalysts consist of a high surface area activated carbon which is usually pre-treated by acid washing. These substrates are very different to the ideal HOPG surfaces studied under UHV, possessing a variety of functional groups which may influence the deposition and stability of the deposited gold.[2] We have studied gold deposition on modified graphite surfaces under conditions that mimic catalyst impregnation methods. The resulting gold distributions have been studied with AFM, XPS and SEM and demonstrate fundamental differences between the treated and untreated surfaces.

[1] G. J. Hutchings, J. Catal., 1985, 96, 292–295.
[2] S. Kwon, R. Vidic, and E. Borguet, Carbon, 2002, 40, 2351–2358.

P2.179 Relation between structure of Pt-ceria catalyst and its tolerance for CO

V Johanek, M Vorokhta and V Matolin

Charles University, Czech Republic

The practical usability of current hydrogen- or methanol-fueled polymer fuel cells (FCs) is often limited due to deactivation of anode catalyst by CO. Catalysts based on cerium dioxide proved to be one of the most promising candidates combining high catalytic activity for hydrogen protonation or methanol decomposition, with its potentially high tolerance against CO poisoning. The unique properties of ceria are attributed to its high oxygen storage capacity. Reactivity and selectivity of a ceria catalyst can be further significantly enhanced using highly-active catalytic materials such as Pt or Rh finely dispersed within oxide layer. In this study, Pt-ceria model catalysts with various thickness, metal concentration, and oxidation state were prepared by high-frequency magnetron sputtering and primarily studied by Reflection Absorption Infra-red Spectroscopy (RAIRS), complemented by electronic and structural information obtained by XPS, SEM, AFM and STM. Pt-ceria thin films were exposed to various concentrations of CO diluted in hydrogen within 300-520 K temperature range, covering typical operating conditions of FCs. It is demonstrated that tolerance of the Pt-ceria catalyst for CO is related to the iconicity of the metal component which is, in turn, influenced by the physical structure of the metal-oxide complex.

P2.180 Theoretical and experimental study of H_2 adsorption on Pd atoms deposited on Cu(111)

M Ramos[1], M Minniti[2], D Farias[2], C Diaz[2], A E Martinez[1], H F Busnengo[1]

[1]Instituto de Física Rosario (CONICET-UNR), Argentina, [2]Universidad Autónoma de Madrid, España

By evaporating small amounts of Pd on Cu(111), Pd atoms act as isolated active sites and make of Pd/Cu(111), an exciting system for single molecule chemistry and for real-world catalysis. In particular, STM experiments have shown that even ~0.01ML of Pd can tremendously increase the reactive sticking probability, S_0, of H_2 on the otherwise inert Cu(111) surface.

In this work we present a theoretical and experimental study of adsorption of H_2 on Pd/Cu(111). By means of supersonic H_2 molecular beam experiments and Helium Atom Scattering techniques, we have determined S_0 as a function of the surface temperature, T_s, used during Pd evaporation and as a function of the molecular impact energy, E_i, for 0.01 ML and 0.1 ML of Pd. We also report DFT activation energy barriers for H_2 dissociation: i) on Pd ad-atoms on Cu(111) terraces, ii) on substitutional topmost layer Pd atoms, and iii) on substitutional subsurface Pd atoms corresponding to the preferred positions of Pd deposited at low, intermediate (~ 350 K) and higher T_s values respectively.

In contrast with the usual belief, DFT calculations show that on Pd ad-atoms (characterized by the lowest coordination) the activation energy barrier for H_2 dissociation is markedly larger than on substitutional topmost layer Pd atoms. This explains the intriguing non-monotonic dependence of the experimental $S_0(T_s)$ which reaches its maximum value for T_s~350K. Moreover, for the latter highest reactivity situation (i.e. for substitutional topmost layer Pd atoms) DFT-molecular dynamics results are also in good quantitative agreement with the experimental $S(E_i)$ data.

P2.181 Study of adsorption of acetophenone and some of its derivatives in aqueous solution on surface of libyan palm charcoal

A A Obeid and M S Sasi

Misurata University, Libya

In this study the adsorption of Acetophenone and some of their derivatives on the surface of palm charcoal has been investigated. UV visible spectrophotometric technique was applied to study the adsorption isotherms

The adsorption isotherms of the studied compounds are marked by similar to S2 and S3 models according to Gills classification. The adsorption on the surface of palm charcoal obey the freundlich equation. The type of adsorption is physical.

The effect of substituted groups and their position on the adsorption of acetophenone compounds also was studied.

P2.182 Reaction of ethanol on Ru(0001)

M Sturm, F Liu, C Lee and F Bijkerk

Dutch Institute for Fundemental Energy Research (DIFFER), The Netherlands

The adsorption and reactions of ethanol on Ru(0001) were studied with temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS). Ethanol was found to adsorb intact onto Ru(0001) below 100 K. Heating to 250 K resulted in formation of ethoxy groups, which undergo further decarbonylation to CO, hydrogen, and surface carbon. No evidence for the formation of significant amounts of other molecules, such as methane, aldehydes, alkanes, alkenes or higher alcohols was found. This suggests that the decarbonylation takes place via beta-hydrogen abstraction, involving an oxametallacycle intermediate, similar to the previously identified decarbonylation mechanism of ethanol on Rh(111) andCo.The deposited surface carbon acts as a poison for subsequent cycles of ethanol decarbonylation, as evidenced by a decreasing CO yield in TPD and RAIRS after an increasing number of adsorption-desorption cycles. Quantification of the TPD results suggests that the reaction of a full monolayer (ML) of adsorbed ethanol results in a CO yield of about 0.1 ML in the first reaction cycle. This limited CO yield can be attributed to desorption of molecular ethanol at temperatures below 250 K. In combination with ethanol clustering upon heating, as was previously evidenced for methanol on Ru(0001) [1], the coverage of ethoxy groups available for decarbonylation is limited to about 0.1 ML.

[1] P. Gazdzicki and P. Jakob, J. Phys. Chem. C 114, 2655-2663 (2010).

P2.183 Desorption of O_2, CO and N_2 from Astronomically Relevant Surfaces

V Frankland, J Lasne, M Collings and M McCoustra

Heriot-Watt University, UK

In the interstellar medium, a range of molecules have been observed in the gas phase or condensed on the icy surface of dust grains. Oxygen (O_2), carbon monoxide (CO) and nitrogen (N_2) are predicted to be among the most abundant small molecules in dense cores. Although the concentrations of most species, such as CO, agree well with the observed molecular abundance using gas-phase chemistry, the models are unable to explain the formation and abundance of several molecules, including O_2 and N_2. Then, the models need to include the adsorption and desorption processes of these species from the icy grains to match the observed abundances. To this aim, we performed Temperature-Programmed Desorption (TPD) experiments to study the desorption kinetics of O_2, CO and N_2 sub-monolayers and multilayers from amorphous silica. The desorption of O_2 from compact and porous amorphous solid water is also reported. Our results show that the morphology of the underlying silica surface affects the desorption kinetics of O_2, CO and N_2.

P2.184 Surface reactivity of Anatase 101 e 001 surfce: a DFT periodic study

A M Ferrari

Dipartimento Chimica Univesita' Torino, Italy

The reactivity of 001 and 101 anatase surfaces has been studied by means of periodic calculation by employing the periodic CRYSTAL09 code and within a density theory approach. Large basis set and PBE0, PBE0-D and B3LYP hybrid functionals have been selected in order to reproduce accurate energy estimates. The interaction with three kinds of molecules has been addressed:

(1) Interaction with probe molecules for acidic and basic surface sites: CO, CO_2, HCOOH, H_2O, NH_3, pyrrole.
(2) Interaction with aminoacids: the case of glycine.
(3) Interaction with dyes for solar cells: the case of a hemisquaraine dye.

The effect of the increasing coverage on the adsorption properties has also been addressed. Results have been compared with available experimental data.

P2.185 The reactivity of the ZnS(110) surface: a periodic DFT study

A M Ferrari

Dipartimento Chimica Univesita' Torino, Italy

The reactivity of ZnS (110) surface has been investigated for the first time by using the periodic ab-initio CRYSTAL code [[1]] within a DFT approach. Several probe molecules and namely water, carbon monoxide and carbon dioxide have been selected. In the case of water probing, several coverages defined by the parameter Q (number of adsorbed molecules per surface zinc site) have been investigated. At the lower coverage (Q = 0.5) only the molecular adsorption mode has been found to be stable with an adsorption energy equal to -17.8 kcal/mol whereas dissociated structures always recombine to the molecular form after geometry relaxation. In particular, two different adsorption structures have been identified that differs for the position of the water molecule with respect to the at surface but presents an almost negligible difference in the stability (about 2.5 kcal/mol). Only for Q>1 it has been possible to localize surface structures characterized by a dissociative adsorption mode although it is never preferred to the molecular one even for Q > 1. CO and CO_2 adsorption reveals a weak basicity and acidity of the surface. Computed data have compared with available data.

[1] R. Dovesi, R. Orlando, B. Civalleri, C. Roetti, V. R. Saunders, and C. M. Zicovich-Wilson. CRYSTAL09. Z. Kristallogr., 220:571, 2005.

P2.186 Spontaneous ester formation controlled by concentration at the liquid -solid interface

N T N Ha[1], T G Gopakumar[2] and M Hietschold[1]

[1]Chemnitz University of Technology, Germany, [2]Christian Albrechts Universität Kiel, Germany

Trimesic acid (TMA) in different solutions is a suitable a model system to carefully analyze the influence of solute concentration. We have used a rather simple sonication method to increase the concentration of TMA in different solvents by increasing the sonication time as a special preparation step. Recently we have shown the formation of a high-density adsorbate structure of trimesic acid (TMA) solved in phenyloctane on HOPG(0001) substrate controlled by the concentration [1] which has never been observed before. Similarly by tuning the concentration of TMA different polymorphs are deposited from solutions in alkanoic acids in a highly controlled manner. There has been found a monotonous correlation between increasing concentration and increasing packing density [2]. With the present study we have shown that the previous observations about the polymorphism of TMA structures in fatty acids are only valid at low concentrations [3]. The influence of concentration on self-assembly of TMA from alcoholic solutions shows a non-monotonous correlation between packing density and concentration of both solute TMA molecules and alcoholic solvents [4]. Here we report a surprising self-assembled 1-undecyl monoester of TMA found at the interface of long-time sonicated TMA-undecanol solutions with the HOPG substrate. This monoester is formed only at the substrate-undecanol interface due to increased concentration of TMA and without any external catalyst. The study demonstrates the role of the external control parameter concentration in self-assembly.

[1] N. T. N. Ha, et al. J.Phys.Chem.C 2010, 114, 3531-3536.
[2] N. T. N. Ha, et al. J.Phys.Chem.C 2011, 115, 21743 –21749.
[3] M. Lackinger, et al.,Langmuir 2005, 21, 4984-4988.
[4] N. T. N. Ha, et al., “Co-operative adsorption of TMA-alcohol mixture controlled by concentration”, in preparing.

P2.187 Investigating interactions between polycyclic aromatic hydrocarbons and atomic hydrogen

A Cassidy, L Nilsson, R Balog, J Thrower, J Rasmussen and L Hornekær

Aarhus Univeristy, Denmark

Polycyclic aromatic hydrocarbons (PAHs) could potentially play an important role in catalysing the formation of molecular hydrogen in the interstellar medium (ISM)[1,2]. PAHs make up 5-10 % of all carbon in the ISM[3] and the chemisorption of hydrogen on coronene to form superhydrogenated species has previously been shown to lead to H_2 formation[4]. Here, scanning tunnelling microscopy (STM) has been used to study the assembly of small PAHs (coronene and pyrene) on both Cu(100) and HOPG surfaces, before and after exposure to atomic hydrogen.

Experiments were performed under ultrahigh vacuum conditions using a liquid nitrogen cooled STM. Atomic hydrogen was produced by thermally cracking H_2 in a tungsten filament. Monolayer coverages of a PAH were obtained by annealing vapour deposited films to remove multilayers. STM images show the formation of a stable, compact monolayer of coronene on both Cu(100) and HOPG. Subsequent exposures to atomic hydrogen lead to changes in contrast on the submolecular scale. Preliminary attempts have been made at matching the observed patterns to calculated patterns in an effort to track the position of the absorbed hydrogen atoms. In this regard, monolayer coverages of pyrene and hexahydropyrene have also been studied and the differences in both packing on the surface and submolecular contrast will be discussed.

[1] W. W. Duley & D. A. Williams, MNRAS, 260, 37 (1993).
[2] E. Rauls & L. Hornekær, ApJ., 679, 531 (2008).
[3] E. Dwek *et al.*, *ApJ.*, 457, 565 (1997).
[4] J. D. Thrower et al., ApJ., 752, 3 (2012).

P2.188 CO oxidation over ultrathin ZnO films on Pt(111)

Y Martynova, S Shaikhutdinov and H-J Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Ultrathin oxide films grown on metals have recently been suggested as interesting catalytic materials showing catalytic properties different from their bulk counterparts. In this work, we studied the structure and reactivity of zinc oxide thin films grown on Pt(111) in the low temperature CO oxidation reaction at near atmospheric pressures.

The experiments were performed in a UHV chamber, equipped with LEED, AES, QMS and a high-pressure cell for reactivity measurements. The films were grown by Zn reactive deposition followed by annealing in O_2 ambient. The film thickness was varied by the deposition time and controlled by CO TPD and AES. The reaction was carried out at 450 K in a CO/O_2 mixture (1:5) in the mbar-range (He balance to 1 bar) and monitored by gas chromatography.

“As prepared” thin films displayed LEED patterns corresponding to ZnO(0001) forming coincidence superstructure on underlying Pt(111). At coverage above one monolayer, the films showed only ZnO(0001)-(1×1) patterns. The films preserved their stoichiometry (AES) and long-range ordering (LEED) after the catalytic test. The reactivity measurements showed complex behavior between CO_2 production rate and nominal film thickness. A monolayer film shows a considerably enhanced activity as compared to thicker (2-5ML) films and bare Pt(111). Submonolayer films promoted the reaction even stronger. No deactivation in time is observed on all ZnO_x films studied.

The results suggest that several reaction pathways may be involved in CO oxidation on ZnO(0001)/Pt(111) depending on the film thickness. Further structural characterization of the film surface and interface with STM are under way.

P2.189 Evaluation of paper surface chemistry during ageing by ToF-SIMS

S Bialczak, A Sundberg and S Willför

Åbo Akademi University, Finland

Paper is one of the oldest man-made products. Using wood to make paper came into practice in late XIX century and today about 90% of global paper production is based on wood. Wood is a complex heterogeneous bio-chemical mixture. The amounts of certain wood components, especially extractives and minerals, vary between wood species and changes seasonally. During the production, storage and usage paper surface undergoes chemical changes, which will affect the paper properties. The content and the composition of lipophilic extractives in the paper have effects on, e.g. strength, paper-to-paper friction, optical properties, as well as on sorption of water, solvents and printing inks. Paper made of termomechanical pulp was submitted to accelerated ageing by heat treatment according to a DIN standard for a maximum time of 7 days. In a previous study the content and composition of extractives was determined by gas chromatography after extraction with acetone:water. The surface properties were investigated by contact angle measurement. It has been shown that aged paper is more hydrophobic than reference fresh paper. The longer the paper was aged, the higher the increase. Extractives are known to naturally migrate to the surface of the paper. However, after already 2 days of ageing they cannot be removed from the paper. They also do not bind to the paper with ester bonds. In this study ToF-SIMS has been used in search of signs of chemical changes and polymerization of surface extractives that cannot be removed from paper, with standard extraction methods, after already 2 days of ageing.

P2.190 Low-pressure oxidation behavior of FeAl –alloys on 600-800°C

H Izzuddin, A Seemayer, G Ankah, J Lengsfeld, P Schneider and F U Renner

Max-Planck-Institut für Eisenforschung, Germany

The low-pressure oxidation behavior of binary FeAl alloys has been examined at different temperatures of 600-800°C. Polycrystalline and single-crystalline samples of $Fe_{90}Al_{10}$ and $Fe_{75}Al_{25}$ were oxidized for 0.5-3 h at 10^{-6} mbar of oxygen in an ultra-high-vacuum chamber (UHV). Prior oxidation, samples were prepared by sputter-annealing cycles in UHV. After oxidation the samples were analyzed by X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM), and Grazing Incidence X-ray Diffraction (GIXRD). The formed oxide layers on the surfaces consist of $FeAl_2O_4$ and Al_2O_3 showing that Al has a dominating role during the oxidation process. From XPS peaks, the composition of the Fe peaks of the oxide layer consists of Fe metal, FeAl-alloys, and FeO. Meanwhile, the composition of the Al peak is changed from Al metal, FeAl-alloys and Al_2O_3 at 600°C to Al metal, FeAl-alloys and $FeAl_2O_4$ on 700°C. From XPS sputter depth profiles, it is shown that the oxide layer was growing with increasing temperature, and the single-crystalline $Fe_{90}Al_{10}$ has a thicker formed oxide layer than poly-crystalline $Fe_{75}Al_{25}$ with same oxidation treatment.

P2.191 H-abstraction reaction from methane in straight channel of H-ZSM-5 zeolite containing O(3P) atom: A D-DFT study

A Palma[1], S Orlanidini[2], M Rutigliano[2], N Sanna[3] and M Cacciatore[2]

[1]Instituto per lo Studio dei Materiali Nanostrutturati (ISMN), Italy, [2]CNR – IMIP, Italy, [3]CASPUR – Roma, Italy

Zeolites are crystalline microporous alumino-silicates characterized by internal cavities and channels of molecular dimensions which allow the use of these materials in different catalytic or separation processes. On the other hand, O(^{3}P) species is well known for its excellent performance in oxidation processes. In this contribution, by first principle Density Functional Theory corrected by semi-empirical dispersion forces (D-DFT)[1,2] calculations, using plane waves expansions and ultrasoft pseudopotentials, we show that triplet oxygen atom, anchored by acidic site in H-ZSM-5 zeolite, plays a catalytic role in the H-abstraction reaction from CH_4 to produce $(OH)^-$ and CH_3 radical. Open shell systems were treated using unrestricted formalism and zeolite was modeled by its crystallographic structure subject to periodic boundary conditions [3]. The reaction is found to be strongly exothermic and a reaction mechanism, with a relatively small energy barrier, is proposed.

Institute of Physics
76 Portland Place, London W1B 1NT, UK
Telephone: +44 (0)20 7470 4800
Fax: +44 (0)20 7637 4266
www.iop.org/conferences

Registered Charity Number: 293851

IOP Institute of Physics

EPS