ELETTRA HIGHLIGHTS



2010-2011





ELETTRA HIGHLIGHTS 2010-2011

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Cover image: The thinnest triangles LEEM image of the faceted step morphology of submonolayer Ni on W(110) at high temperature

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he Elettra Highlights publication for 2010-2011 continues to reflect both the renewed interest of our user community in the enhanced capabilities of Elettra and the great strides recently made in the development of the new free-electron laser (FEL) source FERMI@Elettra.

The Elettra third-generation light source has become one of the few synchrotron radiation sources in the world that operate in top-up mode, and the one and only machine that was not designed for top-up, but has been successfully converted to operate in top-up mode. Elettra routinely operates in top-up mode at both 2.0 and 2.4 GeV, and the users are benefitting from the higher stability and the increased average brightness of the source. In the last year the uptime was 96-97% and the mean time between failures was 140 hours, with a record-breaking uninterrupted top-up stint for users of 195 hours. The major project of realignment of the storage ring has been completed, as has the hardware for the beam-based alignment, increasing the reliability and ease of operation of the machine.

The upgrade of the Elettra beamlines to take full advantage of the new source characteristics continues. For example, a new, redesigned undulator for the SuperESCA/ESCAmicroscopy beamlines was successfully installed, substantially increasing the high-energy beamline performance. A 2M PILATUS detector was installed at the XRD1 beamline. Operation of this detector in the shutterless mode leads to significantly improved data quality and a more than tenfold reduction in data collection time. The CCD detector is now primarily used for data collections for diffraction experiments on smaller molecules. An in-house developed, versatile sample changer holding 50 samples is now in operation, which ensures the optimal benefit from the PILATUS detector. In macromolecular crystallography it is vital that the users can get rapid access to beamtime. Following the great improvements of XRD1, a new beamtime allocation system has been put in place that will enable users to perform measurements 6 weeks after submission of a proposal.

The FERMI@Elettra project has the objective to provide ultraviolet and soft x-ray radiation of unprecedented brilliance in ultrashort and synchronizable pulses for spectroscopy, microscopy, and diffraction applications. The uniqueness of such a project when compared to other FEL projects in the United States (LCLS), Germany (FLASH and XFEL) and JAPAN (SCSS), consists in the use, since its conception, of a *seeding* scheme, that is of a laser optical signal for obtaining the initial stimulated emission from the electron bunches. This allows for a far better control on the intensity and lineshape of the output FEL pulses as compared to machines that use the alternate self-amplified spontaneous emission (SASE) method, where the random nature of the spontaneous emission process yields large variations in pulse intensity and lineshape.

FERMI@Elettra has been planned as an incremental facility, starting with a FEL-1 laser based on a first series of insertion devices of original design and construction and operating between 100 and 20 nanometers, followed by a second, FEL-2 laser. which has been designed to reach few nanometers in the fundamental emission and 1 nm (1248 eV) in the third harmonic. Civil works, carried out in 2007-2010 used low-vibration techniques in order to minimize the disturbance of the regular Elettra operation. The main construction phase, devoted to undulator and experimental halls and to the technological plants, started in 2009 and the beneficial occupancy started already in September 2010.

The FERMI normal-conducting 3 GHz Linac is equipped with 14 RF transmitters of 45 MW peak power, feeding 16 accelerating sections, the photocathode gun and three RF deflectors. The nominal energy is 1.2 GeV for FEL-1 and 1.5 GeV for FEL-2. Repetition rate is at the present 10 Hz and will be upgraded to 50 Hz in 2012. The seed laser specifications are set by the High Gain Harmonic Generation (HGHG) FEL scheme adopted; in particular the seed laser is tunable down to 200 nm, with a peak power above 100 MW over the tunability range. Synchronization in the femtosecond range between the seed laser and the electron beam, as well as along the whole facility, is provided by an all-optical timing distribution system.

The commissioning of the machine started in Summer 2009 with the operations on the first part of the machine where electrons are created and accelerated up to 100 MeV. Since then, commissioning runs have been alternating with long shutdown periods to allow machine installation progress. The FEL-1 line, consisting of a planar undulator (the modulator) and six APPLE-II undulators (the radiators) was completed in November 2010. The wavelength of the FEL radiation can be varied thanks to the variable undulator gap, down to 10 mm. Furthermore, the use of APPLE II undulators allows control of the FEL polarization that can be varied from linear to circular. Few weeks after completing the installation of FEL-1, on December 13, 2010 first evidence of coherent emission in the 60 to 20 nm range was obtained.

The benefit of using external seeding in terms of spectral bandwidth and photon energy stability was evident since the very first days of FEL operation, when spectral measurements showed that the pulse bandwidth was close to the Fourier limit. During 2011 the FEL-1 performance improved greatly. In July 2011, after increasing the bunch charge from 250 to 450 pC, with other minor changes in the accelerator and FEL optimizion on the TEM₀₀ Gaussian mode, clear evidence of FEL exponential gain was obtained. At 43 nm the measured photon flux increased from about 10⁹ photons per pulse (December 2010) to more than 10¹³ photons per pulse. Similar flux intensities have been measured at 52 nm and at 32.5 nm. At the lower wavelength limit of FEL-1, 20 nm, the photon flux achieved was larger than 10¹² photons per pulse.

Once FEL operation is optimized, its stability over a few hours is truly remarkable: the central wavelength jitter is below 10^{-4} , the spectral bandwidth stability is below the 3% level and the intensity jitter is about 10%. Comparison with the spectral intensity observed from the FLASH SASE facility in Hamburg, Germany shows that while for the seeded FERMI@Elettra FEL the emission is a single mode TM₀₀, for the SASE FEL a complex, multi-mode emission is observed. This, together with the dramatically increased stability in wavelength, spectral bandwidth and intensity, are important advantages that seeded FELs such as FERMI offer relative to SASE FELs.

The success achieved last December was instrumental in convincing the Italian government to include the ELETTRA-FERMI-EUROFEL project as one of 14 "Flagship Projects" within the Italian "Programma Nazionale della Ricerca 2011-2013" with a proposed funding of 45 MEURO over the four years. This funding will be an extremely important complement to the operation budget and a safeguard for implementing an efficient scientific program on FERMI.

While commissioning of FEL-1 continues, four beamlines are being completed - Diffraction and Projection Imaging (DIPROI), TIMEX and TIMER within the Elastic and Inelastic Scattering (EIS) program, Low Density Matter (LDM) - in the new experimental hall. A call for proposals for user beamtime will be published by the end of 2011 with beamtime assignments to external users expected to begin in the second half of 2012.

Installation of the FEL-2 undulator will start at the end of 2011. The FEL-2 line runs parallel to the FEL-1 line at a distance of 1 meter. An HGHG double cascade scheme is adopted for FEL-2, thus there is a first stage with one modulator and two radiators followed by a second stage with one modulator and six radiators. The permanent magnets periodicity of the final radiators is lower than in FEL-1, all other specifications being similar. The first harmonic wavelength for FEL-2 will range from 20 nm to 4 nm. Commissioning of FEL-2 is expected to start in the first half of 2012.

Some twenty-seven new international partner institutions are involved in the upgrade of Elettra and in the development and use of the new FERMI@Elettra source. Some of the new strategic directions opening up for us and for our partners will be addressed by the thematic workshops that will take place as part of the XIX Elettra Users' Meeting: "New Frontiers in Atomic, Molecular and Cluster Physics and Chemistry", and "Nanoenergetics: Theoretical and Experimental Approaches". Such workshops will serve the purpose of engaging a broader user community, and our partner institutions will have prominent roles in the above events.

We take this opportunity to thank our employees, our Partners and external Users for their enthusiasm and dedication over the years. We trust that with their help we will be able to meet the major challenge of fully exploiting an upgraded Elettra light source while developing the new FERMI@Elettra FEL source.

Alfonso Franciosi

Chief Executive Officer Sincrotrone Trieste S.C.p.A.

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RESEARCH HIGHLIGHTS



ATOMIC AND MOLECULAR PHYSICS

Connection between acoustic dissipation and density of states on glass-formers

B rillouin spectroscopy, at visible, ultraviolet and X-ray frequencies, combined with incoherent neutron scattering has been used to identify a strict relation between acoustic power dissipation and density of states. The connection has been verified, over an extended frequency range between 0.5 GHz and 5 THz, on a prototypic system when it passes from the liquid to the glassy phase. A simple but general formalism has been employed to interpret the experimental results, thus clarifying some key aspects of the fast dynamics in glass-formers.



Figure 1. Normalized isotropic Brillouin susceptibilities $\chi_{l,s}''(\omega)$ shown together with tagged-particle susceptibilities $\chi_{lNS}''(\omega)$, obtained from neutron scattering data, and imaginary part of longitudinal acoustic compliance data, $J''(\omega)$.

The dynamics of glass-forming systems covers a broad frequency range. When a liquid transforms into a glass, the structural relaxation, always present in liquids, slows down involving molecular rearrangements that progressively get slower under cooling (from picoseconds to hundreds of seconds). The study of this relaxation is now accredited and a number of theories have been formulated about its microscopic origin. Besides being sensitive to this relaxation, phononlike excitations are also strongly affected by a fast relaxation dynamics (GHz-THz) that emerges, in light and neutron scattering spectra, as a broad Quasielastic contribution (QES) deeply temperature dependent. Though the nature of this feature has been widely studied, a general agreement on its interpretation is still lacking. Overall, the existing literature proposes a connection between the QES intensity and the damping of the acoustic waves, suggesting that the temperature behavior of these two quantities might be the same. The main limitation, in the past, for putting this concept to the test was the lack of experimental data for the acoustic attenuation in a frequency range wide enough to be directly compared to the QES data. Only recently the development and advance of spectroscopic techniques, such as inelastic X-ray and Ultraviolet Brillouin Scattering (IXS and IUVS, respectively), have enabled overcoming the problem and measuring the acoustic attenuation in previously unexplored regions. Here, approaching the case-study glycerol, we describe how the combined use of Brillouin spectra, collected in different frequency regions, and incoherent neutron spectra represents a powerful tool for finely investigating the correspondence between acoustic dissipation and density of states of a

glass forming system. The Brillouin experiments on a sample of glycerol have been performed at the optical laboratory in Perugia (BLS), at the Inelastic Ultra-Violet beamline (Elettra) in Trieste (IUVS) and at the Inelastic x-ray scattering ID16 beamline (ESRF) in Grenoble (IXS). The incoherent neutron scattering measurements have been done at the cold neutron time-of-flight spectrometer IN5 of the Institut Laue-Langevin in Grenoble (INS). In Fig. 1 normalized isotropic Brillouin susceptibilities $\chi_{LS}''(\omega)$ are shown together with tagged-particle susceptibilities $\chi_{INS}''(\omega)$, obtained from neutron scattering data. In the same figure, acoustic compliance data $J''(\omega)$ are also reported, obtained by fitting the spectra around the Brillouin peak through a Damped Harmonic Oscillator (DHO) (squares) and by using a simultaneous fullspectrum analysis (continuous curves). A weakly temperaturedependent scaling factor allowed matching the light scattering data to the neutron scattering ones. The fine superposition between the imaginary part of longitudinal compliance and the scaled neutron susceptibility suggests the existence of a notable correspondence between these two quantities at all temperatures and in the whole explored frequency range. We investigate this connection recalling that, in mechanical

experiments, $\omega J''(\omega)$ is proportional to the energy dissipation per unit time, and, in incoherent neutron scattering experiments, $\omega \chi_{INS}''(\omega)$ is proportional to the Fourier transform of the velocity autocorrelation function $g(\omega)$, which, in the solid, exactly corresponds to the vibrational density of states. Our results thus indicate a direct link between $g(\omega)$ and the dissipation of acoustic energy, i.e. a relation between $g(\omega)$ and the damping $\Gamma(\omega)$ of acoustic phonons as estimated from the width of Brillouin peaks. Using a standard field-theory approach, we have calculated $g(\omega)$ as the superposition of longitudinal and transverse acoustic waves contributions, obtaining the observed agreement with $\Gamma(\omega)$ in conditions of low acoustic absorption and provided that a T-independent Cauchy-like proportionality holds between longitudinal and transverse acoustic modes. Our approach, independent of any theoretical consideration on the microscopic origin of the acoustic attenuation, holds in an astonishingly wide frequency range, comprising both structural and fast relaxation in a wide temperature range, from the liquid to the supercooled and the glassy regime, thus promising to provide a general link between single particle and collective properties of disordered systems. Experiments on other systems are actually in progress to test its generality.

ORIGINAL PAPER

L. Comez, G. Monaco, C. Masciovecchio, A. Paciaroni, A. Gessini, F. Scarponi, G. Ruocco, and D. Fioretto, *Phys. Rev. Lett.* **106**, 155701 (2011)

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sp hybridization in free carbon nanoparticles: presence and stability observed by NEXAFS spectroscopy

Free carbon nanoparticles are known to exist in the interstellar space but their exact physical nature is still unidentified and strongly debated. At the University of Milano a pulsed microplasma cluster source has been developed for the study of free clusters at the Gas Phase beamline. The presence and stability of *sp* hybridized atoms in free carbon nanoparticles was investigated by NEXAFS spectroscopy. The experiments show that a predominant fraction of carbon atoms is found in linear *sp*-chains and that conversion into sp^2 structures proceeds already at low temperature and in the gas phase.

The discovery and synthesis of fullerenes led to the hypothesis that they may be present in interstellar space and responsible for some of the "diffuse interstellar bands", a long standing mystery in astronomy. In the laboratory, high yield production of fullerenes from carbon plasma is obtained only when condensation occurs at T > 1000 K while at lower temperatures socalled "carbon soot", built up from ill-defined carbon nanoparticles (NPs), is favoured. Theoretical models of the fullerene formation predict the existence of intermediate highly disordered but remarkably stable pre-fullerenic NPs with not only of sp^2 and sp^3 hybridized carbons but also a significant amount of sp hybridization. Formerly sp hybridization in solid state



Figure 1. (A) Electron yield measured for free carbon NPs as a function of the delay time between the PMCS discharge and the electron detection (i.e. the NP residence time in the source). (B) NEXAFS spectra of the free NPs acquired in the 11 delay time windows shaded in panel (A), compared to the in situ NEXAFS spectrum of the NP assembled film deposited at RT (dep. 300K). The acetylene and ethylene π^* resonances are indicated as dotted lines(C) Evolution of X_{sp} with the delay time; the value of X_{sp} for the deposited film is indicated as a dashed line.

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carbon was considered very unlikely because sp carbon chains, when deposited, react exothermically to form sp^2 structures due to the dangling bonds at their extremities. Nevertheless, the feasibility of producing *sp*-rich solid carbon was demonstrated a few years ago by some of us by depositing, at room temperature and in high vacuum, pure carbon NPs produced by a Pulsed Microplasma Cluster Source (PMCS). In this source NPs are produced via aggregation of carbon atoms ablated from a graphite rod through He sputtering at a remarkably lower temperature than in standard fullerene sources. After aggregation, the mixture of NPs and He expands through a focusing nozzle into the vacuum chamber, forming a highly collimated molecular beam which could be crossed with the photon beam at Elettra. The mass distribution of these pre-fullerenic NPs ranges between 10² and 10³ atoms. While the spectroscopic study of free prefullerenic NPs is essential for a better understanding of the intermediate steps of carbon NP formation, prior to our experiments at Elettra, sp chains had been examined only in the solid state and not as free NPs prior to deposition.

Fig. 1 presents the first gas phase characterization performed by Near Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS) of the bonding structure of sp-rich prefullerenic nanoparticles produced by a PMCS. The NP size and structure evolves with residence time in the source but after exiting from the cavity, their further evolution is quenched by the collisionless and cool environment of the molecular beam. Fig. 1A shows the electron yield measured at different delay times after the electrical discharge producing carbon vaporization (shading highlights the time windows applied for time-resolved data shown in Fig. 1B and 1C). The

delay time is the residence time of the NPs in the source cavity plus a small interval (~1 ms) due to the time of flight from the source to the interaction region. Fig. 1B presents the NEXAFS spectra for each of the delay time intervals marked in Fig. 1A. A NEXAFS spectrum of a film of NPs deposited at 300 K on copper is shown for comparison. A clear evolution can be observed: the spectra of the first NPs exiting from the source are sharply peaked at ~285.7 eV, an energy consistent with the acetylene-type $\pi^*_{C=C}$ resonance at 285.9 eV (marked by a dotted line in the figure). Thus the first NPs exiting the source are characterized by a predominantly sp bond structure. To the best of our knowledge this is the first NEXAFS spectrum of a pure carbon system displaying a sharp π^* peak indicative of sp hybridization. As the delay time increases (going

As the delay time increases (going from spectrum 1 to 11 in Fig. 1B), the peak at 285.7 eV progressively decreases, though remaining the predominant feature at the π^* edge of the spectrum, while a shoulder at ~284.7 eV (*i.e.* $\pi^*_{C=C}$) grows. Finally, in the spectrum of the deposited film, the acetylene-type $\pi^*_{C=C}$ peak is not any longer the predominant feature and the $\pi^*_{C=C}$ peak shows a similar intensity.

Fig. 1C shows the evolution of the fraction of NEXAFS signal related to *sp*-bonds (X_{sp}) , calculated from

the integral intensities of the π^*_{C-C} and $\pi^*_{C=C}$ peaks the spectra in Fig. 1B (shaded in Fig. 1B), versus delay time (i.e. NP residence time inside the source). The amount of sp bonds present in the NPs decreases monotonously with delay time, remaining nevertheless much higher than in the NP-assembled film (dashed line in Fig. 1C). This indicates that during all phases of the NP formation, the aggregates are composed of a major fraction of sp carbon chains, in good agreement with theoretical predictions. The chains evolve progressively towards sp² structures during residence time in the source; nevertheless a relevant fraction is able to survive even after NP deposition at room temperature, confirming that the end-capping of the chains by bonding to sp^2 groups affords a remarkable stability to carbon atomic wire structures. In conclusion, we demonstrated the sp hybridization of free carbon NPs by NEXAFS and followed the evolution of their structure on a millisecond time scale under low temperature conditions in an inert atmosphere. Our results show that free carbon NPs can have a complex structure with varying relative amounts of sp and sp^2 bonds. This has very important consequences for a wide variety of fields where carbon NPs play a role such as astrochemistry and environmental sciences.

ORIGINAL PAPER

L. Ravagnan, T. Mazza, G. Bongiorno, M. Devetta, M. Amati, P. Milani, P. Piseri, M. Coreno, C. Lenardi, F. Evangelista, and P. Rudolf, *Chem. Comm.* **47**, 2952 (2011)

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The valence electronic structure and conformational flexibility of epichlorohydrin

The valence electronic structure of epichlorohydrin, because of its importance as a model chiral system, has been investigated by Angle-Resolved- and Threshold-Photoelectron Spectroscopies (ARPES and TPES) using circular and linear polarized light. The controversial assignments of the valence electronic structure of the molecule impede a full understanding of chiroptical properties such as the circular dichroism exhibited in the valence photoelectron angular distribution of its enantiomers. Addressing this issue by a combined experimental and theoretical investigation is here highlighted.

Epichlorohydrin

(chloromethyloxirane, C₃H₅ClO) is a very versatile chemical intermediate used in a wide variety of applications, namely in the production of epoxy glues, resins and textiles of special properties, glycerol, plastics, elastomers, biologically active pesticides, bactericides, and fungicides, and to prepare pharmaceutical agents. Its chemical structure is characterized by the highly reactive threemembered oxirane ring and the oxygen and chlorine heteroatoms. The presence of one asymmetric carbon atom and the relatively small molecular size and rigidity, makes this organic compound particularly interesting as a model optical active system to study chiroptical properties from a fundamental point of view.

This molecule is generally present in the gas phase, at room temperature, as a distribution of stable conformers associated with the internal rotation of the –CH₂Cl substituent group to the oxirane ring, namely *gauche-II*, *gauche-I*, and *cis* (see Fig. 1). The most stable and dominant structure *gauche-II* is reported as inset in Fig. 1.

Figure 1. Potential energy curve of (R)epichlorohydrin for internal rotation of the -CCIH₂ group calculated as a function of the C-C-C-CI dihedral angle. The three minima correspond to the stable conformers. The inset shows the molecular structure of the most stable gauche-II conformer, which is the dominant species. Theoretical and experimental investigations of optical rotatory dispersion in gas phase enantiomers of epichlorohydrin were focused on the effect of the conformational flexibility on this chiral property, and agreed on the existence of the three stable conformers abovementioned. Novel spectroscopic techniques based on ionizing synchrotron radiation with circular polarization and aimed at studying chiral properties of optically active free molecules have recently been developed. In such investigations, the circular dichroism measured

in the angular distribution of photoelectrons emitted by free chiral molecules enables any photoionization process to characterize intrinsic properties of chiral molecules. In this context, the knowledge of the electronic structure (e.g. the nature of the ionized molecular orbitals) might be valuable for a deeper understanding of the relationship between chiral and molecular properties. Previous studies of epichlorohydrin pointed out the difficult assignment of the most important part of the Photoelectron (PE) spectrum, the



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HOMO region, which displays substantial band overlap with two bands containing several cation states within a narrow energy range (2 eV). A further source of spectral complexity is the conformational flexibility that influences the interaction between the oxygen (n_0) and chlorine (n_{cl}) nonbonding orbitals and therefore the photoionization energetics. The epichlorohydrin was therefore investigated by a combined experimental and theoretical study. High statistics PE Spectra and Threshold Photoelectron spectra (TPES) of sufficiently high resolution (4 meV) were recorded in the gas phase using room temperature

samples. The TPE spectrum of the HOMO region, reported in Fig. 2, shows four main components: an intense second band displaying three main structures and a much weaker first band, at 10.6 eV, whose fine structure is partially resolved. The effect of the conformational flexibility on the photoionization energetics was studied by Density Functional Theory (DFT) and 2h-1p configuration interaction methods. Strong breakdown of the Koopmans theorem was obtained for the four outermost ionizations (HOMO region), which were further investigated by higher level ab initio calculations. The full assignment of the spectrum was put

on a firm basis by the combination of experimental and theoretical results. The orbital composition from correlated calculations was found closer to the DFT orbitals, which were then used to analyze the electronic structure of the molecule. The HOMO and HOMO-2 are n_0/n_{cl} mixed orbitals, HOMO-1 is a pure n_{cl} orbital, while HOMO-3 is mainly localized on the oxirane ring with a C-C-O bonding character. The nature of each valence MO is generally preserved in all the conformers, although the magnitude of the n_0/n_{cl} mixing in the HOMO and HOMO-2 varies to some extent with the C-C-C-Cl dihedral angle.



Figure 2. Valence TPE spectrum of epichlorohydrin (T = 23 °C) recorded in the HOMO region with 4 meV resolution.

ORIGINAL PAPER

S. Stranges, M. Alagia, P. Decleva, M. Stener, G. Fronzoni, D. Toffoli, M. Speranza, D. Catone, S. Turchini, T. Prosperi, N. Zema, G. Contini, and Y. Keheyan, *Phys. Chem. Chem. Phys.* **13**, 12517 (2011)

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Dissociative double photoionization of benzene molecules in the 26-33 eV energy range

time-of-flight mass spectrometer has been used to study the dissociative double ionization of benzene by UV synchrotron radiation. The threshold energy for the main dissociative processes, leading to $CH_3^+ + C_5H_3^+$, $C_2H_3^+ + C_4H_3^+$ and $C_2H_2^+ + C_4H_4^+$ ion pairs have been characterized by exploiting a photoelectron-photoion-photoion-coincidence technique, giving 27.8 ± 0.1, 29.5 ± 0.1, and 30.2 ± 0.1 eV, respectively. Theoretical calculations of the energy and structure of dissociation product ions have been also performed to provide further information about the dynamics of these processes.





Figure 1. Lower part: the time-of-flight mass spectrum of photoions detected with the photon energy set to 32.10 eV. Upper part: plot of coincidences at the same energy. The points in the area "B" define the events for $CH_3^+ / C_5H_3^+$ coincidences, while those in "C" the $C_2H_3^+ / C_4H_3^+$ and the $C_2H_2^+ / C_4H_4^+$ coincidences. The $C_3H_3^+ / C_3H_3^+$ coincidences are contained in the diffuse spot "A", mixed with $C_6H_6^{-2+}$ dications and with $C_3H_3^+$ ions also formed by single ionization of benzene.

Figure 2. The relative photon energy dependence for the three dissociative channels following the double photoionization of benzene in the 26-33 eV range.

Benzene may be considered as the basic unit for polycyclic aromatic hydrocarbons, which are a large class of conjugated π -electron systems of great importance in many research areas, such as combustion and environmental chemistry, material science, and astrochemistry. Several studies have been published on the double photoionization of benzene. It is presently well established that for the molecule in its ground state the threshold photon energy for the formation of the $C_6 H_6^{2+}$ dication is 24.65 ± 0.03 eV and such a dication remains undissociated when the energy is increased by few eV. However, when the photon energy is further increased, some ion-ion separation reactions start to occur. These charge separation processes have been studied by detecting the two product ions in coincidence, using a VUV lamp, or applying synchrotron radiation. With increasing photon energy the following charge separation reactions, listed in the order of increasing energies, have been characterized:

 $C_{6}H_{6}^{2+} \rightarrow C_{5}H_{3}^{+} + CH_{3}^{+}$ $C_{6}H_{6}^{2+} \rightarrow C_{4}H_{3}^{+} + C_{2}H_{3}^{+}$ $C_{6}H_{6}^{2+} \rightarrow C_{3}H_{3}^{+} + C_{3}H_{3}^{+}$

Theoretical calculations have been also performed in connection with the electronic structure and energy of the molecular benzene dication and with the structure and energy of the ions formed in some of the dissociation reactions. We report here on a study of the charge separation reactions of the benzene dication when this ion is formed by double photoionization of benzene molecules in the 26-33 eV photon energy range, providing new information about the photodissociation dynamics. The experimental results have been interpreted by the use of theoretical calculations performed *ad hoc* to characterize energetics and structure of product ions.

The present study has shown that the dissociative channel leading to $CH_{3}^{+} + C_{5}H_{3}^{+}$ opens at 27.8 eV, while the onset for channels leading to $C_2H_3^+ + C_4H_3^+$ and $C_{2}H_{2}^{+} + C_{4}H_{4}^{2}$ are at 29.5 and 30.2 eV, respectively. The first channel remains dominant in the whole investigated energy range, while the third appears to be always the least effective one. These reactions have also been characterized by studying theoretically energy, structure and spin multiplicity of the dication and of the dissociation product ions. Combining these results with the observed kinetic energy release into the products it has been possible to obtain new information about the most probable structure and internal energy of final ions.

The main dissociation channel, namely the one producing $CH_{3^{+}} + C_{5}H_{3^{+}}$, appears to proceed via "metastable" ion formation, with the precursor dication $C_{c}H_{c}^{2+}$ exhibiting a lifetime longer than the characteristic detection time of our instrument (~50 ps). The lifetime is shorter in both of the other two dissociation reactions. This can be easily rationalized considering that such a "metastable" dissociation channel requires a rearrangement of two C-H bonds with a following transfer of two hydrogen atoms. These conclusions suggest, as a logical future development, the measurement of the same processes also with mono-deuterated benzene. This could provide not only an improvement of the statistics of the collected data, in order to better study the precursor dication lifetime, but also the investigation of the symmetric dissociation leading to $C_3H_2D^+ + C_3H_3^+$, a channel not resolved in the coincidence plots that we have measured in the present work. We are planning such experiment in the near future.

ORIGINAL PAPER

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Condensed Matter: Structure, Electronic and Magnetic Properties

Indium zinc oxide micro-pyramids with pinholes and nanopipes

runcated micropyramids of indium-zinc-oxide (IZO) exhibiting pinholes and nanopipes have been grown by thermal treatments of compacted InN and ZnO powders. X-ray Photoelectron Spectroscopy (XPS) and microscopy measurements recorded at the ESCAmicroscopy beamline are used to discuss the Zn incorporation as a dopant and the formation of Zn_kIn₂O_{k+3} ternaries, and the results are correlated with cathodoluminescence (CL) and Energy-Dispersive X-ray (EDS) measurements. A growth model is proposed from the morphology evolution of the pyramids during the formation of the IZO ternary compounds.



Figure 1. (a) SEM image of pyramids with a pinhole at the apex. (b) XPS image showing micropyramids obtained using the signal ratio between In 3d and Zn 3d peaks.

Indium-Zinc-Oxide (IZO) micro and nanostructures with different amounts of Zn and In have potential applications as transparent conductors, field emitters, gas sensors and in luminescence and optoelectronic devices. The variable composition of crystalline IZO (from In doped ZnO to Zn doped In_2O_2) enables to modulate structural and electronic parameters of interest for applications. In addition, the ternary can have the form of a $Zn_k ln_2 O_{k+3}$ compound with k integer. The present study on the growth and characterization of IZO micropyramids enables us to propose a growth model taking into account the morphology evolution of the structures and the formation of ternary $Zn_k In_2O_{k+3}$ compounds. This is demonstrated using the XPS technique at the ESCA microscopy beamline of the Elettra synchrotron working with a 640 eV photon energy and a resolution of 0.2 eV. Moreover, the combination of these results with others obtained by means of scanning electron microscopy related techniques as cathodoluminescence or EDS, allows the correlation between the microstructural features and the optical and electronic properties of individual micropyramids. IZO micropyramids, with a square (400) base and four (222) triangular faces, have been grown by thermal treatment of InN and ZnO precursor powders. Some of the pyramids with rough surfaces and truncated tips show pinholes with regular

crystalline facets forming an inverted pyramid with square base (Fig. 1a). The apexes of these pinholes present a hollow core or pipe, which could be related to a dislocation driven growth of rods. EDS mappings and local spectra enable the identification of the rough surfaces of the pyramids with a secondary deposition of a Zn enriched material. The Scanning Photoelectron Microscope (SPEM) can work in both spectroscopy and imaging modes with a zone plate focusing optics to obtain a microprobe with a diameter of 150 nm. Fig. 1b shows an XPS image displaying the ratio between In 3d and Zn 3d signals. Bright regions in Fig. 1b at the edge of pinholes or at the apex of well formed pyramids denote a higher In to Zn ratio in these regions, in agreement with the EDS results. Fig. 2 shows the XPS spectra of O 1s, In 3d, and Zn 3d core levels acquired in regions with a high or low Zn concentration as well as the valence band XPS spectra. XPS O 1s core level spectra (Fig. 2a) consist of two components centered at 529.7 and 531.8 eV whose relative intensities depend on the probed area. The lower binding energy component is usually associated to oxygen in the indium oxide lattice, whereas the higher binding energy component could be originated from oxygen in oxygen-deficient regions. The lower binding energy component is significantly increased in regions with a high Zn concentration.

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This implies that the crystalline nature of the material improves with increasing Zn concentration reducing the oxygen-defective regions and leading to an enhancement of the luminescence in these regions. A luminescence band at 2.32 eV could be related to the incorporation of Zn. The 3.2 eV near band gap emission, observed only in regions with a high Zn/In ratio, appears to be associated with the formation of $Zn_k In_2O_{k+3}$ compounds. The shift measured in the position of the Zn 3d core level (Fig. 2c) indicates a variation in the Zn chemical environment as areas with increasing Zn content are probed. This is attributed to the presence of ternary compounds instead of to the direct Zn^{2+} to In^{3+} substitution. The estimated Fermi level position with respect to the valence band minimum is increased by 0.35 eV in the Zn rich regions, which is consistent with an enhanced n-type behavior.

In conclusion, XPS assessment of the IZO pyramids provides information on the chemical content, the charge state of dopants and their effect on the Fermi level or the valence band, key factors to control doping for improving the potential applications of these structures.

Figure 2. XPS peaks corresponding to different elements and the Valence Band (VB) from regions with high (upper graph) and low (lower graph) Zn to In ratio. Reprinted with permission from J. Phys. Chem. C, 115, 8354 (2011). Copyright (2011) American Chemical Society.



ORIGINAL PAPER

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Bulk sensitive X-ray absorption and magnetic circular dichroism investigation of Mn- and Co-doped ZnO thin films

Provide the measured transmission L_{2,3} X-ray magnetic circular dichroism spectra on Mn- and Co-doped ZnO thin films grown on soft X-ray transparent silicon nitride membranes. The lineshapes of the absorption spectra rule out dopant clustering and are consistent with the presence of Mn and Co divalent ions substituting Zn ions. XMCD spectra did not give evidence of ferromagnetic behavior of the Mn and Co ions. The lack of dichroic signal indicates that the ferromagnetism witnessed by VSM measurements could arise from delocalized magnetic moments, due to itinerant electrons associated with defects.



Figure 1. Mn (a) and Co (b) L₂₃ – edge XAS spectra of Mn-doped ZnO films.

We investigated Mn- and Codoped ZnO thin films by X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) in order to gain an insight into the controversial origin of the Room Temperature Ferromagnetism (RT FM) in dilute magnetic oxides. Inspite of the many reports of ferromagnetism the origin of the magnetic behavior still remains unclear. In the literature there is a general agreement about the presence of RT FM for dilute oxides when investigated by using techniques able to measure the global sample magnetization like SQUID or VSM magnetometry. However, an inhomogeneous scenario appears when the magnetic properties are explored by site sensitive techniques, such as XMCD. This can be attributed to small sampling depth of the total electron yield detection mode (2-3 nm at L-edges) or to surface magnetic dead layers, impurities and contaminants, as the sample is usually grown or synthesized ex situ and eventually cleaned by ion sputtering. In this study such controversial issues have been avoided by performing XAS and XMCD investigations of thin Mn- and Co-doped ZnO films in transmission mode that is probing the whole film thickness and therefore almost nullifying the influence of the near surface layer on the measured curves. The sensitivity to the whole film volume of global and element specific magnetometry allowed the results of

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the measurements, performed on the same samples, to be compared so that possible sources of FM could be consistently indicated. Mn- and Co-doped ZnO thin films with dopant concentration between 0 and 10 at.% were grown ex situ by using pulsed laser deposition on Si_3N_4 membranes which are nearly transparent to soft X-ray radiation. The films thickness was about 300 nm. The XRD spectra exhibit only the 002 reflection which indicates the presence of the only wurtzite phase, with preferential 001 growth and good crystallinity. Magnetization versus field measurements, performed at RT by means of a commercial VSM, showed clear ferromagnetic behavior with saturation values of about 1.5 emu/g (~0.20 μ_{B} per dopant ion). XAS/XMCD experiments were performed on the Circular Polarization beamline at Elettra synchrotron radiation facility (Trieste, Italy) on as-received Mn- and Codoped ZnO films grown on Si₂N₄ membranes. Absorption spectra were acquired at RT in transmission yield mode. XMCD spectra were measured by using right-handed (ρ^+) and left-handed (ρ^-) circularly polarized radiation in the presence of a magnetic field of 0.4 T which, according to the VSM data, allowed the films to reach the saturated magnetization state.

Fig. 1a shows the XAS spectra of Mndoped ZnO films at Mn L₂₃- edges. The lineshapes, different from those of MnO₂, Mn₂O₃ and Mn metal, look similar to the divalent MnO ones, suggesting that Mn ions are divalent and do not form Mn metal clusters. Also Co-doped films (Fig. 1b) exhibit Co L_{2,3} spectra which resemble the ones of divalent Co ions substituting Zn ones in tetrahedral coordination. The investigation of element specific magnetic properties was done by performing XMCD at Mn and Co L₂₃-edges and the spectra are shown in Fig. 2. The spectra did not show any dichroic effect at the Co and Mn edges, independently of the dopant

concentrations (Mn or Co). As Mnand Co-doped films exhibited a global RT ferromagnetic moment a delocalized magnetic response, associated with electrons trapped at vacancies or other defects, may occur. FM is attributed to itinerant electrons occupying a narrow impurity band (Stoner model); here the dopant ions do not carry any magnetic moment but it is supposed to induce defects that add suitable electronic levels in the material. In conclusion we performed bulk sensitive XAS and XMCD experiments on sample films grown *ex situ* and exhibiting a net global ferromagnetic moment at RT. The lineshape of the $L_{2,3}$ XAS spectra and the different global and local ferromagnetic behavior indicate that the FM can be due to a spin-split impurity band of itinerant electrons associated with defects.



Figure 2. XMCD spectra of selected Mn- and Co-doped films at (a) Mn $L_{2,3}$ - and (b) Co $L_{2,3}$ - edges.

ORIGINAL PAPER

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Revealing the high-energy electronic excitations underlying the onset of high-temperature superconductivity in cuprates

Studying how High-Temperature Superconductivity (HTSC) affects the high-energy physics associated with Mott-like excitations is challenging. The novel time- and energy-resolved optical spectroscopy, developed at the T-Rex@Elettra laboratories and at the Department of Physics of Università Cattolica in Brescia, allowed to clarify the relationship of many-body CuO₂ excitations and the onset of high-T_c superconductivity.



Figure 1. Pictorial representation of the CuO_2 planes, characteristic of superconducting cuprates. The charge transfer process (hole from the Cu 3d to the O 2p states) is represented by the yellow arrow. The Zhang-Rice singlet is indicated by the gray thick square.

Figure 2. Energy- and time-resolved reflectivity on $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$. The dynamics of the reflectivity is measured over a broad spectral range. The two-dimensional scans of $\delta R/R(\omega,t)$ are reported for three different doping regimes (first column: Underdoped (UD), $T_c = 83$ K; second column: Optimally Doped (OP), $T_c = 96$ K; third column: Overdoped (OD), $T_c = 86$ K), in the normal (first row), pseudogap (second row) and superconducting phases (third row). The insets display schematically the position of each scan in the T-p phase diagram of $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$. The white lines (right axes) are the time traces at 1.5 eV photon energy.



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The high-T_c copper-oxide (cuprate) superconductors are a particular class of strongly correlated systems in which the interplay between the Cu 3d and the O 2p states determines both the electronic structure close to the Fermi level as well as the high-energy properties related to the formation of Zhang-Rice singlets (i.e. hole shared among the four oxygen sites surrounding a Cu, and antiferromagnetically coupled to the Cu spin) and to the charge-transfer processes (see Fig. 1). One of the unsolved issues of high-T_a superconductivity is whether the electronic many-body excitations at high-energy scales are involved in the condensate formation in the under- and over-doped regions of the superconducting dome. Solving this problem, that defies an explanation within the BCS theory, would provide a benchmark for unconventional models of high-T superconductivity. Conventional optical spectroscopies have been widely used to investigate high-T_c superconductors at equilibrium. Although these techniques have revealed a superconductivity-induced modification of the CuO₂-planes'

optical properties involving energy scales in excess of 1 eV, the identification of the high-energy electronic excitations involved in the onset of high-temperature superconductivity has remained elusive. The main reason is that, at

equilibrium, this effect is hidden by the temperature-dependent

narrowing of the Drude-like peak,

describing the low-energy optical

properties of the free carriers. Here we solve this problem adopting a non-equilibrium approach to disentangle the ultrafast modifications of the high-energy electronic excitations from the slower broadening of the Drude-like peak induced by the complete electron-phonon thermalization. The impulsive suppression of $2\Delta_{sc}$ is achieved by photoexciting superconducting $Bi_2Sr_2Ca_{0.92}Y_{0.08}Cu_2O_{8+\delta}$ crystals (Y-Bi2212) through an ultrashort light pulse (pump). The supercontinuum spectrum produced by a nonlinear photonic crystal fibre is used to probe the high-energy (1.2-2.2 eV)modifications of the CuO₂-plane's optical properties, as a function of the delay from the excitation. In Fig. 2 we report the time- and frequency-resolved reflectivity variation $(\delta R/R(\omega,t) = R_{neq}(\omega,t)/\omega$ $R_{eq}(\omega,t)$ -1, where $R_{neq}(\omega,t)$ and $R_{eq}(\omega,t)$ are the non-equilibrium (pumped) and equilibrium (unpumped) reflectivities), for the normal (top row), pseudogap (middle row), and superconducting (bottom row) phases at three different dopings.

While the $\delta R/R(\omega,t)$ measured in the normal and pseudogap phases can be reproduced assuming an impulsive modification of the Drude model parameters, in the superconducting phase the structured variation of the reflectivity at high energies is accounted for only by assuming a dopingdependent modification of both the 1.5 eV and 2 eV oscillators. These results unveil an unconventional mechanism at the base of HTSC both below and above the optimal hole concentration required to attain the maximum critical temperature. Superconductivity-induced changes of the optical properties at high-energy scales seem to be a universal feature of high-temperature superconductors, suggesting that this issue will be decisive in understanding high-temperature superconductivity. The technique developed in this

work will trigger the next generation of optical spectroscopies, where the temporal axis is added to the frequency axis, aimed at clarifying a variety of unsolved issues in solidstate and condensed-matter physics.

ORIGINAL PAPER

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Collapse of short-range magnetic order in CoO at the Néel temperature

Dichroic Effect in Angle Resolved Auger Photoelectron Coincidence Spectroscopy (DEAR-APECS) has been measured on a CoO thin film above and below the magnetic transition Néel temperature (T_N) . Sharp high-spin and low-spin structures has been identified in spite of the otherwise featureless conventional Auger spectra, typically found for openband systems. The disappearance of the dichroism just above T_N indicates a collapse of the surface short-range magnetic order.



Figure 1. AR-APECS measured below T_N in the two geometric configurations NN (upper panel), and AN (lower panel). The dichroic effect (difference between red and blue lines) allows to disentangle low spin (red peak) and high spin (blue peak) multiplet terms.

In Auger Spectroscopy (AES) Auger matrix elements include two body Coulomb operators and, when core-valence-valence spectra are measured, final states are characterized by two additional holes in the valence band. This makes AES a valuable "two-body" tool for probing electronic properties of highly correlated materials and magnetic systems. Nevertheless, while Photoemission Spectroscopy (XPS), which can be considered a "one-body" probe, has became an established tool for the study of electronic structure, the apparent featureless lineshape of most of AES measurements has hampered its potentiality. It is indeed a paradox that in magnetic systems, where exchange and correlation play a fundamental role, AES displays broad lineshapes which do not change upon crossing magnetic transitions. The point is that, while in XPS emission angle and kinetic energy of the photoelectron (the one directly involved in the ionization event) typically project onto well defined states with sharp energy distributions, emission angle and kinetic energy of the Auger electron (one of the two ones participating to the auto-ionization event) do not. It is like if an integration over all the possible paths of the second (not detected) electron, leaving the valence band and filling the core hole, should be taken into account. An indirect detection of the second electron is achieved in Angle Resolved Auger Photoelectron Coincidence Spectroscopy (AR-APECS) where the Auger electron is detected in time coincidence with its parent photoelectron. Selection rules and matrix elements establish a tight relation between the two detected electrons (Auger and photoelectron) and the two holes created in the valence band, giving rise to a

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selectivity on the final spin state. In the present work AR-APECS has been measured across the antiferromagnetic transition of a CoO thin film grown on Ag(001). Co 3p_{3/2} photoelectrons, excited by 250 eV linearly polarized photons, have been detected in time coincidence with Co MVV Auger electrons at two different temperatures: 170 K (below the Néel temperature T_N and 295 K (just above T_N) and in two different geometries referred to as NN, where both electrons are not aligned (N)with the photon polarization vector e and AN, where the photoelectron is aligned (A) with e, and the Auger electron is not aligned (*N*). As previously demonstrated NN configurations enhance low spin final states while AN ones favor high spin states.

In Fig. 1 at $T < T_N$ a dichroic effect, that is a difference between AR-APECS spectra in NN and AN configurations (red and blue lines, respectively) allows to single out low spin (red peak) and high spin (blue peak) multiplet terms for a *d*⁵ configuration associated to the unrelaxed part (two hole contributions) of the spectrum at high kinetic energies. The relaxed portion of the Auger intensity associated with the screening of the primary core hole and which includes one-hole and two-holeone-electron configurations, contributes at lower kinetic energies. At 295 K, just above T_N the dichroic effect has completely disappeared and in Fig. 2, high and low spin multiplet terms are no longer discriminated. It is interesting to note in Fig. 2 that, despite the dramatic change in the DEAR-APECS, conventional AES does not display any change upon crossing T_{N} . The drop of the dichroism above T_{N} has been attributed to a collapse of

the surface short-range magnetic order. Magnetic correlation existing between first neighboring atoms below T_N affects core hole screening and leads to a higher contribution of unrelaxed Auger intensity where high and low spin multiplet terms are identified. Above T_N a higher contribution of the relaxed portion leads to a dramatic suppression of the dichroic effect. The conclusion is supported by the fact that dichroic effect in open-band systems is seen when the valence band splits and leads to a fully occupied spin polarized sub-band where the Cini-Sawatzky model applies and electron correlations further separate in energy low and high spin contributions.



Figure 2. AR-APECS measured just above T_N in the two NN and AN configurations: the dichroic effect is absent. In the lower part conventional AES no shows difference when crossing the magnetic transition.

ORIGINAL PAPER

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Direct observation of a dispersionless impurity band in hydrogenated graphene

e show with angle-resolved photoemission spectroscopy that a new energy band appears in the electronic structure of electron doped hydrogenated monolayer graphene (H-graphene). Its occupation can be controlled with the hydrogen amount and allows for tuning of graphene's doping level. Our calculations of the electronic structure of H-graphene suggest that this state is largely composed from hydrogen 1s orbitals and remains extended for low H coverage.

Doping is at the heart of modern semiconductor technology because it allows for control of the charge carrier density and is therefore the basis for all electronic circuit elements. Doping is usually done by the inclusion of foreign atoms to the material which is still silicon for most applications. However, the search for ever smaller and faster devices requires new materials. Graphene is one of the latest developments in this direction and one of the most promising materials for implementation in the next generation electronic devices. Due to graphene's unique electronic properties (massless Dirac Fermions) alternatives to classical charge transport come into reach, that allow unprecedented speed of the graphene based transistors. However, being a zero-gap semiconductor, pure graphene is not ready for its direct implementation as an active element in a field effect transistor. Here we show that hydrogenation of graphene leads to the formation of a bandgap and a new impurity level. The C-H bond is well defined and H/C ratios equal to 25% have been realized (see sketch in Fig. 1a). In the experiment, we synthesize and functionalize graphene samples in situ and measure Angle-Resolved Photoemission Spectroscopy (ARPES) at the BaDElPh beamline. Functionalization of graphene was performed by intercalating

potassium below graphene followed by hydrogenation. Fig. 1b shows ARPES spectra of graphene with an increasing potassium coverage. Clearly, the Dirac point shifts away from the Fermi energy to higher energies with increasing potassium coverage. Intercalation of potassium below graphene (bottom right of Fig. 1b) yields a much larger separation between π and π^* bands. This can also be seen in the Energy Dispersion Curves (EDCs) shown in Fig. 1c: upon potassium intercalation the energy separation increases from 400 meV to 800 meV. In Fig. 2a we present ARPES spectra of a hydrogenation series that was performed on fully n-doped graphene. We observe: i) a general



Figure 1. (a) A sketch of hydrogenated graphene. (b) ARPES intensities around the K point of the Brillouin zone of graphene intercalated with one monolayer Au for increasing potassium doping. The last viewgraph (bottom right) denotes the photoemission intensities of graphene intercalated with potassium in between the graphene / Au interface. (c) Energy dispersion curves taken at the K point for the six doping steps.

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broadening, ii) a shrinkage of the Fermi surface, iii) the energy gap increases with hydrogenation and, most importantly, iv) a new state appears within this gap. The new state is almost dispersionless and its ARPES intensity increases as hydrogenation is proceeding. The increased ARPES intensity of the midgap state and the shrinkage of the Fermi surface of the π^* band, as indicated by the two black vertical lines on top of each panel in Fig. 2a, go together and are attributed to an electron transfer from the π^* band to the midgap state. From Fig. 2b it is clear that already at ratios of H/C = 0.9% the energetic distance between the π and π^* bands increases from 0.8 eV to 1.6 eV which we attribute to the partial sp³ hybridization. These results are in good agreement with calculations showing this midgap state is largely composed from hydrogen 1s orbitals (see Fig. 2c and Fig. 2d).

In conclusion, we have found a new electronic state in H-graphene that is located in the energy gap. In the case of n-doped H-graphene the midgap state becomes available for electrons and directly observable with ARPES since it is then situated below the Fermi energy. Therefore, the H impurity band likely acts as an electron acceptor level which provides the possibility to control the electron concentration in H-graphene via the H/C ratio.



Figure 2. (a) ARPES intensities of hydrogenated n-doped graphene with increasing H/C ratios as denoted. The size of the Fermi surfaces is indicated by two black vertical lines on top. The dots in the last panel are a guide to the eye and depict the dispersionless midgap state. The photoemission intensity scale is depicted and applies to all graphs. (b) EDCs of the ARPES intensity at the K point. (c) DFT calculation of the electronic energy bands and (d) the partial DOS of HC_{32} . The dispersionless band in blue color corresponds to the midgap state.

ORIGINAL PAPER

D. Haberer, L. Petaccia, M. Farjam, S. Taioli, S.A. Jafari, A. Nefedov, W. Zhang, L. Calliari, G. Scarduelli, B. Dora, D.V. Vyalikh, T. Pichler, Ch. Wöll, D. Alfè, S. Simonucci, M.S. Dresselhaus, M. Knupfer, B. Büchner, and A. Grüneis, *Phys. Rev. B* **83**, 165433 (2011)

Extrinsic screening of ferroelectric domains in PbZr_{0.48}Ti_{0.52}O₃

n a ferroelectric thin film, a stable polarization charge of defined polarity can be established at its boundaries, which will be screened by intrinsic and extrinsic carriers. For the first time, we were able to directly observe the extrinsic charge screening by adsorbates at a Pb(Zr_{0.48}Ti_{0.52})O₃ (PZT) surface. We used energy-filtered PEEM and mirror-electron microscopy at the SPELEEM of the Nanospectroscopy beamline to monitor the polarity-related chemical and electronic changes at both the adsorbate-covered and clean PZT surface.

Ferroelectric (FE) materials have the intriguing property that a their structural and electronic state can be voltage-controlled. The interest is now turning towards surface-related effects, such as voltage-controlled surface catalysis and adsorbateinduced modification of the FE state. The latter effect is of vital importance since it bears an enormous potential for sensor applications, and may in addition deliver answers to the vivid debate on why the FE state is stable in ultrathin films. Here, we address this question by Photoemission Electron Microscopy (PEEM) and Mirror-Electron Microscopy (MEM) using the SPELEEM at the Nanospectroscopy beamline at Elettra.

A (001)-oriented PZT layer was grown by high pressure sputtering on a conducting SrRuO₃ (SRO) back electrode on SrTiO₃(001). The PZT film was polarity-patterned by conductive tip AFM applying a dc bias voltage. The outer square shown in Fig. 2c was written by a bias of +5V, inducing a negative polarization pointing inwards (P⁻),





the inner square was overwritten by -5V (P⁺). Writing was followed by a reading step using AFM and Piezoforce Microscopy (PFM). PFM confirmed that the written patterns correlate with the FE state. AFM showed no topographic changes by the writing.

The structured sample was investigated in the SPELEEM. After transfer into UHV, the sample surface is always covered by adsorbates screening part of the net FE charge at the surface. To investigate this effect, the sample was measured with and without adsorbates. Cleaning was performed at an O₂ partial pressure of 4.8×10^{-5} mbar with annealing at 400 °C for several hours. Surface contamination was monitored by energy-filtered PEEM. Oxygen annealing removes the O 1s high binding energy component (Fig. 1a) stemming from chemisorbed CO_{γ} , as confirmed by the missing C 1s core level peak in the annealed state (Fig. 1b). The cleaning changes the valence band as well, removing states related to surface carbon near the Fermi-level, (Fig. 1c). The gap between 0 and 2.6 eV is typical for a clean PZT surface.

Fig. 2 shows the LEEM measurements. For very low energy of approaching electrons, reflection occurs above the surface. At higher energies the electrons are able to penetrate the surface, and the reflectivity drops considerably (*MEM-LEEM transition*). The energy of the transition E_m depends on the surface

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potential which is influenced by the FE polarization, as can be seen in Fig. 2c. The difference in E_m between P^+ and P^- polarized regions directly corresponds to the different surface electronic structure as shown in the density functional theory calculations in Fig. 2a. The FE net charge near the surface changes the position of the valence band onset and, if a constant electron affinity is assumed, also the work function in the same manner.

The theoretically-predicted energy difference of 0.5 eV is larger than the experimentally observed one (<100 meV), because in the calculations adsorbates are not taken into account. The screening effect of the latter reduces the FE related surface potential change. Theory qualitatively confirms our results indicating that a P⁺ state has a higher work function than P⁻ and thus an earlier onset of the reflectivity drop

when increasing the kinetic energy of the approaching electrons. Summarizing, we have measured the MEM-LEEM transition as a function of the FE polarization of polarity-patterned PZT. A clear FErelated surface potential difference is observed. The screening effect of adsorbates is demonstrated. The results are explained by an image charge model and supported by DFT calculations.



Figure 2. a) DFT calculations with FE stabilization by an external field. b) Schematic of the electronic structure of a FE thin film with intrinsic and extrinsic screening. c) Top: LEEM-Images of the FE domains across the MEM-LEEM transition (from left to right: 0.8, 1.45, 1.85, and 2.45 eV). Inner square: P^* , outer: P^- , unwritten PZT: P^+ imprint. Middle and bottom: Local electron reflectivity curves extracted from the regions of interest in the inset before and after in situ surface O, annealing.

ORIGINAL PAPER

I. Krug, N. Barrett, A. Petraru, A. Locatelli, T.O. Mentes, M.A. Niño, K. Rahmanizadeh, G. Bihlmayer, and C.M. Schneider, Appl. Phys. Lett. **97**, 222903 (2010)

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Orbital topology, interlayer spin coupling, and magnetic anisotropy of the CuFeO₂ compound

-ray absorption spectroscopy performed on a CuFeO₂ single crystal reveals the pivotal role of the Cu ions in the discussion of the anisotropic properties of the compound. In particular, it is shown that there is a 3d hole density on the nominal 3d¹⁰ Cu⁺ ions which may lie at the origin of the intriguing low temperature magnetic properties of CuFeO₂. In addition, the finding has important consequences regarding the field-induced ferroelectricity of the system.

The class of complex oxide materials exhibits an extremely rich variety of intriguing phenomena: superconductivity, colossal magnetoresistance, and multiferroicity, to name a few. Because the intricate physical mechanisms responsible for such material properties typically involve the interplay between multiple coupled degrees of freedom, often the details of these interactions ultimately determine the macroscopic behavior. In the different types of multiferroic materials for example, the soughtafter spin-charge coupling frequently involves lattice and orbital degrees of freedom as well. One particularly intricate system is the geometrically frustrated and multiferroic CuFeO₂ (Fig. 1), in which the magnetism and ferroelectricity have been linked to spin-lattice and spin-orbit coupling respectively. The multitude of complex antiferromagnetic states at low temperature and in applied magnetic fields can be accounted for by the strong correlation between lattice distortion and the degree of magnetic frustration. However, the stability of the low-temperature magnetic ground state has been somewhat of a puzzle since its discovery, as the set of in-plane exchange constants required to model the system is peculiar to say the least. Moreover, an accurate system description also requires a



Figure 1. a) Schematic crystal structure of CuFeO₂ (R3m, a = b = 3.03 Å, c = 17.17 Å). The 3d electronic congurations of the Fe and Cu ions result in a mutual antiferromagnetic superexchange interaction J_{se} . b) The low temperature phase transition ($T_{c2} = 11$ K) involves a tilting of the O-Cu-O "dumbbells", resulting in a network of effectively ferromagnetic interlayer Fe-Fe interactions that stabilizes the magnetic structure, as illustrated by the projection in the [110] c-plane.
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magnetic anisotropy term that is coupled to the lattice distortion, the origin of which has remained enigmatic thus far. Finally, the exact relation between these magnetic terms and the ferroelectricity observed in the field-induced magnetic spiral state has yet to be clarified.

The present X-ray absorption study of $CuFeO_2$ reveals the interlayer Cu ions to be a crucial missing link in its microscopic understanding. The specific lattice-induced orbital topology is shown to induce partial holes and thus finite spin density in the 3d orbitals of the Cu⁺ ions (Fig. 2), which were thus far considered magnetically idle. The addition of this degree of freedom to the intricate system of interactions unravels the peculiar low temperature magnetic order and anisotropy, while simultaneously introducing new aspects to the ferroelectricity mechanism. Having established the presence of (partial) 3d holes on the Cu ions (3d^{10-x}), it is justified to assume a corresponding unpaired spin density in the Cu 3d band. The existence of such unpaired Cu 3d spin density on the interlayer Cu ions in CuFeO₂ (Fig. 2) uncovers a crucial "hidden" aspect of the already complex system of coupled degrees of freedom, which allows us to shed light on several previously unresolved issues. Firstly, the interaction pathway for the recently discovered magnetic exchange between consecutive triangular high spin Fe-layers is now discovered to be a double superexchange across the bridging O-Cu-O "dumbbells".

Secondly, the results suggest a highly plausible physical origin of the puzzling low temperature anisotropy. The presence of holes of prevalent 3d, character on the Cu ions partially restores the guenched Cu orbital momentum along the c-axis. Consequently, the local spin-orbit coupling dictates alignment of the associated Cu spin density along the crystallographic c-axis. Lastly, the Cu degrees of freedom described here complicate the issue of ferroelectricity in the spiral phase of CuFeO₂. The mechanism thought to be responsible for the fieldinduced ferroelectric moment along the [110] direction invokes the incommensurate variation of the hybridization of Fe 3d and O 2p states which is shown here to involve Cu 3d orbitals as well.



Figure 2. Copper a), iron b) $L_{2;3}$ and oxygen K c) polarization dependent XAS spectra (solid lines). The measured spectra are compared to corresponding XAS spectra of reference compounds. d) Comparison of the Cu a) and Fe b) 3d and O 2p c) p-DOS (solid lines) to the calculated XAS spectra (dashed lines). The filled curves denoted "H-V" are the linear dichroic signals.

ORIGINAL PAPER

M. Malvestuto, F. Bondino, E. Magnano, T.T.A. Lummen, P.H.M. van Loosdrecht, and F. Parmigiani, *Phys. Rev. B.* **83**, 134422 (2011)

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Optical properties of (SrMnO₃)_n/(LaMnO₃)_{2n} superlattices

Where measure the optical conductivity $\sigma_1(\omega)$ of $(SrMnO_3)_n/(LaMnO_3)_{2n}$ superlattices (SL) for n = 1, 3, 5, and 8 between 10 and 400 K. Data show a T-dependent insulator to metal transition for n = 3, driven by the softening of a polaronic mid-infrared band. At n = 5 that softening is incomplete, while at the largest period n = 8, the MIR band is independent of T and the SL remains insulating. One can thus first observe the Insulator-to-Metal Transition (IMT) in a manganite system in the absence of the disorder due to chemical doping.

Since decades, manganites attract the greatest attention of the condensed matter community. This is due either to the Colossal MagnetoResistance (CMR), which makes them appealing for applications, and to the rich doping-temperature phase diagram, which is of great interest for basic research. In particular, several studies have been devoted to the Insulator-to-Metal Transition (IMT) coupled to ferromagnetic ordering at hole-doping levels ~1/3. The IMT is understood through the double-exchange mechanism, once the localization tendency due to polaron formation has been taken into account. Today it is widely recognized that quenched disorder weakens long range order and causes ferromagnetism to break up into clusters, whose sudden alignment in the presence



Figure 1. $\sigma_1(\omega)$ as extracted from a Drude-Lorentz fit to the reflectivity at T = 10 K, for the n = 1, 3, 5, 8 compounds, showing the Mott transition induced by the proximity between the layers. $\sigma_1(\omega)$ at T = 300 K, for n = 16 is reported as well. Data on single crystals of LaMnO₃, La_{0.9}Sr_{0.1}MnO₃ and SrMnO₃ at 10 K are also shown for comparison.

of a magnetic field is an essential ingredient of CMR.

Recent progresses in the growth of atomic-scale multilayers open exciting opportunities in the design of materials with novel properties. The so-called "electronic reconstruction" effect produces a new 2-D metallic state at the interface between a band insulator as SrTiO₃ and a Mott insulator like LaTiO₃. Manganite superlattices with alternating layers of insulating anti-ferromagnets SrMnO₃ (SMO) and LaMnO₃ (LMO) have been recently studied as well. Thanks to electronic reconstruction, both metallicity and ferromagnetism can be induced in these nano-structured Superlattices (SLs). The (SrMnO₃)_p/(LaMnO₃)_{2p} SL system corresponds to an effective hole doping 1/3. When n < 3, the spacing

between interfaces is so small, that the 3-D charge distribution throughout the film is believed to be uniform. For n = 1, an IMT below a temperature $T_{IMT'}$ comparable to that of the corresponding La_{2/3}Sr_{1/3}MnO₃ alloy, takes place in the absence of random disorder. For sufficiently low temperatures, dc measurements show that the film made up of two insulators becomes metallic for small n. Nevertheless, the way the IMT is approached for decreasing n, the excitations involved, and the SL low-energy electrodynamics are still to be investigated. One may also ask whether the dc resistivity reflects the carrier dynamics at the interfaces or that in between, and whether the

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optical properties resemble or not those of the bulk materials. We have addressed these problems by means of infrared spectroscopy, a tool which has been successfully used to probe the low-energy electrodynamics and the mechanism of the IMT in a number of oxides. We have shown that such heterostructures are characterized by novel electronic states, profoundly different from those of doped bulk manganites. At the largest lattice period (n = 8) the spectra indicate an insulating or poorly metallic behavior at low temperatures, with the presence of a mid-infrared band around 10000 cm⁻¹, which is not observed in bulk SMO or LMO and may be attributed to strongly localized charges (small polarons), not available at the interface (see Fig. 1). The same band is found at lower energies both at n = 5 and n = 3, where its slight softening at low T is accompanied by the building of a small Drude term. At n = 1, where eventually the charge reaches a uniform distribution throughout the film, a dramatic softening of the mid-infrared band triggers a double-exchange-

Figure 2. $\sigma_1(\omega)$ at different temperatures for n = 8, 5, 3 and 1, in comparison with the low-temperature conductivity of cleaved $La_{0.825}Sr_{0.175}MnO_3$ single crystals and $La_{2/3}Sr_{1/3}MnO_3$ films.

driven insulator-to-metal transition around room temperature. As T lowers (see Fig. 2), the mid-infrared band continues to increase in intensity and to displace toward zero frequency, assuming a large polaron character, thus providing low-energy states to the Drude term. The polaronic character of the charges is confirmed by an effective mass, which at n = 1 is m*/m_b~7. The optical data, once extrapolated to $\omega = 0$, provide an alternative determination of the superlattice resistivity, which is not affected by paths perpendicular to the interfaces. Probably for this reason, they do not show the low-T upturn exhibited by dc-measurements. As a whole, this optical study of the $(SMO)_n/(LMO)_{2n}$ system shows that such heterostructure has its own properties, characterizing a novel electronic state which is profoundly different from those of doped bulk manganites except for the smallest interlayer spacing at n = 1, where however the metallization at T_{IMT} takes place in the unusual absence of disorder.



ORIGINAL PAPER

A. Perucchi, L. Baldassarre, A. Nucara, P. Calvani, C. Adamo, D.G. Schlom, P. Orgiani, L. Maritato, and S. Lupi, *Nano Letters* **10**, 4819 (2010)

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Emergence of a magnetic charge crystal in artificial dipolar spin ice

Agnetic frustration effects in artificial kagome arrays of nanomagnets are investigated using Monte Carlo simulations and X-ray photoEmission electron microscopy. Spin configurations of demagnetized arrays reveal unambiguous signatures of long range, dipolar interactions between the nanomagnets, and the emergence of a magnetic charge crystal.



Figure 1. XMCD-PEEM magnetic image of an artificial array of 470 x 70 x 10 nm³ nanomagnets. The partly superimposed dots highlight the nodes of the kagome lattice. Field of view is 5 µm. The direction of the incoming X-rays is indicated by the hv arrow. Black and white contrast is observed according to the sign of the magnetization component along this X-ray direction, as sketched in the two panels below the image. The spin state of each nanomagnet, and thus the magnetic charge carried by each vertex, are measured.

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Frustration is a general concept in physics and can be found in many condensed matter systems. Frustration arises when all pairwise interactions can not be satisfied at once, for example due to the system geometry. In some cases, frustration effects lead to an extensively degenerate ground state, i.e. a low temperature manifold built with a large number of configurations with identical energy. Pauling's description of the low-temperature proton disorder in water ice was perhaps the first example of frustration in condensed matter physics, and remains its paradigm (see L. Pauling, Journal of the American Chemical Society 57, 2680 (1935)). At the end of the nineties, new magnetic compounds have been synthesized, in which the disorder of the magnetic moments at low temperature is analogous to the proton disorder in water ice. Because of this analogy, these compounds have been named spin ice. Recently, this correspondence between the physics of water ice and its magnetic equivalents has been pushed further with the realization of artificial, two dimensional arrays of ferromagnetic islands. One important advantage of these mesoscopic lattices compared to the spin ice compounds found in condensed matter physics is to allow magnetic imaging of individual spins, i.e. the visualization in real space of how spins accommodate frustration.

Using lithography techniques, we have fabricated geometrically frustrated arrays of nanomagnets on a kagome lattice, i.e. a lattice of triangles sharing their corners on which the nanomagnets are located as seen in Fig. 1. The magnetic configuration of each nanomagnet is then probed using X-ray Magnetic Circular Dichroism

PhotoEmission Electron Microscopy (XMCD-PEEM), a technique available at the Elettra synchrotron facility (Nanospectroscopy beamline). Due to their elongated shape, magnetization within the nanomagnets can only point along the long axis of the elements. A nanomagnet can thus be considered as an Ising spin. Each center of the triangles, called a vertex, is then defined by the spin state of a set of three Ising spins (see Fig. 1). Eight states are possible: two have a high energy and correspond to the 3-in or 3-out spin configurations, and six have a lower energy and correspond to the 1-in/2-out or 2-in/1-out spin configurations. Each spin of the array being a magnetic dipole, the X-in/Y-out configuration of a vertex can also be characterized by the magnetic charge it carries: the 3-in or 3-out configuration are equivalent to a magnetic charge state ± 3 , while the other spin configurations are equivalent to a charge state of ± 1 . In other words, these spin models on a kagome lattice can also be seen as a magnetic charge model on a hexagonal network. **Combining Monte Carlo simulations** and XMCD-PEEM magnetic imaging on artificial arrays of cobalt nanomagnets, we found an important result. Contrary to what was thought until now, the long range (i.e. beyond nearest neighbors) dipolar interactions between the nanomagnets cannot be neglected. This result has profound consequences: while the main

interest for frustrated compounds arises from the massive degeneracy of their ground state, this degeneracy is fully lifted when long range, dipolar interactions are included in the model. Understanding whether or not these long range interactions influence the local spin configurations in artificial arrays of nanomagnets is thus essential, especially because these arrays are often considered as a playground to study magnetic frustration effects on a mesoscopic scale. One argument we used to demonstrate this result was to compare predictions from dipolar spin ice models and our experimental observations. In particular, as the system reaches low-energy spin configurations when we demagnetize the arrays, it goes through a (predicted) phase transition where spins fluctuate while the magnetic charges at the vertices crystallize to form a perfectly ordered arrangement of alternating +1 and -1 magnetic charges. In this phase, all vertices are in one of the six low-energy configurations (we say that the system satisfies the ice rule), but these configurations are such that a vertex carrying a magnetic charge +1 can only be surrounded by three vertices carrying a charge -1 (and vice versa). The novelty of our work was to observe the emergence of this phase, in which magnetic charges crystallize due to the presence of long range interactions between the nanomagnets.

ORIGINAL PAPER

N. Rougemaille, F. Montaigne, B. Canals, A. Duluard, D. Lacour, M. Hehn, R. Belkhou, O. Fruchart, S. El Moussaoui, A. Bendounan, and F. Maccherozzi, *Phys. Rev. Lett.* **106**, 057209 (2011)

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Surface and bulk electronic structures of LaFeAsO studied by angle-resolved photoemission spectroscopy

We studied the electronic structure of LaFeAsO, a parent compound of iron-arsenic superconductors, by angle-resolved photoemission spectroscopy (beamline APE at Elettra, beamlines 1 and 9 at HSRC, Japan). By examining its dependence on photon energy, polarization, and sodium dosing, both the bulk and the surface contributions are identified. For the surface states, both the LaO-terminated and FeAs-terminated components are revealed. Our data suggest that the band reconstruction may play a crucial role in the spin-density-wave and the structural transitions observed in this system.



Figure 1. Fermi-surface mapping and band structure of LaFeAsO along G-M in the normal state (170 K). (a) ARPES intensity map at $E_{\rm F}$ overlaid by the Fermi crossings. (b) Different Fermi surfaces are constructed by tracking the Fermi crossings. (c) Photoemission intensity plot along G-M (cut 1 in panel a). The dashed curves are the guides to the eye. (e) Calculated bulk electronic structure of LaFeAsO along G-M based on density functional theory.

The discovery of superconductivity in LaFeAsO_{1-x}F_x has declared the advent of iron-based hightemperature superconductors (Fe-HTSCs). After intensive research, the record superconductivity transition temperature T_c of Fe-HTSCs is still held by this so called 1111 series. Resembling the cuprates, superconductivity emerges from the antiferromagnetic ordered ground state upon doping. Therefore the intimate relationship between superconductivity and magnetism is maintained.

In the parent compounds of 1111 series, the structural and Spin-Density-Wave (SDW) transition temperatures are separated, which provides an opportunity to reveal the origin of the structural transition uniquely and its influence on the electronic structure. Angle-Resolved Photoemission Spectroscopy (ARPES) has already been employed to study the electronic structure of various Fe-HTSCs, revealing the electronic structure, superconducting gap, and the electron-boson coupling. However, due to the covalent Ln-O bonding, LnFeAsO (Ln = La, Sm, Ce, etc.) exposes a polar surface with charge redistribution after cleavage. There are two types of surfaces, the LnO-terminated and FeAsterminated. A recent detailed band calculation of LaFeAsO shows that the electronic structure of the two types of surfaces deviates strongly from each other and from that of the bulk. Since ARPES is essentially a surface probe, the measured band structure is strongly complicated by the surface states. Therefore,

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the bulk electronic structure of LnFeAsO could not be established. This prevents the understanding of so far the highest T_c series of Fe pnictides, which in turn hampers the construction of a global picture of electronic structure in Fe-HTSCs. In order to illustrate the difficulties mentioned above, we present in Fig. 1 the measured electronic structure and the Fermi surface in the normal state (170 K). The observed Fermi surface consists of three hole pockets, two electron pockets and a tiny patch like feature around the G point as well as one electron pocket around M. This is very different from the calculated bulk electronic structure and the band structure of other Fe pnictides. The band structure as indicated by the dashed curves in Fig. 1c is resolved by tracking the local minimum locus in the second derivative of the ARPES intensity plot with respect to energy (Fig. 1d). In total, we observed nine bands and five Fermi surface sheets around G, significantly more than in the bulk band structure calculations. By carefully conducting photon energy, polarization, and Na-dosing dependence studies, we could distinguish states from the bulk and the surface, and the results are summarized in Fig. 2. As a result, the nature of the SDW state is linked to the bulk band reconstruction at low temperatures.

We therefore obtained a comprehensive picture of the electronic structure in LaFeAsO by distinguishing bulk and surface contributions. Due to the surface charge redistribution in the 1111 series, the measured electronic structure of LaFeAsO is heavily "contaminated" by the surface states. For this reason, great caution has to be taken when interpreting the ARPES data obtained on this series of Fe pnictides (for example, the measured superconducting gap on a surface band might be caused by the proximity effects, and the strong kink on a surface band does not necessarily suggest strong electronphonon interactions in the bulk bands).

Our temperature-dependent data further show that the large

downward shift of the bulk band saves the total energy of the system and drives the phase transitions. The onset of this shift at the structural transition temperature further evidences the occurrence of a fluctuating magnetic ordered phase that might play a role in the structural transition. The results in the 1111 series are consistent with the observations in the 122 and 111 series of iron pnictides, suggesting the universality of the electronic response to the structural and magnetic phase transitions. Our results could therefore contribute in constructing a global picture of the Fe-HTSC physics.



Figure 2. The summary of (a) the bulk and (b) the surface band structures that can be measured. (c) The diagram for the origin of the measured bands.

ORIGINAL PAPER

L.X. Yang, B.P. Xie, Y. Zhang, C. He, Q.Q. Ge, X.F. Wang, X.H. Chen, M. Arita, J. Jiang, K. Shimada, M. Taniguchi, I. Vobornik, G. Rossi, J.P. Hu, D.H. Lu, Z.X. Shen, Z.Y. Lu, and D.L. Feng, *Phys. Rev. B* **82**, 104519 (2010)

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Growth of spatially ordered Ge nanoclusters in an amorphous matrix on rippled substrates

The influence of periodically corrugated-rippled substrates on the self-assembly of Ge quantum dots in fused silica matrix was investigated. The rippled substrate highly influences the arrangement of Ge quantum dots in the matrix; it ensures a substantial improvement in the regularity of their ordering and a narrowing of their size-distribution. The Grazing Incidence Small Angle X-ray Scattering (GISAXS) technique was shown to be amazingly efficient in the determination of the above mentioned structural properties and the characterization of the self-assembly process.

The production of materials containing Quantum Dots (QDs) attracts great attention due to their highly-applicative properties. Especially interesting are semiconductor QDs, embedded in solid amorphous matrices. The properties of such systems can be easily manipulated by the QD composition, size and arrangement. Ge is one of the most interesting semiconductor materials because Ge QDs have strongly size-tuneable electronic properties, electro and photo luminescence, non-linear optical properties and unusual melting-freezing conditions. Recently we have developed a



Figure 1. Atomic-force microscopy picture of a rippled Si surface, and its Fourier transformation (in the inset) [M. Buljan et al. Phys. Rev. B 82, 125316 (2010). Copyright (2011) by the American Physical Society].

method for the production of selfassembled Ge QDs in amorphous silica matrix. The method is based on diffusion-induced nucleation combined with the effect of surface morphology. Ge QDs were created by the deposition of $(Ge+SiO_2)/SiO_2$ multilayer films on a flat Si(111)substrate at an elevated temperature. The benefits of the method are a simple and efficient production of the material, a relatively narrow size distribution as well as a rather regular arrangement of the dots in the matrix. The main problem with the produced material is that the regular ordering appeared in small domains randomly rotated with respect to the normal to the film surface.

Our new investigation, performed at the Austrian SAXS beamline of Elettra, solved the above-mentioned problem and resulted in a further improvement of the material properties. Instead of flat substrates, we have now used periodically corrugated-rippled substrates. These substrate surfaces exhibit a very small periodicity (10-20 nm) and they can be easily produced on large surface areas by ion erosion. Fig. 1 shows an Atomic Force Microscopy (AFM) image of a rippled surface, used as substrate for the multilayer deposition. Thin films containing five, ten and twenty (Ge+SiO₂)/SiO₂ periods were simultaneously deposited onto rippled and on flat Si(111) substrates by magnetron sputtering. The Transmission Electron Microscopy (TEM) micrograph of a

multilayer containing 20 periods, taken in the direction perpendicular to the direction of the ripples is shown in the Fig. 2: the QDs appear in the valleys between the ripples, so they follow the substrate morphology. The correlation of the dot positions at different interfaces (indicated by dashed lines in Fig. 2) is visible in the whole depicted sample area showing that the dots form a large three-dimensional QD lattice. From the analysis of the TEM cross-sections taken in directions parallel and perpendicular to the ripples follows that the QDs are ordered indeed within one large domain, while small randomly oriented ordered regions appeared

previously in samples deposited on flat substrates.

The regularity of the quantum dot positions is nicely visible in the GISAXS maps of the films, shown in the right panel of Fig. 2. The GISAXS map of the rippled substrate prior to deposition shows only two lateral streaks stemming from the periodicity of the ripples. After the deposition of a 5 bi-layer film a beautiful GISAXS intensity distribution is obtained showing that the arrangement of the formed QDs follows the morphology of the rippled substrate. Increasing the number of deposited layers to ten, the lateral features in the **GISAXS** images become slightly

broader, showing a small increase in the QD position disorder with increasing number of layers. We have performed a numerical analysis and fitting of the 2D GISAXS maps obtained in different azimuthal directions of the probing beam and for films deposited on flat and rippled substrates. From this analysis follows that a rippled substrate improves the ordering of QDs and causes a narrowing of the size distribution of the QDs compared to the flat substrate.

The prepared Ge QD arrays were found to be very efficient in charge trapping, so the prepared films have good potential for usage in QDbased memories.



Figure 2. Left: transmission electron micrograph of the cross-section of a $(Ge+SiO_2)/SiO_2$ multilayer deposited on a rippled substrate taken in the direction across the ripples. The arrows indicate the correlations in the positions of the dots. Right: GISAXS maps measured on a rippled substrate prior to the deposition, and on multilayer containing 5 and 10 periods in direction perpendicular to the ripples [M. Buljan et al. Phys. Rev. B 82, 125316 (2010). Copyright (2011) by the American Physical Society].

ORIGINAL PAPER

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Seeding metal organic frameworks using ceramic nano-flaked microparticles

etal-Organic Frameworks (MOFs) may have an integral role in future catalysis, filtration and sensing applications because of their surface areas of thousands of square metres per gram, controlled pore size and distribution. In general, for MOF-based device fabrication, well-organized or patterned MOF growth is required, and thus conventional synthetic routes are not suitable. Here, we explore the use of nanostructured poly-hydrate zinc phosphate (α -hopeite) microparticles as nucleation seeds for MOFs in combination with patterns obtained using Deep X-Ray Lithography.

The ability to fabricate devices based on porous and ultraporous materials is an important technological hurdle. Metal-Organic Frameworks (MOFs) are a new emerging class of hybrid porous materials with a unique combination of porous properties (high surface area and tuneable pore size architecture, size, distribution) and customizable chemical composition. However, there is still a lack of knowledge on controlling the MOF position of growth locations. Here we present the discovery of a ceramic micro-particle which acts as exceptional seeds for MOFs nucleation. Such particles have been named "Desert Rose Microparticles" (DRMs) because of the similarity with a mineral. Once a surfactant (Pluronic F127) is added to a traditional MOF-5 precursor solution, this particular surfactant coordinates the Zn²⁺ ions and simultaneously provides an abundant source of phosphate. These factors enable the rapid formation of inorganic poly-hydrate zinc phosphate nano-flaked microparticles.

As the DRM formation precedes the growth of MOF-5, DRMs can effectively act as heterogeneous nucleation seeds for the framework crystals.

During the first 3 h of reaction, the only micron-sized species to form within the surfactant suspension are the α -hopeite DRMs of Fig. 1.



Figure 1. Scanning electron microscopy of a Desert Rose Micro-particle (DRM). Such nanostructured poly-hydrate zinc phosphate (α -hopeite) micro-particles can be used as nucleation seed for Metal Organic Frameworks (MOF-5).

After 3 h, heterogeneous nucleation of MOF-5 takes place on the nanometre-sized flakes of the DRMs to form cubic crystallites. Prolonging this growth time allows single crystal or multifaceted MOF-5 crystallites to develop, with sizes as large as 100 µm.

During a single-pot synthesis, α -hopeite DRMs can be isolated before MOF-5 nucleates, and consequently re-dispersed into a variety of solvents as exogenous nucleation seeds. When incubated in a fresh N,N-diethyl formamide (DEF)-based MOF-5 growth medium, a significant improvement in crystal quality can be achieved. The use of the nucleating agents in this case more than doubles the crystal growth rate compared with control samples. The seeded nucleation mechanism for the growth of MOF-5 can be adapted directly to solid substrates. This feature is demonstrated for α -hopeite DRMs deposited directly onto 200 nm porous alumina or silicon substrates. The immersion of this substrate into a fresh DEF-based MOF-5 precursor solution results in crystallite growth of the framework exclusively from the microparticles. Optical imaging through the focal plane of the frameworks reveals that several α -hopeite DRMs can be detected within the crystals. The existence of embedded microparticles and the truncated shape of the otherwise cubic crystals suggest a heterogeneous nucleation mechanism.

In a subsequent experiment, the DRM seeding effect was tested

using a support with a complex 3D geometry. A 100-µm thick film of commercial SU-8 resist was deposited on a silicon substrate and patterned using Deep X-ray Lithography (DXRL) at the Elettra Synchrotron, to obtain an array of high aspect ratio vertical wells (30-50 µm diameter). Under optimized conditions, more than one DRM could be deposited per well (Fig. 2a). Immersion of the DRM infiltrated surface into a MOF-5 growth solution caused framework crystals to nucleate inside the wells (Fig. 2c,d). The crystallite sizes were found to be constrained until they had outgrown

the well height, whereupon they grew freely in all directions. Further evolution of the system resulted in the merging of MOF crystals to form an interpenetrated crystalline structure (Fig. 2c).

This structure could be detached from the silicon wafer to form a free-standing support, with the channels in the SU-8 resin occupied by MOFs. Therefore, DRMs combined with DRXL has shown the capability to address a controlled growth of MOF-5 crystals in specific location. This technique opens new perspectives on MOF based device fabrication.



Figure 2. Scanning electron microscopy of Desert Rose Micro-particles used as seeds in a patterned membrane using Deep X-Ray Lithography (DXRL). a) DRMs located in a hole of the substrate after the drop-casting and drying processes. b,c) MOF-5 crystals growing within the seeded lithographed holes. The micrograph was taken after 5 h reaction time at 95 °C in the MOF-5 growing medium. d) Substrate after 10 h reaction at 95 °C. MOF-5 crystals have grown out of the seeded holes.

ORIGINAL PAPER

P. Falcaro, A.J. Hill, K.M. Nairn, J. Jasieniak, J.I. Mardel, T.J. Bastow, S.C. Mayo, M. Gimona, D. Gomez, H.J. Whitfield, R. Riccò, A. Patelli, B. Marmiroli, H. Amenitsch, T. Colson, L. Villanova, and D. Buso, *Nat. Commun.* **2**, 237, (2011)

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Tuned bandgap nanodimensional alloys: towards next generation solar cells

ruly alloyed PbS_xSe_{1-x} (x = 0-1) nanocrystals (~5 nm in size) have been prepared. Their resulting optical properties are red-shifted systematically as the sulfur content of the materials increases. The alloyed structure of the nanocrystals is confirmed by depth-profiling X-ray Photoelectron Spectroscopy (XPS) carried out at the SuperESCA beamline and by energy filtered transmission electron microscopy which show a homogeneous distribution of sulfur and selenium within the nanocrystals. XPS is also used to study the surface oxidation of the nanocrystals.

Global power consumption is currently 13 TW, and is set to double by 2050. Currently less than 1 TW of our power requirements are provided by all renewable sources, while 120,000 TW are provided from the Sun. There is an urgent requirement both to improve the efficiency of solar cells and to produce a step change in the cost of solar technology. Small nanocrystals of semiconducting material or "quantum dots" offer great potential as the light-harvesting elements in next generation solar cells, in particular because under certain conditions it is possible to generate more than one set of current carriers for every photon absorbed,

a phenomenon known as "multiple exciton generation" or MEG. Socalled "colloidal" nanocrystals, produced from solution, also offer the prospect of a cheap, low temperature synthesis. However, it has proved difficult to synthesise nanocrystals with uniform and reproducible composition, and they may be susceptible to rapid surface oxidation.

In this work, we demonstrate the production of truly alloyed PbS_xSe_{1-x} nanocrystals (NCs) of uniform composition. Because the band gap of the material varies uniformly with composition, this offers the tantalizing prospect of being able to tune the energy of the light absorbed

by the NC just by adjusting the composition. A crucially important aspect of the work is the demonstration of a uniform composition. Depth-profiling XPS at the SuperESCA beamline was used to probe the composition of the NCs, and their surface degradation. This was complemented by Transmission Electron Microscopy (TEM) carried out at the University of Manchester, UK. Compositionally-tuned PbS_Se_{1.x} NCs were prepared by adding specific amounts of sulfur and selenium (in the form of TMS or TMSe) to a PbO solution at 130 °C. Energy-filtered TEM (Fig. 1) shows NCs of around 5 nm diameter, with a homogeneous



Figure 1. PbS_xSe_{1-x} NCs, imaged using energy-filtered TEM. a) Se jump ratio map (obtained by dividing the post-edge EDAX signal by the pre-edge signal at the Se M-edge), b) S jump ratio map, obtained at the S L-edge. The white cross marks identical nanoparticles.

distribution of sulfur and selenium within the NCs. XPS confirms the S/Se ratios are close to the nominal compositions. UV absorption and photoluminescence spectroscopies were used to measure the energy gap of the NCs. This showed that the energy gap varies continuously between that of 5 nm PbSe NCs (1.4 eV) and that of PbS NCs (1.0 eV) as x is increased. This range is ideal for optimum absorption of the solar spectrum. The optical properties are red-shifted systematically as the sulfur content of the materials increases. The variation can be described by a Vegard'stype relationship with a bowing parameter of 0.190 ± 0.45 eV. Thus the energy gap can be controlled by changing the NC composition while keeping the size of the NCs constant. XPS was used to probe the surface oxidation of the NCs, using the SuperESCA beamline. Fig. 2 shows Pb 4f, S 2p and Se 3p signals obtained at the lowest photon energy used (250 eV). This gives a sampling depth (taken as 3 times the electron mean free path length) of only 1.7 nm, i.e. this experiment probes only the surface layers of the NCs. In the S 2p/Se 3p spectrum (Fig. 2b), most of the intensity lying between 167 eV and 171 eV binding energy is due to oxidation of PbS to PbSO₄ and PbSO₃. Strong oxidized components are also evident in the Pb 4f spectrum. In each case, quantification shows that around half of the signal is due to surface oxidized components. We have recently found very similar results for PbS NCs, corresponding to a surface oxidation layer of around 0.5 nm thickness (in this case, around a third of the volume of the NC).

This oxidation acts to blue-shift the optical properties as a function of NC ageing (as the core of the NC

contracts), and must be controlled if these NCs are to find application in next generation solar devices.



Figure 2. Core level XPS with component fits for 5 nm NCs of composition $PbS_{0.5}Se_{0.5}$. The photon energy is 250 eV, and the sampling depth is ca. 1.7 nm. a) Pb 4f core levels. Doublet Pb1 (blue) is due to PbSe and PbS, Pb2 (violet) and Pb3 (gold) to oxidation products. b) S 2p and Se 3p core levels. Doublet Se1 (black) is due to PbSe, S1 (red) to PbS, S2 (gold) to neutral S, S3 (green) and S4 (blue) to oxidized PbS (sulfite and sulfate).

ORIGINAL PAPER

J. Akhtar, M. Afzaal, M. Banski, A. Podhorodecki, M. Syperek, J. Misiewicz, U. Bangert, S.J.O. Hardman, D.M. Graham, W.R. Flavell, D.J. Binks, S. Gardonio, and P. O'Brien, J. Am. Chem. Soc. **133**, 5602 (2011)

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Fast fabrication of large area, nanostructured arrays out of polymers and carbon nanotubes by wet-processing

A novel, fast and low-cost wet-processing method for the creation of large area, ordered arrays of filamentary nanostructures, has been developed at the Chemistry Laboratory at Sincrotrone Trieste. The technique, named Auxiliary Solvent-Based Sublimation-Aided NanoStructuring (ASB-SANS), allows to obtain, within minutes and over areas as large as thousands of µm², ordered arrays of fibers, starting from materials as diverse as organic polymers, carbon nanotubes, ITO nanoparticles. Dimensions and topology of the fibers can be easily defined varying the deposition conditions.

When fabricating high aspect ratio nanostructures on planar substrates, wet-processing techniques are preferable to vacuum-based ones, because of lower costs and higher versatility. In particular, patterns of nanofibers can be obtained by self-assembling, contact printing or electrospinning, but these methods do not allow to achieve features homogeneity over areas as large as thousands of μ m² in reasonable times and at acceptable costs. A novel, fast, low-cost and versatile wet-processing method for the creation of large area, ordered arrays of filamentary nanostructures has been developed in the Chemistry Laboratory of Sincrotrone Trieste. The technique, named Auxiliary Solvent-Based Sublimation-Aided NanoStructuring (ASB-SANS), is applied as depicted in Fig. 1, and exploits an organic crystal able to sublimate (SS) as a templating matrix for the material to be structured/ patterned (Target Material, TM). Both materials are dissolved in an appropriate auxiliary solvent (AS).



Figure 1. Sketch of the ASB-SANS process. The Target Material (TM, green spheres), the Auxiliary Solvent (AS, blue liquid in the beaker) and the Sublimating Substance (SS, red cubes) are mixed together (step a) to form a homogeneous ternary solution (step b), which is deposed onto a substrate (step c). After the evaporation of the AS (step d) and of the SS (step e), the nanostructured TM is left onto the substrate (step f). Arrays of parallel fibers, interconnected (path I) or well separated (path II), depending on the used SS/TM ratio, are obtained.

This approach allows to deposit the desired TM on any substrate and in a liquid form, which in turn enables the use of widely available deposition techniques, like for example inkjet printing, spray coating, and so on. The process can be carried out at room temperature and ambient pressure. The proper choice of the AS and SS allows an extreme versatility in terms of patternable TMs. In particular, proof-of-concept of these principles was demonstrated presenting patterns fabricated within minutes out of organic polymers

(Fig. 2a and Fig. 2b) and carbon nanotubes (Fig. 2c and Fig. 2d). The so-developed patterns cover several hundreds, or even thousands, of µm² of the substrate with a notable homogeneity. The size of the obtained features can be controlled varying the growth conditions, in particular the SS/TM ratio, allowing to tune the fibrous pattern dimensions from a few tens of nm to a couple of mm. Also the topology of the fabricated patterns can be controlled in this way, switching easily from connected to isolated fibers arrays (Fig. 2).

Using synchrotron light, investigations are being carried out on the effects of the ASB-SANS process on the crystallinity of polymers. Applications of this technique in fields as different as tissue engineering, energy storage or nanoelectronics are possible, and are currently under scrutiny. Overall, the reported results, achieved in very simple fabrication conditions (i.e., no use of clean rooms or of sophisticated deposition techniques), suggest that ASB-SANS may become a widely diffused nanostructuring technique.



Figure 2. SEM photos evidencing the effects of the ASB-SANS process on poly(methylmethacrylate) (a and b) and carbon nanotubes (c and d). Independently from the considered TM, low SS/TM ratios deliver arrays of interconnected, parallel fibers (a, c), while high TM/SS ratios (b, d) allow to obtain arrays of still parallel, but well separated, fibers. Scale bars: a, 10 µm; b, 2 µm; c, 20 µm; d, 10 µm.

ORIGINAL PAPER

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Valence band photoemission of the Zn-phthalocyanine/Ag(110) interface: charge transfer and scattering of substrate photoelectrons

The valence band region of organic/metal interfaces formed by depositing Zn-phthalocyanine molecules on Ag(110) are studied using high-resolution ultra-violet photoemission spectroscopy at the BaDElph beamline. For the ordered first monolayer, we find an interface state related to charge transfer which leads to the partial filling of the lowest-unoccupied molecular orbital. Important changes in the spectral region of the Ag 4d bands are attributed to the indirect effect of the ordered monolayer on the changed escape conditions of substrate bulk photoelectrons (surface umklapp).



Figure 1. Left panel: UPS spectra showing the evolution of the low-energy region of the valence band of ZnPc/Ag(110) for increasing ZnPc coverage, starting from the clean Ag(110) (normal emission, hv = 21 eV). Right panel: Valence-band angle-resolved UPS spectra (hv = 21 eV) of (upper panel): pristine Ag(110) and (lower panel) 1 monolayer ZnPc/Ag(110), for three light incidence angles ($\zeta = 50^{\circ}$ corresponds to normal emission $\theta = 0^{\circ}$). The lower panel also shows the UPS spectrum from a polycrystalline Ag sample at hv = 21 eV (figure adapted from L. Giovanelli et al., Phys. Rev. B **82**, 125431 (2010)).

Recent impetus in the field of organic electronics is paving the way for the next-generation nanolectronic devices. In this context, organic ultra-thin films deposited on singlecrystalline metal surfaces are currently a fertile testing ground for a range of specific electronic properties related to an eventual charge transfer between π -conjugated molecules and the metal. Electron spectroscopies are fundamental tools to explore their electronic properties. In particular, Ultraviolet Photoelectron Spectroscopy (UPS) is sensitive to tiny modifications of frontier molecular orbitals and the appearance of hybrid interface states. Among the π -conjugated molecules known as organic semiconductors, the planar Metal-Phthalocyanines (M-Pc) are flexible molecular building blocks since their optical, electronic and magnetic properties can largely be tuned, e.g. through the choice of the central metal atom. Moreover, the presence of a doubly-degenerate Lowest-Unoccupied Molecular Orbital (LUMO) opens a whole range of complex fundamental effects related to a partial LUMO-filling upon electronic doping. For example, recent theoretical studies have suggested that electron-doping of non-magnetic M-Pc may result in correlated systems resembling those of doped fullerenes. In particular, close to LUMO halffilling, a metallic state would be the precursor of a superconducting phase which has not, up to now, been observed by UPS. Electron doping of M-Pc may be realized at organic-metal interfaces upon charge transfer from the substrate. The present work deals with high-resolution UPS measurements of the ZnPc/Ag(110)interface electronic properties

obtained at the BaDElph beamline. The ordered ZnPc/Ag(110) interface shows intriguing behaviour and specific electronic and vibrational properties with respect to a thick film, e.g. the presence of Ramanactive modes coupled to electronic interface states. We have compared the spectral features in the Valence Band Density-Of-States (VBDOS) characteristic of the clean substrate, the thick molecular film and the interface.

Zooming in the low Binding Energy (BE) region, in addition to the molecular HOMO above 1.5 eV, a feature attributed to interface states specific to the first-layer molecules appears following a charge transfer from the substrate to the LUMO (Fig. 1 left panel). This LUMOderived interface state is a clear fingerprint of the molecule/substrate interaction, which is likely to be of a covalent nature with a sizeable charge transfer. The presence of such a low-lying finite DOS may explain the observed vibrational features in the framework of a dynamical charge-transfer model, but the spectral shape is rather peaked at about 0.3 eV below E_r. Due to the presence of a substrate contribution up to this energy, it is not yet clear whether the DOS related to the partly-filled LUMO actually extends up to the Fermi level. This behaviour is at variance with the clear DOS increase at E_r for other molecular monolayers like C₆₀ on noble metals. Another kind of prominent features is promoted by the molecular adsorption, lying in the substrate

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Ag 4d bands emission region where the sensitive angle-dependence observed for the pristine substrate is lost (Fig. 1 right panel). Although it would be tempting at first sight to assign these features to new interface states, we argue that they are completely understandable by considering the diffraction of substrate VB photoelectrons by the ordered monolayer. The latter provides new 2D reciprocal lattice vectors which are able to fold back bulk direct transitions which appear in off-normal direction to normal emission, a phenomenon known as "surface umklapp". Due to the large molecular lattice parameter, a whole range of 2D reciprocal vectors are able to affect the escaping photoelectron, which leads to an effective averaging of direct transitions from several directions of the Ag 3D Brillouin zone. The resulting UPS line-shape accordingly reflects an averaged Ag 3D DOS which mimics the emission from a polycrystalline Ag sample (Fig. 1 right panel). In conclusion, we show that the presence of the molecular 2D overlayer changes the escape conditions of the photoelectrons emitted from the Ag substrate through surface umklapp. The strong Ag-derived features appearing throughout the valence band should not be confused with eventual genuine interface states characteristic of a covalent or charge transfer molecule/substrate interaction. We have indeed also detected such a state near the Fermi level of the ZnPc/Ag(110).

ORIGINAL PAPER

L. Giovanelli, P. Amsalem, T. Angot, L. Petaccia, S. Gorovikov, L. Porte, A. Goldoni, and J.-M. Themlin, *Phys. Rev. B* **82**, 125431 (2010)

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Bottom-up approach towards titanosilicate mesoporous pillared planar nanochannels for nanofluidic

anofluidic transport in lab-on-chip devices requires nanochannels that are difficult to fabricate. We present an alternative to construct large areas of extremely homogeneous Pillared Planar Nanochannels (PPNs) for nanofluidic applications, which are made of mesoporous titanosilicate pillars, 20 nm in diameter, supporting a continuous sealing layer of the same material. They have been characterized with small angle X-ray scattering. This complex hierarchical structure is achievable when combining diverse bottom-up processing strategies with powerful top-down techniques such as deep X-ray lithography.



they require challenging top-down technological approaches. We present a bottom-up, scalable, low-cost and robust alternative to construct large areas of mesofluidic Pillared Planar Nanochannels (PPNs). Microscopy images displayed in Fig. 1 are representative of the whole system, and show the typical PPN layers made of dense and mesoporous materials organized into vertical nanopillars supporting a continuous roof. Such conformation is homogeneously present all over the coated substrate. They have been obtained upon combining self-assembly of block copolymer, nanostructured solgel coatings and highly controlled liquid deposition processing. The mesoporous structure contains two types of porosity. The first one is the fully open and accessible interpillar porosity with characteristic dimensions adjustable between 20 and 400 nm, which is necessary to allow facile diffusion despite the double layer effect. The second one is present inside the pillars and the roof, and is composed of less than 10 nm pores, which aim at increasing the surface area. Both layer structures have been characterised by Grazing Incidence Small Angle X-ray Scattering (GISAXS). Pillar ordering can be assessed by GISAXS analysis as shown in Fig. 2 for F127-templated titanosilicate systems.

Nanofluidics transport in lab-onchip devices requires nanochannels that are difficult to fabricate since



The intense Bragg diffraction signal at $q_v = 0.14 \text{ nm}^{-1}$, together with its first harmonic at $q_v = 0.28 \text{ nm}^{-1}$, is associated to both (01)p and (02)p diffractions of the highly ordered 2D lateral hexagonal structure formed by the pillar array with a corresponding inter-pillar distance of 51 nm (d(01) = 44 nm). The latter dimensions can be found on TEM and SEM images whatever the type of inorganic material used for impregnation. The fact that the (01)p diffraction has a vertical tail (diffraction rod) extending only in the z direction, suggests a high degree of vertical alignment of the pillars. For the F127-templated titanosilicate layers, the GISAXS

diagram (Fig. 2) exhibits, together with the previous (01)p diffractions of the pillars at low q, the characteristic (110)m, (101)m and (1-10)m diffraction points of the Im3m mesostructure, revealing that the nanoporous network is composed of a contracted body centred cubic arrangement of pores with extended domains having the [110] direction normal to the surface. The lateral periodicity is found to be 14.5 nm, which corresponds to the structure obtained for plain continuous films, for which pores sizes were deduced from ellipsometry porosimetry to be around 6 nm. The high order structure is clearly observed in SEM and TEM, see the corresponding

images in Fig. 1c-f. Interestingly, the SEM image 1c reveals that the pillars do not have the same texture as the roof. The TEM image of Fig. 1f, 1g, shows that the pillars are actually hollow cylinder (tubes) below the roof.

These pillared planar nanochannels showed the ability to vehicle fluids in the inter-pillars porosity through natural capillary forces, for which the classical Washburn model of diffusion is verified. In addiction PPNs are compatible with lithography techniques, such as deep X-ray lithography, for the production of complex designs and thus demonstrating to be ideal candidates for micro/nano fluidic applications.



Figure 2. GISAXS pattern of Im3m mesoporous (F127 templated) 10%SiO₂-90%TiO₂ mesofluidic pillared planar nanochannels.

ORIGINAL PAPER

M. Faustini, M. Vayer, B. Marmiroli, M. Hillmyer, H. Amenitsch, C. Sinturel, and D. Grosso, *Chem. Mater.* **22**, 5687 (2010)

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Non destructive XRD investigations on grisaille paint layers on stained glass windows

A comprehensive study of the alteration products in grisaille paints is very important to understand the complex processes involved in the decay of this type of glass decoration. An exhaustive characterization of these products and so a full understanding of the mechanism of their formation may lead to the development of new protective materials for conservation and restoration. Non destructive and innovative XRD experiments on the MCX beamline allowed us to recognize the alteration products on the grisailles surface and to propose a mechanism for the formation of alteration patinae.

Since the end of the XIX century the study of glass corrosion and its weathering products was considered of great interest for cultural heritage science. In the last decades the interest of the scientific community was mainly focused on the characterization of glass corrosion products, their formation processes, and on the development of new systems for the protection of the glass surface. An interesting and breaking research field, still nowadays almost unexplored, regards the investigations on stained glass windows alteration, especially on those painted by the grisaille method. Grisaille can be defined as a painting mixture formed by a finely powdered pigment (mainly



Figure 1.Stained glass windows fragment SSGP1; The XRD patterns a) and b) were collected in section a), and b) respectively.

transition metal oxides) and highly fusible glass (lead rich glass) forming a coloured layer applied on the glass surface, the adherence to the glass being guaranteed by a low temperature firing of the grisaille without melting the glass support. From a chemico-physical point of view, the obtained material is a system in which the crystalline phases (pigments) are embedded in an amorphous phase (low melting glass) which acts both as a dispersing medium and as an agent fixing the pigments onto the substrate (the stained glass window). The interaction of this surface with the environment (i.e. the effect of pollutant agents) promotes the formation of alteration crusts involving both the grisaille paint layer and glass window surface. The aim of the present article deals with the characterization of the alteration products of ancient and modern grisaille paint layers. The understanding of the complex chemical and structural nature of alteration products leads to an exhaustive comprehension of the deterioration processes and will be helpful to propose a correct project for the conservation and restoration of grisaille stained glass windows. Non invasive and non destructive X-rays diffraction, performed by synchrotron light, is a perfect tool to obtain information on these products. The possibility to use an X-ray beam focused on a small area of the surface of the sample allows the investigation of very small fragments and its high

brilliance allows the collection of a highly resolved XRD pattern. The MCX beamline has the possibility to use a relatively large sample holder and for this reason it is very suitable for cultural heritage non destructive investigations. In spite of this valuable opportunity, this technique is still very seldom used and so the results we report may be considered as very innovative and rich of consequences. The experiments were performed on two different sets of fragments: the first one (5 fragments) belongs to the stained glass windows of the XV century Basilica of SS. Giovanni e Paolo in Venice, while the second one (2 fragments) to the XX century church of San Giovanni in Polegge (Vicenza). In the present paper we will focus our attention only on SS. Giovanni e Paolo sherds, hereafter SSGP, showing the most interesting results. These fragments, with dimensions included between 4 and 50 cm², present the painted surface partially or totally covered by blackbrownish to white crusts. Chemical analyses were performed by using a non invasive and transportable Bruker AXS Artax µ-XRF spectrometer. XRPD pattern were collected in grazing angle geometry in the 5-60 2θ range, with a step size of 0.01° and exposure time of 1 sec and λ of 1.319 nm. The glass composition for the main element of all the fragments is similar, and the difference among them regards only the presence of different chromophore metals. Fig. 1 shows fragment SSGP1, a green glass

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painted with a dark grisaille and partially covered by a brown-whitish patina. XRPD pattern collected on the dark grisaille, section a) in Fig. 1 shows the presence of CoAl₂O₄, together with CaSO₄, BaSO₄ and lead hydroxychloride, Pb(OH)Cl. The color of cobalt aluminate, a deep blue pigment, which turned to dark, may be due to candle soot deposition or to the overfiring of the glass during the fixing process. The presence of CoAl₂O₄ is almost surprising, because the pigment was first synthesized in the XVIII century; this evidence is indicative of a substitution/restoration of the original XV stained glass windows. Furthermore, the analysis performed on the white patina, section b) in Fig. 1, reveals also the presence of sulphates, CaSO₄, PbSO₄, and of iron oxyhydroxides, FeOOH. Similar results were obtained for the other fragments, in which sulphates are the predominant species on the alteration patinae. On the basis of these evidences, a deterioration mechanism can be proposed. An aggressive environment with large thermal variation, typical of the Venice lagoon, can promote microcracking on the grisailles surface. These micro-breaks, together with the natural roughness of the grisailles layer, may favour the condensation processes on the surface. In this way, the formation of a deterioration-induced porous system can act as a series of micro-reactors for leaching phenomena with the subsequent salt precipitation.

ORIGINAL PAPER

R. Bertoncello, B. Dal Bianco, A. Lausi, L. Nodari, J.R. Plaisier, E. Rebollo, U. Russo, and A. Vezzoli, *The alteration processes in stained glasses: a comparison between modern and ancient Italian stained glass windows*, presented at SR2A-2010, Amsterdam, The Netherlands, 7-10 November 2010

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Elastic properties, residual stress and texture gradients in protective nickel coatings

The bending magnet beamline MCX at the Italian synchrotron Elettra offers a perfect design and geometrical set-up for residual stress and texture analysis by X-ray diffraction. The high brilliance of synchrotron radiation reduces considerably the acquisition time of standards $\sin^2\psi$ -plots for stress analysis, while the possibility of using different beam energies allows the study of property gradients. This work presents an example of application of X-ray diffraction to the study of residual stress and texture gradients in electrodeposited nickel coatings.

Thin films and coatings often show preferred crystalline orientation and a residual stress state as a consequence of the competitive grain growth process taking place during the deposition on the substrate. Moreover, as the film thickness increases and substrate ceases to directly interact with newly formed layers, gradients of preferred orientation and stress can be generated.

Residual stress and texture measurements are conveniently performed by means of X-ray diffraction, as the technique is contact-free and non destructive, hence it does not alter the sample during the observation. However, diffraction does not measure stresses directly, but rather strains. To retrieve the former, an appropriate constitutive equation needs to be applied, implying knowledge of the material's elastic properties and mechanism of grain interaction. The task is made complicated by possible preferred orientation and properties gradients, as well as by the lack of a priori information on the specific properties of the thin film, which are frequently different from those

of the corresponding bulk materials. So far, fairly complex models have been proposed to account for the elastic grain interaction in thin film residual stress analysis, but the agreement with the experimental data, in many cases, is still poor. An elegant solution consists of performing in-situ mechanical testing on specimens during X-ray diffraction strain measurement, so to allow a simultaneous determination of residual stress and elastic constants, thus providing a complete outlook of the component's mechanical properties.



Figure 1. Measured 2θ -sin² ψ map for E=8.3 keV (left) and intensity contour plots for both energies (right). Pole figures sections for the (200) reflection (centre).

When a gradient of either stress or texture is present, characterization is further complicated by the introduction of additional degrees of freedom. The issue can be addressed by repeating a measurement using differently penetrating X-rays, so to modulate the thickness of the sampled volume. As beam absorption is a function of energy, repeating a measurement using different photon energies allows reconstructing the property gradient over material thickness. Whereas conventional X-ray sources produce monochromatic radiation, synchrotron light covers a broad wavelength range; photon energy can be easily selected by employing a single crystal double mirror, tilted by a suitable angle.

A material's linear absorption coefficient generally decreases as a function of photon energy. However, sharp changes are found across the absorption edges. In other words, beam penetration depth can change by an order of magnitude or more within a few eV. This can be exploited to study property gradients: when a measurement is repeated just above and just below the material's main constituting element absorption edge, a layer of very different thickness is involved in diffraction, but also almost identical instrumental conditions apply. This is especially useful when a comparison between data sets is presented, as the need for accurate corrections for instrumental effects is loosened.

As a case study, stress and texture gradients were measured on an electrodeposited nickel coating on steel. These coatings are very common in corrosion protection applications, and constitute an ideal case study as their residual stress state, as well as preferred orientation of crystalline domains sensibly vary as a function of deposition conditions. In this case, the 20 µm thick film was deposited in a standard Watt's bath, under pulsed current and continuous solution stirring to promote homogenization and minimize porosity. X-ray stress and texture measurements (Fig. 1) have been repeated using an incident beam photon energy of 8.3 and 8.4 keV, respectively (the K absorption edge of nickel being 8.33 keV). Measurements showed that, while a slight texture gradient can be appreciated after observing the pole figure peak width decreasing with beam penetration, a stress gradient is non-existent (Fig. 2). This information, which would have been impossible to achieve with conventional laboratory instruments, provides useful feedback to the coating technologists, to optimize the deposition process and resulting properties of the protective coatings.



Figure 2. $sin^2 \psi$ -plot for the (220) reflection at 8.3 keV (filled squares) and 8.4 keV (empty circles). Connecting lines are shown as a guideline for the eye.

ORIGINAL PAPER

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Highly anisotropic Dirac cones in epitaxial graphene modulated by an island superlattice

e present a new method to engineer the band gap, charge carrier mobility and its directional dependence in epitaxial graphene by using metal cluster superlattices self-assembled onto the moiré pattern formed by graphene on Ir(111). Angle-Resolved Photoemission Spectroscopy (ARPES) at the VUV photoemission beam line reveals three-fold symmetry in the band structure associated with strong renormalization of the electron group velocity close to the Dirac point giving rise to highly anisotropic Dirac cones. Moreover, the cluster superlattice widens the band gap between Dirac cones.



Figure 1. a) Sketch of the π -band for g/Ir(111) close to K-point and Fermi level $E_{\rm F}$. The Dirac cones are mostly symmetric and only a small gap opens at K-point. b) STM image of the moiré structure of g/Ir(111). c) ARPES intensity of the p-band of g/Ir(111) around the K-point and along the ΓK direction and perpendicular to it. d) Sketch of the π -band for Ir/g/Ir(111). The cluster superlattice induces a strong anisotropy in the Dirac cones and the opening of a large gap at K-point e) STM image of Ir cluster superlattice grown on g/Ir(111) ($\theta = 0.15 \text{ ML}, T_{dep} = 375 \text{ K}$). f) ARPES intensity of the π -band for Ir/g/Ir(111). In c) and f) the dots represent the peak positions of the momentum distribution curves.

Graphene (g) is a 2D honeycomb lattice made of carbon atoms with the conduction electrons in sp²-hybridized Bloch states. Its exceptional charge carrier mobility and optical transparency of 98% make g an ideal material for fast transistors and for solar cell top electrodes, respectively. Close to the K points of the Brillouin zone, the bands have a linear dispersion that is well described by the relativistic Dirac equation for massless neutrinos. The resulting Dirac cones of the conduction and valence bands touch each other at their summits at the Dirac point located at the Fermi level E_r. Therefore, freestanding g is a zero-gap semiconductor with symmetric π – π * bands (cones) close to the K points. However, most electronic device applications require a band gap. Moreover, the speed with which information can be transmitted along g depends on the charge carrier group velocity. For this reason an issue equally relevant for applications is the ability to create and tailor anisotropies in the g band dispersion.

Theory has suggested that band gap and anisotropies in the group velocities may derive from an external long-range periodic potential. Such a potential is created when putting graphene onto a lattice mismatched closepacked metal surface. The resulting moiré structures exhibit periodic stacking alternations between C rings localized on top of metal atoms, implying that both C atoms of the g unit cell are on substrate hollow sites, and C rings centred above one or the other of the two non-equivalent substrate hollow sites, implying that either one of the two C atoms is localized on top of a substrate atom. The g-substrate binding has a significant van der Waals contribution; however, directed chemical bonds can be formed where C atoms are on top of substrate atoms. Their strength depends on the substrate; on Ir only a weak covalent bond forms resulting in g slightly corrugated and "floating" above the Ir(111) surface. For the same system it has been shown that adsorbing metal clusters on top leads to a local sp³ hybridization with one C atom binding to an Ir substrate atom below and the other to an Ir cluster atom on top. This is expected to strongly enhance the corrugation of the electron potential. Fig. 1 shows our ARPES and STM results for g/Ir(111) and Ir clusters on g/lr(111) together with sketches of the respective systems. For g/lr(111) (upper panels) the ARPES data reveal a weakly perturbed π

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Brillouin zone with the Dirac point at $E_{\pi} = (-70 \pm 20)$ meV. Assuming charge neutrality, this implies a small gap $E_{g,g/lr} = (140 \pm 40)$ meV. The ratio of the group velocities along the gK and pTK direction is with $v_{\rm TK} / v_{\rm pTK} =$ (16 ± 2) % very close to the value $v_{\rm rK} / v_{\rm prK} = 5\%$ expected for unperturbed g due to the trigonal warping. The small difference is the result of the soft periodic potential resulting from the moiré alone. On the contrary, on Ir/g/Ir(111) (lower panels) the cluster superlattice potential induces a strong group velocity anisotropy together with a significant band gap opening. ARPES data in Fig. 1e give group velocities of $V_{\Gamma K} = (4.90 \pm 0.06) \text{ eV Å and}$ $V_{\rm pFK} = (2.90 \pm 0.05) \text{ eV Å},$ corresponding to an anisotropy of $v_{\rm rK} / v_{\rm prK} = (70 \pm 5)$ %. This value is 12 times larger than the anisotropy expected for unperturbed g. Moreover, the Ir cluster superlattice shifts the π summit down to $E_{\pi} = (-200 \pm 20)$ meV, while the $\pi^{\hat{*}}$ -band stays above E_{F} . For the cluster lattice a small charge transfer was observed. We find that the C 1s level shifts down by (30 ± 30) meV and the top of the s-band at the M point of the second Brillouin zone by the same amount. With $E_D = -30$ meV, we find $E_{g' lr/g/lr} = 340 \text{ meV}.$

ORIGINAL PAPER

Dirac cone at the K-point of the

S. Rusponi, M. Papagno, P. Moras, S. Vlaic, M. Etzkorn, P.M. Sheverdyaeva, D. Pacilé, H. Brune, and C. Carbone, *Phys. Rev. Lett.* **105**, 246803 (2010)

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SURFACE SCIENCE AND CATALYSIS

Pentacene film on Cu(119)

The molecular structure of thin pentacene film grown on a Cu(119) surface has been studied by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and Scanning Tunnelling Microscopy (STM) at beamline APE. The interaction between the π -molecular orbitals delocalized on the aromatic rings and the underlying copper substrate was established with C 1s NEXAFS spectra. The present study demonstrates that highly ordered pentacene films can be obtained on Cu(119) vicinal surface both in a flat orientation for low coverages and in a bulk-like herringbone orientation for higher coverages.

Substantial research has sought to understand the diverse structural and electronic properties of the molecular films grown on insulator and metallic substrates since molecular films are increasingly implemented as constituent of electronics devices (organic transistors, solar cell, etc.). Polyacenes, π -conjugated organic molecules, made up of benzene rings, are promising candidates among other molecules, since conjugation provides a good conduction channel. Furthermore, the small size of the molecule permits a joint experimental and

theoretical research approach. The growth mode of the molecular film has been demonstrated to affect its final electronic structure and transport properties. Pentacene has attracted the interest of the scientific community because of its highly anisotropic charge transport and high carrier mobility. In bulk phase, pentacene has a layered herringbone-like structure, whereas at interfaces with single crystalline substrates the first layer molecules lie down when deposited on strongly interacting metallic surfaces and stand up when deposited on weakly interacting substrates.

We investigated the growth of pentacene film on Cu(119) by NEXAFS spectroscopy and STM, with the aim to determine the molecular orientation at the surface of pentacene at subsequent stages of deposition from the interface layer to a multilayer thickness and to clarify the role of polyacene-substrate and molecule-molecule interactions in the formation of organic films. We reported in Fig. 1 the STM images relative to pentacene film of thickness of 4 nm and > 4 nm. A dense packed molecular structure with the molecules aligned along the step directions is observed up



Figure 1. (a-c) STM images of pentacene film of thickness 4 nm (a) and > 4 nm (b-c). The pentacene unit cell is drawn in panels (a) size: 7.5 x 18 $Å^2$, (c) size: 7.4 x 6.5 $Å^2$; (d) Pentacene growth mode scheme for Cu(119) surface.

to a thickness of 4 nm (Fig. 1c). A two-dimensional unit cell contains one molecule and has dimensions of $a = 7.5 \pm 0.8$ Å, $b = 18 \pm 0.8$ Å. Hereafter, we will refer to this growth mode of pentacene on Cu(119) as phase A.

At coverage > 4 nm we observe a different ordered structure (Fig. 1b, 1c). The molecules appear as elongated balls with a well defined periodic arrangement. The denselypacked film arranges in rectangular adsorption structure with molecules oriented upright with respect to the substrate surface. We define a unit cell between nearest neighboring molecules and measure the lattice parameters of 7.4 x 6.5 $Å^2$ as indicated in panel c of Fig. 1. Each cell contains 2 pentacene molecules. Fig. 1d illustrates the molecular growth mode on Cu(119) in phase A and phase B.

Fig. 2 shows representative C 1s NEXAFS spectra for free pentacene

in gas phase (blue curve in panel a) and pentacene films on Cu(119) of thickness 4 nm (red curve) and > 4 nm (black curve). Likewise other polycyclic hydrocarbons, the NEXAFS spectra of pentacene films are characterised by two different energy regions: the first below 290 eV is relative to the 1s- π^* transitions; at higher photon energies are due to the transition 1s- σ^* transitions. NEXAFS line shape from the monolayer (0.3 nm) up to 4 nm thick films is similar. In the case of a monolayer the hybridization with copper induced the modification of the aspect of 1s- π^* transition. This hybridization is certainly limited to the interface layer, but the intra layer bondings of pentacene in the A phase remains strong up to a critical thickness. NEXAFS line shape relative to phase B is similar to the one of pentacene in gas phase, i.e. typical of less interacting molecules.

Angle dependent C 1s NEXAFS indicates a molecule tilting angle α of 5° for (2 and 4 nm thickness) and angle ~10°, i.e. the molecules are oriented almost parallel to the surface. On the other hand, angle dependent C 1s NEXAFS for pentacene of thickness > 4 nm gives the evidence of upright orientation of the molecules.

The growth of pentacene on Cu(119) is characterized by a strong interface interaction stabilizing the first pentacene layer in a dense line-wave geometry that is followed by a few layers of dense flat lying molecules (phase A), progressively acquiring some tilt both with rotations about the long axis and about the short axis. Beyond 4 nm a substantial part of the film converts to an upright geometry (phase B) including both the newly deposited pentacene molecules and partially those from the topmost layers of the phase A.



Figure 2. C 1s NEXAFS spectra of pentacene in gas phase (blue line) and pentacene films on Cu(119) of thickness 4 nm (red curve) and > 4 nm (black curve).

ORIGINAL PAPER

E. Annese, I. Vobornik, G. Rossi, and J. Fujii, Langmuir 26, 19142 (2010)

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A link between corrugation and thermal stability of epitaxial graphene

We report about a novel approach, based on the combined use of synchrotron radiationbased techniques and DFT calculations, to investigate the link between the corrugation of epitaxial graphene on Re(0001) and its thermal stability. Our results prove that graphene on Re(0001) is strongly corrugated, and point out an unambiguous relationship between corrugation and thermal stability. In fact, the high temperature disruption of the carbon network, which is mediated by diffusing vacancies, turns out to be more likely in the buckled, strongly interacting regions of the moiré cell.

In the last few years, epitaxial graphene has attracted a staggering interest in the fields of nanotechnology due to its outstanding properties. It is acknowledged that the strength of the graphene-substrate interaction and its thermally-induced modifications can deeply affect not only the electronic, chemical and geometrical structure of the carbon layer, but also its heat transport properties.

In this respect, graphene corrugation plays a key role in determining the properties of the carbon sheet and its high temperature stability. In supported graphene, corrugation arises from the strain caused by the lattice mismatch between the carbon network and the substrate, which leads to the formation of a moiré long-range periodic superstructure. Our work focuses on the investigation of the properties of epitaxial graphene on Re(0001). The combined use of core level photoelectron spectroscopy and Density Functional Theory (DFT) allowed us to pinpoint a clearcut link between corrugation and thermal stability and to shed light on the microscopic mechanisms involved in the carbon layer breakup.

The single-layer graphene sheet on Re(0001) is uniform and well-ordered on a large scale, as proved by the Low Energy Electron Microscopy (LEEM) images (Fig. 1b). The C 1s core level spectrum of the graphene-covered surface is reported in Fig. 1d. The spectrum shows two main components, which is typically the hallmark of a strongly-interacting graphene/metal system. Ab initio DFT calculations performed on a (10×10)/(9×9) moiré unit cell (according to the stoichiometry suggested by electron diffraction measurements (Fig. 1a)) revealed that the carbon layer is strongly corrugated (Fig. 1c), with C-Re distances ranging between 2.1 and 3.8 Å and a buckling of ~1.6 Å. Interestingly, the computed C 1s core level binding energies of the 200 C atoms in the cell show a clear dependence on the C-Re distance: the closer a C atom is to the metal surface, the higher its Binding Energy (BE) is.



Figure 1. (a) LEED pattern of graphene/Re(0001). (b) LEEM image of the graphene-covered substrate, showing the long-range order of the C film on the surface. (c) Top and side views of the simulated structure (the color scale reflects the C-Re distance). (d) Comparison between the experimental (empty circles) and the simulated C 1s spectrum (solid line); below is shown the calculated spectral distribution originated by the 200 C atoms.

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Starting from the calculated BE, we subsequently fitted the experimental spectrum to a convolution of 200 components: the agreement between experimental and theoretical data (Fig. 1d) proves that what lies beneath the two-peak shaped spectrum of graphene is actually an almost continuous distribution of the C-Re distances.

The determination of graphene corrugation provided us the starting point to address the issue of thermal stability.

Annealing graphene to high temperature (>1000 K) leads in the initial stage to a substantial depletion of the high BE C 1s component, leaving the peak at lower BE almost unaffected (Fig. 2a,b). We performed a series of experiments at different temperatures, in order to monitor the evolution of the high BE C 1s component and measure its temperature-dependent decay rate. From the Arrhenius plot of these data, we estimated an effective activation barrier for C-C bond breakup of 3.5 ± 0.7 eV. In order to shed light on the mechanisms of carbon layer disruption we used DFT. As it turned out, a realistic reaction path

involves the formation of carbon vacancies, which can diffuse at 1100 K from the weakly to the strongly interacting regions of the moiré cell (Fig. 2c). In the presence of diffusing vacancies, the overall barrier for C-C bond breaking in the strongly interacting parts amounts to 4 eV, which matches the experimentally estimated value. In conclusion, our work

highlighted a clear correlation between graphene corrugation and its thermal stability, a key achievement especially in sight of the high temperature applications of supported graphene.



Figure 2. (a) Evolution of the C 1s spectrum during annealing of the graphene-covered substrate at 1100 K. (b) Intensity decay of the two C 1s core level components (S = strongly, W = weakly interacting) during the annealing. (c) Simulated reaction path for graphene layer breaking in the presence of diffusing vacancies. Initial-, Transition- and Final-states are reported.

ORIGINAL PAPER

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In situ X-ray spectromicroscopy investigation of the stability of SOFC metal interconnects in operating electrochemical cells

e studied electrochemical processes occurring in Cr/Ni bilayers in contact with Yttria-Stabilized Zirconia (YSZ), in order to gain molecular-level understanding of durability issues of Solid-Oxide Fuel-Cell (SOFC) interconnects. We demonstrate the potentiality of SPEM and micro-XPS in following the evolution of chemical state and local elemental distribution, as a function of applied potential in a cell working at 650 °C in 10⁻⁶ mbar O₂ ambient. We pinpointed temperature-induced and potential-dependent diffusion and oxidation-reduction of Ni and Cr resulting in specific morpho-chemical dynamics.



Figure 1. (A) Sketch of the cell and experimental set-up. (B) Evolution of Ni and Cr distributions under different reaction conditions. The sketches summarize SPEM results: the arrows indicate the Ni (white) and Cr (black) spreading directions. The dashed-white lines indicate the initial patch borders. (a) Room temperature, initial state; (b) 650 °C, open-circuit; (c) 650 °C, biased; (d) 650 °C, open-circuit at the end of the experiment. (C) XPS spectra taken, under electrochemical control, at the Cr and Ni patches of the cathode side and inside the YSZ electrolyte close to the Ni patch.

SURFACE SCIENCE AND CATALYSIS

The efficiency, environmental friendliness and prospective fuel flexibility of Solid-Oxide Fuel-Cells (SOFC) makes them attractive energy generation systems. Notwithstanding the appeal of this technology, a major drawback militating against large-scale implementation of SOFCs is durability, crucially impacted by material degradation. In particular, interconnects, which provide physical separation between the air and fuel, in addition to electric connection between the anode and cathode of adjacent cells, are one of the critical components of SOFC stacks. The reduction of operating temperature to and below ~750 °C has allowed replacement of ceramic interconnects with more convenient Fe-, Cr- and Ni-based alloys, chiefly ferritic stainless steels. Use of this material is nevertheless yielding problems owing to the release of volatile Cr-species that poison the catalysts as well as to the formation of resistive oxides. In the study of the degradation of SOFC materials, using benchmark characterization schemes that mimic SOFC processes is not sufficient, since a real device entails multiple processes at different length scales and reacting interfaces that may be imbedded and not always accessible to analytical tools. For this reason, the development of in situ X-ray based approaches offers unique opportunities of gaining an insightful understanding of the physical chemistry underlying durability issues. In order to carry out SPEM measurements at ESCAmicroscopy, we fabricated a

cell containing the chief components of an SOFC (Fig. 1A): Cr represents the interconnect, Ni is the catalyst and YSZ is the electrolyte. Electrochemical experiments in the SPEM chamber were run at 650 °C in O_2 10⁻⁶ mbar.

Fig. 1B (a-d) illustrate the evolution of the device after heating, followed by voltage application; the sketches in each panel summarize the events occurring under different conditions. The SPEM images in Fig.1B (a) prove that the initial state has well defined Cr and Ni patches. Fig. 1B (b-d) report the elemental distribution across the cell, evolving upon heating and electrochemical polarization. As a result of annealing without bias, Ni and Cr diffuse from their original patches. The spectra in Fig. 1B (b), measured in the indicated spots within the Ni patch and inside the YSZ, evidence Cr spreading on the Ni patch and Ni diffusion on YSZ. Fig. 1B (c) shows that at the polarized cathode Ni diffuses also towards the Cr patch, while Cr partially retracts, whereas at the anode the diffusion directions of Cr and Ni preserve the OPC behavior. Reversing the potentials results in spreading of Cr and Ni all over the cell (Fig. 1B (d)). The evolution of the elemental distribution is accompanied by changes in the chemical state of Ni, Cr and YSZ, clearly evidenced by the Cr 2p, Ni 3p, Zr 3d and Y 3d spectra, taken in different parts of the cell. Representative spectra measured under different conditions are displayed in Fig. 1C. The bottom

spectrum in each panel is measured under Open-Circuit Potential (OCP) conditions (650 °C, 10^{-6} mbar O₂ ambient) before applying bias. As can be expected, the top Ni and Cr layers are oxidized under OCP conditions, whereas Zr and Y preserve their oxidation states. The deconvolution of the Cr 2p spectrum requires three components, two of them with binding energy corresponding to the metallic Cr⁰ and stoichiometric Cr₂O₃ (Cr³⁺) and a third dominant one with intermediate binding energy. The Ni 3p binding energy of the bottom spectrum in panel Ni + Cr. measured inside the Ni patch under OCP condition, corresponds to pure NiO (Ni²⁺) state, which indicates that the formed oxide layer is thicker than our probing depth. The spectrum also shows the presence of Cr that has diffused from the Cr patch. The bottom Y 3d and Zr 3d spectra in panels Zr and Y measured at OCP confirm Y^{3+} and Zr^{4+} oxidation states and evidence YSZ partial reduction at -3 V.

In conclusion, the results obtained in this research contribute to: (i) the rationalization of the damage mechanisms undergone by metallic materials employed in SOFCs, such as metallic interconnects; (ii) the fundamental understanding of high-temperature corrosion in terms of electrochemical mechanisms; (iii) the knowledge of the effects of coupling YSZ to metallic – and possibly multimetallic – systems in applications like thermal-barrier coatings.

ORIGINAL PAPER

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A supramolecular engineering via chemical modification of 2H-tetraphenylporphyrin: in situ metalation and flat conformation

A chemical modification of 2H-Tetra-Phenyl-Porphyrins (2H-TPP) monolayer on Ag(111) was observed after the annealing above 550 K. A selective carbon de-hydrogenation, with the formation of new aryl-aryl bonds between the phenyl groups and the macrocycle, as well as the rotation of the phenyl rings in a flat conformation has been suggested. A combination of NEXAFS, STM and theoretical calculations proves the predicted chemical reaction. This system provides a stable template for macrocycle adatom metalations as we demonstrate for Fe metalation.

Organic monolayers on metal surfaces allow the realization of new compounds, of low-dimensional metal-organic architectures and patterned surfaces, which cannot be achieved by conventional methods. Porphyrins are one of the most studied molecules, since they play a key role as main building blocks in important biological molecules such as cytochrome P-450 and hemoglobin as well as for magnetic systems and catalytic processes. Chemically very stable and versatile, they can be modified with different functional groups (meso-substituents) while the molecular core (macrocycle) can host a wide range of metals at the center of the ring, forming metallo-porphyrins. The interaction of the metal at the center of the molecule with the substrate atoms may play a fundamental role in the adsorption behavior as well as in the electronic and chemical properties of the systems. In our recent investigations we have demonstrated that one monolayer of 2H-TPP, prepared by thermal desorption of the corresponding multilayer at 550 K on Ag(111), adsorbs with the macrocycle and the phenyl flat. This information



Figure 1. NEXAFS spectra at the N 1s (a) and C 1s (b) absorption thresholds for the 2H-TPP multilayer and monolayer on Ag(111). The monolayer was obtained by sublimating the multilayer at 550 K. The spectra were collected in two geometries: with the linear light polarization parallel ($\theta = 0^{\circ}$) and perpendicular ($\theta = 90^{\circ}$) to the substrate surface. The vertical dotted line roughly separates the π^* and the σ^* regions. Calculated and experimental STM images of the 2H-TPP monolayer in constant current mode (-0.4 V, 30 pA): Simulations are shown for the spiral (c) and the normal (d) 2H-TPP on the top while the STM experimental micrograph is shown on the bottom (e). Pictorial view of the predicted theoretical reaction (f).


show features sensitive to the molecular bond orientation. They put in evidence a flat configuration for the macrocycle and showed that the phenyl groups remain flat after the incorporation of Fe. We have found that the influence of the modification of porphyrins, i.e. the Fe metallic center in the porphyrin core has only minor structural effects in the monolayer: the initial after the multilayer desorption, with

has been directly addressed

by means of X-ray absorption

(Fig. 1a,b) and photoemission

this adsorption conformation,

experiments. In order to explain

theoretical calculations suggest a

possible molecular reaction and

de-hydrogenation of eight carbon

atoms in the remaining monolayer

the formation of four new aryl-aryl carbon bonds. While the reaction

takes place also in the deposited monolayer annealed at 550 K, the initial presence of the multilayer favors a decrease of the aryl-aryl coupling barrier and the selection of a spiral conformation in the dehydrogenated molecule (Fig. 1f). The chemical reaction produces

a stable molecule that forms a

(Fig. 1 c,d,e) that can be further modified by the introduction of

In situ Fe atom coordination

of 2H-TPP macrocycles, in the

monolayer regime, has been then

valence band photoemission and NEXAFS using synchrotron radiation light, has followed the subsequent

coordination steps for the monolaver (see Fig. 2). X-ray photoemission

spectra provide the straightforward

evidence of the Fe coordination.

In particular, the N 1s spectrum

of the porphyrin is expected to change when the iron is bound at

the center of the macrocycle. In fact, the N 1s spectrum of 2H-TPP

has two easily resolved components

because of the two N species (iminic

and pyrrolic), whereas the N atoms are equivalent in Fe-TPP, and just

one peak is expected. The X-ray

absorption spectra, taken varying

the synchrotron light polarization,

successfully reproduced in vacuum on Ag(111). An extensive surface characterization, by means of XPS,

central metal atoms.

patterned square lattice on Ag(111)

conformation of the phenyl legs and the interaction with the substrate reduce the degrees of freedom of the whole molecule. Both core level and valence band photoemission results give evidence that the metallic state of the first molecular layers evolves with Fe-complexation because of Fe-d_z state hybridization with the s-p bands of the substrate.



Figure 2. (top) Sketch of the metalation process for the in-situ formation of Fe-Tetraphenylporphyrin. (bottom left) N 1s XPS spectrum of 2H-TPP monolayer before and after Fe deposition steps. The formation of the peak at BE = 398.4 eV gives evidence of the N-Fe coordination. (bottom right) N 1s and C 1s absorption spectra of the 2H-TPP before and after the metalation.

ORIGINAL PAPERS

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The structure and the molecule-substrate interaction in a Co-octaethyl porphyrin monolayer on the Ag(110) surface

The morphological and electronic properties of an ultra-thin film of Co-octaethylporphyrin (Co-OEP) molecules deposited on the Ag(110) surface has been studied by density functional theory calculations, scanning tunneling microscopy, near-edge absorption and UV photoemission spectroscopy with synchrotron radiation (APE, ALOISA and GASPHASE beamlines). The single layer shows a long-range order where the molecules are arranged in a non-commensurate rectangular lattice. The strong molecular interaction with the substrate leads to the electron transfer from the metal substrate to the molecule, mostly involving the Co metal center.

Porphyrins are metallorganic molecules with planar structure and a metal atom in the centre. Beside their important role in several bio-systems (e.g. chlorophyll and haemoglobin), they recently raised interest for their optical, catalytic and sensing properties. The study of thin layers of porphyrins in Ultra High Vacuum (UHV) allows the investigation, by means of surface science techniques, of their interaction with metallic surfaces and of the possible occurrence of self-assembling. We have chosen Co-octaetyl porphyrin also to see whether it is possible to obtain a

long-range ordered periodic array of magnetic atoms.

The morphology of the single layer of Co-OEP, which has been obtained by thermal desorption of a deposited multilayer, has been firstly characterized by means of Scanning Tunneling Microscopy (STM). In Fig. 1a a long range STM image is presented where the film clearly shows a long-range order. The molecules are arranged in a non-commensurate rectangular lattice. Despite this, the molecular lattice is aligned with the high symmetry direction of the Ag substrate and their presence induces a reconstruction in the substrate step shape. STM measures at low temperature (70 K) allow us to distinguish sub-molecular features, i.e. the ethyl groups surrounding the porphyrin core (Fig. 1b), and to see that the molecules are not completely flat on the surface. In order to have more information about the absorption configuration, angle-dependent Near-Edge X-Ray Absorption Spectroscopy (NEXAFS) data have been collected. The data indicate that they are tilted $20^{\circ} \pm 5^{\circ}$ off the surface. Moreover, NEXAFS spectra at N 1s and Co 2p show significant differences with the



Figure 1. STM images of the Co-OEP single-layer: a) long-range image of the highly ordered molecular lattice at room temperature; b) high resolution image at 70 K. In the inset a ball-and-stick model of the Co-OEP molecule is shown.

data collected on the multilayer and in the gas-phase. Interesting differences between the single layer and the multilayer have also been observed in the UV Photoemission Spectroscopy (UPS) data (Fig. 2a): an extra density of states is present close to the Fermi edge. The explanation of these phenomena requires an investigation of the interaction between the molecules and the substrate.

In order to understand the porphyrin-Ag interaction, Density Functional Theory (DFT) calculations have been performed both for the isolated molecule and the adsorbed one. In the isolated molecule the Lowest Unoccupied Molecular Orbital (LUMO) is the quasi-atomic d_{z2} orbital, which is strongly localized on the Co atom and oriented normally with respect of the molecular plane. The calculation in the adsorbed molecule configuration shows that this orbital hybridizes with the Ag bands and becomes a broad feature which partially shift across the Fermi edge (Fig. 2b). In summary, DFT calculations indicate that a charge transfer from the Ag substrate to the molecule takes place upon adsorption, and that this interaction mostly involves the Co atom.

Figure 2. a) UPS valence band spectra comparison between single-layer, multi-layer and Ag substrate; in the inset the feature close to the Fermi level is shown.
b) the DFT calculated density of states of the molecule adsorbed on the substrate. The projections on N and Co atoms are green and blue respectively. The spatial distributions of the orbitals are sketched on side. The spatial distribution at the Fermi level is sketched in the inset.

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This explains the observed valence band feature appearing in the single-layer spectra (Fig. 2a), which can be regarded as a partial filling of the LUMO upon the charge transfer. This is also in agreement with the numerical simulations of the Co 2p NEXAFS spectrum, which indicate a strong hybridization between the Co states and the Ag bands. The interaction with the Ag surface induces a partial reduction of the Co²⁺ ions, which likely leads to a reduction of their magnetization. This latter effect, which requires deeper investigation to be quantified, is a shortcoming if one wants to exploit the magnetic properties of such an ordered array of magnetic atoms.



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Support nanostructure boosts oxygen transfer to catalytically active platinum nanoparticles

Pt/ceria model catalyst. Two types of M-O interactions were observed: (1) the electron transfer from Pt nanoparticles to the oxide, and (2) the oxygen transfer from ceria onto Pt. Both effects trigger the oxidation state change from Ce⁴⁺ to Ce³⁺. Extraordinarily high sensitivity of the used resonant enhanced photoelectron emission is crucial for detection of these effects.

A typical solid catalyst is composed of metal nanoparticles supported on the surface of an oxide. At first it was implied that the activity of the catalyst is exclusively determined by the dispersed metal nanoparticles while the oxide support remains *inert*. Recently the benefits of an *active* oxide support captured attention. Interplay between nanoparticles and the active oxide opens up new reaction channels and gives rise to new reaction mechanisms on the surface of the catalyst.

The M-O interaction often involves a transfer of electrons or active atomic species between the metal and the oxide support. For example, CeO_2 (ceria) support easily releases its lattice oxygen that could be dispatched onto the surfaces of metal nanoparticles. This process is called reversed oxygen spillover. It provides additional functionality to the catalysts, in particular, a unique resistance to poisoning by carbon. The reversed oxygen spillover is considered to be the key step in several catalytic reactions on CeO₂. However, it is so difficult to detect that it has never been clearly identified experimentally. To do so we have employed **Resonant Photoelectron** Spectroscopy (RPES) at the Materials Science Beamline. We used the fact that during spillover, the released oxygen anion donates two of its electrons to two neighbouring cations changing their oxidation states from Ce⁴⁺ to Ce³⁺. RPES allows precise tracking of the oxidation

states of cerium cations.

The experiment was conducted on well defined Pt/CeO₂(111) supported model catalyst formed on Cu(111). The method is based on measuring the valence band spectra at photon energies of 121.4 and 124.8 eV corresponding to 4d → 4f resonant photoelectron emission enhancement either in Ce3+ or Ce4+ cations. An additional spectrum is measured at photon energy of 115 eV under the off-resonance condition. The corresponding resonant features (D(Ce3+) and $D(Ce^{4+}))$ emerge in the valence band spectra at 1.5 and 4.0 eV, respectively. The ratio of the resonant enhancements (RER), D(Ce³⁺)/ $D(Ce^{4+})$, directly reflects the $Ce^{3+}/$ Ce⁴⁺ concentration ratio.



Figure 1. Experimental verification of two types of metal-oxide interaction.

The developments of the RER on CeO₂ and Pt/CeO₂ as a function of temperature are shown in Fig 1. Additionally, the valence band spectra taken under in- and off-resonance conditions from CeO₂ before and after Pt deposition as well as after annealing to 700 K are displayed. Unlike on bare CeO₂, where RER was constant and close to zero, a significant rise of RER after Pt deposition and its following dependency on the temperature was observed on Pt/ceria. In order to understand this behavior we employed a Density Functional Theory (DFT). The calculations have been done using two models of ceria: one of the ideal (singlecrystal) CeO₂(111) surface and another of a real (rough) ceria film composed of oxide nanoparticles (chosen to be $Ce_{40}O_{80}$). Interactions of each of the models with a Pt. cluster have been studied. The calculations revealed significant interaction between Pt and oxide that causes a facile electron transfer from the Pt (partial oxidation) to ceria (partial reduction) on both, surface and particle models. Indeed, the increase of RER observed directly after Pt deposition manifests the formation of Ce³⁺ ions at Pt/ceria interface. Temperature dependent development of RER has been analyzed considering formation of oxygen

vacancies. The models recreating detachment of one oxygen atom due to oxygen release and oxygen spillover to Pt particle are shown in Fig 2. The calculations show that neither oxygen release nor oxygen spillover are feasible for Pt supported on the surface ceria. However, the reverse oxygen spillover becomes energetically favorable for Pt supported on ceria nanoparticles. The spillover is associated with a substantial activation barrier. We find a rapid increase of the Ce³⁺ concentration upon annealing above 500 K. The pronounced ceria reduction is consistent with the oxygen reverse spillover, in accord with DFT calculations.



Figure 2. DFT calculations: oxygen release versus oxygen spillover.

ORIGINAL PAPER

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, and J. Libuda, *Nature Materials* **10**, 310 (2011)

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Ordered vacancy network induced by the growth of epitaxial graphene on Pt(111)

Where the studied large areas of $(\sqrt{3}x\sqrt{3})R30^\circ$ graphene commensurate with a Pt(111) substrate. The combination of our in-house STM measurements and the synchrotron based XPS performed at the SuperESCA beam line with *ab initio* density functional calculations leads us to conclude that this structure is originated by the formation of a surface reconstruction at the Pt surface, which consists of an ordered vacancy network formed in the outermost Pt layer and a graphene layer covalently bonded to the Pt substrate.

Epitaxial graphene on transition metal surfaces is nowadays a very active research field. Depending on the procedure used to grow graphene different phases, including defective structures, can be formed on metal substrates. Epitaxially grown graphene arranges in coincidence structures, better known as moirés, which show different periodicities and crystallographic orientations for each transition metal substrate. The stability of these moirés is related to the minimization of the strain between the substrate and the graphene overlayer as it can be

observed in Scanning Tunnelling Microscopy (STM) experiments. Moreover, there is a direct relationship between the strain and the portion of surface covered by every one of these moirés. In some metals, as in the case of Pt, there exist many different phases fulfilling this rule. In the case of graphene grown on Pt(111) we have shown that there are 21 stable structures that minimize the stress and whose extension is directly proportional to the strain. We focused our study on the smallest of these superstructures, namely the $(\sqrt{3}x\sqrt{3})R30^\circ$. This phase

corresponds to the structure holding more strain of all the existing moires on Pt(111). The large mismatch between the $(\sqrt{3}x\sqrt{3})R30^\circ$ periodicity and the Pt(111) surface causes a large strain within the graphene sp² bonds, making this structure, in principle, unstable. However, experimental STM images show large areas of this particular phase covering a portion of the surface area much bigger than it could be a priori expected from its calculated strain. Also our high resolution experimental STM images reveal an anomalous high corrugation



Figure 1. Top view (left) and side view (right) of the structural model derived from XPS, STM images and DFT calculations for the $(\sqrt{3}x\sqrt{3})R30^\circ$ reconstruction. Smaller sizes on the spheres represent deeper atoms. The side view is slightly tilted for a better visualization of the vacancy channels and interaction between C (black) and surface Pt (gray (yellow)) atoms.

inside the graphene reconstructed unit cell. These are the reasons why this crystallographic phase could be different than a simple moiré over layer and therefore, a deeper analysis is required in order to understand the origin and stability of this particular superstructure. We propose that this structure is related to a reconstruction at the Pt surface consisting of an ordered vacancy network formed in the outermost Pt layer covalently bonded to the graphene layer (see Fig. 1). We have found that the formation of an ordered network of Pt vacancies at the outermost layer leads to an energetically stable structure compatible with the STM images. After trying many different structures (including lateral shifts

in the graphene layer, extra carbon atoms, and vacancies in both layer and surface), our best-fit model is depicted in Fig. 1.

The XPS spectra of the Graphene/ Pt(111) system measured at the SuperESCA beamline is in good agreement with our model. We have measured the C 1s and Pt 4f_{7/2} peaks for samples grown using large polycyclic hydrocarbons (C₆₀ in the present study) and ethylene. The C 1s peak of the sample grown with ethylene can be understood in terms of a single sp² component coming from a weakly interacting graphene over layer on the Pt(111)surface. This result is consistent with the STM studies that do not report the $(\sqrt{3}x\sqrt{3})R30^\circ$ when using this recipe for growing graphene.

However, when measuring the C 1s peak of graphene grown using C_{60} precursors two extra components are found. These two extra components can be assigned to the graphene layer highly interacting with the Pt vacancy network and the C atoms covalently bonded with the substrate.

In Fig. 2 we compare both the best fit density functional theory calculated STM images, including multiple scattering formalism, with the high-resolution low temperature STM measurements. The agreement between both images is quantitatively (see profiles in the main reference) very good. We invite the interested reader to the main reference for a deeper understanding of our work.



Figure 2. STM image (V = 0.1 V) for the ($\sqrt{3}x\sqrt{3}$)R30° experimental (left) and simulation best-fit structure using a multiple scattering formalism (right). A schematic atomic model has been overlaid. Both images are merged in the central part.

ORIGINAL PAPER

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Enhanced spin relaxation in a quantum metal film by the Rashba-type surface

We employed angle-resolved photoemission spectroscopy to interpret the magnetoconductance measurements of a ultrathin Ag(111) film covered with a bare or a $\sqrt{3}x\sqrt{3}$ -Bi/Ag -terminated surface as a function of the applied magnetic field. The experimental magneto-transport data were analyzed by introducing the results of photoemission Fermi surfaces, obtained at the VUV-photoemission beamline, into the Hikami-Larkin-Nagaoka formula to derive the characteristic fields of the two systems. The formation of the Rashba-type surface alloy was found to reduce the spin relaxation time in the quantum film by nearly 85 %.

Spin and current controls in solids have been one of the central issues in researches of electron and spin transport. Nowadays, electronics/ spintronics deals with nanometeror atomic-scale structures, where manipulations of single charge/spin channels and related functional properties have become accessible. Miniaturization of these systems implies the emergence of various quantum phenomena. For example, valence electrons of films with the thickness comparable to the electron wavelength form discrete Quantum-Well States (QWSs) under opportune conditions of confinement (quantum size effect). Furthermore, the size reduction also increases the surface/volume ratio and a film possibly changes its electronic (spin) properties by the surface effect. Concerning metal films, the quantum size effect requires the thickness in a range of nanometers and the length corresponds to several tens of atoms, indicating the very large ratio of a surface (interface) monatomic layer to film atomic layers. Thus, we were



Figure 1. Magnetoconductance data for the bare and $\sqrt{3}x\sqrt{3}$ -Bi/Ag-covered ultrathin Ag(111) films on Si(111). Solid and broken lines are fits to the data according to the Hikami-Larkin-Nagaoka formula. Two possible curve fits were performed for the Bi/Ag(111) film with the different fitting parameters. σ_{co} is the quantum unit of conductance.

interested in combining the quantum size effects and the surface effect on the metal films to induce new physical phenomena. In the present research, we used angle-resolved photoemission to understand the magneto-transport data of bare and $\sqrt{3}x\sqrt{3}$ -Bi/ Ag-covered ultrathin Ag(111) films. Prior to beamtime at VUV-Photoemission beamline, we made *in situ* magneto-conductivity measurements of these films, prepared under UHV condition, in our laboratory. Nanometersthick Ag(111) films were grown epitaxially on a Si(111)7x7 surface and the $\sqrt{3}x\sqrt{3}$ -Bi/Ag surface was prepared by the subsequent Bi deposition. Fig. 1 shows variation of the magnetoconductance, $\sigma(B) - \sigma(B=0) = \Delta \sigma$, as a function of the applied magnetic field B, for the bare and $\sqrt{3}x\sqrt{3}$ -Bi/Agterminated 15-ML Ag(111) films. The magnetoconductance curves of both systems display signatures of weak antilocalization (decrease of $\Delta \sigma$) under weak magnetic field and weak localization effects (increase of $\Delta \sigma$) under strong magnetic field, with a reversing field of 0.1 T for the bare Ag and about 0.4 T for the Bi-covered film. These two quantum interference effects are quantitatively described by the Hikami, Larkin, and Nagaoka (HLN) formula using four characteristic field parameters. The experimental data were well-fitted with the formula (Fig.1) and the fitting values are the characteristic magnetic fields that can be

converted to spin and coherence relaxation time if density-of-state, $N_{DOS'}$ of the system is known. To obtain the exact values of N_{DOS} for the two film systems, we mapped their Fermi surfaces and the band dispersion curves over the whole two-dimensional Brillouin zone by angle-resolved photoemission spectroscopy at the VUV-Photoemission beamline. Figures 2a and 2b show Fermi surfaces and Fig. 2c and 2d show band dispersion curves for (a), (c) the bare and (b), (d) the $\sqrt{3}x\sqrt{3}$ -Bi/Ag-covered 15-ML Ag(111) films. All circular

and hexagonal-like Fermi energy contours in Fig. 2a are subbands of quantum-well states (QWS's), except for the spot at the center, which is the Ag(111) surface state (SS). These QWS's have basically free-electronlike in-plane dispersion (Fig. 2c). The electronic structure of the $\sqrt{3}x\sqrt{3}$ -Bi/Ag(111) film (Fig. 2d), instead, appears to be more complex, due to several surface-state bands (SS_{Bi/Ag}'s), spin-split by the Rashba interaction, which disperse downward from the center of Brillouin zone. A N_{DOS} value is calculated from a shape of a Fermi surface and Fermi velocity

at each Fermi vector. Then, the experimental $N_{\mbox{\tiny DOS}}$ were derived from the photoemission data (Fig. 2) and they were related with the characteristic magnetic fields (Fig. 1) to obtain various relaxation time. We found that the $\sqrt{3}x\sqrt{3}$ -Bi/Ag (Rashbatype) surface appears to reduce by almost one order of magnitude the spin-relaxation time of the electrons in the ultrathin metal film, without affecting the phase coherence time. The present data demonstrate quantum controls of electrons in a nanomteter-thick metal film by a surface atomic layer.



Figure 2. Photoemission Fermi surfaces and band diagrams of (a,c) bare and $(b,d) \sqrt{3}x\sqrt{3}$ -Bi/ Ag-terminated 15-ML Ag(111) films measured at hv = 49.6 eV. Red solid lines are obtained from parabolic fits of band dispersion of QWS's near the Fermi level (EF).

ORIGINAL PAPERS

N. Miyata, H. Narita, M. Ogawa, A. Harasawa, R. Hobara, T. Hirahara, P. Moras, D. Topwal, C. Carbone, S. Hasegawa, and I. Matsuda, *Phys. Rev. B* 83, 195305 (2011).

K. He, Y. Takeichi, M. Ogawa, T. Okuda, P. Moras, D. Topwal, A. Harasawa, T. Hirahara, C. Carbone, A. Kakizaki, and I. Matsuda, *Phys. Rev. Lett.* **104**, 156805 (2010)

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Correlating sulfur reactivity of Pt_xPd_{1-x} nanoparticles with a bimetallic interaction effect

anoparticles of Pt_xPd_{1-x} (x = 0.5, 0.3 or 0) nanoparticles submitted to H_2 reduction and posterior H_2S sulfidation at 300 °C were characterized by *ex situ* and *in situ* X-ray Absorption Spectroscopy (XAS), measured at Elettra (Italy) and LNLS (Brazil). The XAS experiments allowed us to monitor short-range order changes around the Pt and Pd atoms induced by the thermal processes. The EXAFS (Extended X-ray Absorption Fine Structure) data analysis demonstrated that the number of chemisorbed sulfur atoms is proportional to the quantity of Pd in the vicinity of Pt.

Considerable attention has been paid recently towards the development of catalysts with high activity for the hydrogenation of aromatics (HYD) and hydrodesulfurization (HDS) reactions. Such studies indicate that particulate emissions in diesel engines exhaust gases can be reduced by decreasing the fuel's sulfur content. A few highly active systems for the HYD have already been obtained, though they are very susceptible to sulfur poisoning, which means a dramatic loss of their activity due to formation of sulphur compounds on the active sites.

Thus, the use of these catalysts is still limited by severe pre-treatment requirements until sulfur tolerance can be greatly improved. One possible approach to lower the sulfur poisoning of a noble metal catalyst is to alloy the active component with another metal. Bimetallic systems enable the tailoring of catalytic activity and selectivity, which is referred in the literature as occurring through a "cooperative effect". In a recent work, our group used in situ XAS to study non-supported Pt_vPd_{1-v} (x = 1, 0.7 or 0.5) nanoparticles under hydrogen reduction and



Figure 1. Relation between the number of Pt-S bonds (N_{PtS}) and the amount of Pd in the Pt_xPd_{1x} nanoparticles (x). The inset represents the larger sulfur reactivity of the core-shell PtPd nanoparticles.

and we observed that the reduction process is a necessary step prior to the occurrence of any sulfur reaction and that Pd migrates toward the surface, forming a Pt-rich core - Pdrich shell structure. Here we report on our investigations for systems with higher contents of Pd, *i.e.*, non-supported Pt Pd₁, (x =0.5, 0.3 or 0) nanoparticles. The use of non-supported catalysts, instead of catalysts supported on zeolites or γ -Al₂O₃, allows evidencing any interaction between Pt and Pd. The samples were submitted to reduction and sulfidation at 300 °C in the presence of a H₂ or H₂S containing atmosphere, respectively. Both Pt L₃ and Pd K edges were characterized by XAS to reach more detailed structural information. The use of Elettra XAFS beamline was crucial since it is not possible to probe the Pd K edge at LNLS. The atom-specific short-range order investigation by XAS provided a way of monitoring local structural changes induced by reduction and sulfidation processes. Our experiments probed the number and type of atoms in the vicinities of Pt and Pd, including the formation of metal-sulfur bonds (Pt-S, Pd-S). Using the structural parameters obtained from the fitting of the EXAFS oscillations, we searched for a correlation

posterior sulfidation. Only the Pt L₂

absorption edge was monitored

between the sulfur reactivity of the nanoparticles and the bimetallic interaction effect.

Our results firstly confirmed that bimetallic PtPd nanoparticles are more reactive with sulfur than either pure Pd or pure Pt. A comparison of the number of Pt-S bonds formed in terms of the nanoparticles' composition (investigated in the present and in the previous work) is displayed in Fig. 1. The variation of the average number of Pt-S bonds (N_{Pt-S}) is plotted as a function of the Pd concentration. The trend observed shows that for higher Pd concentration (lower x values), the number of observed Pt-S bonds is larger. We conclude that the higher reactivity is related to a modification in the electronic structure of the metals due to a charge transfer effect from the Pd to the Pt atoms in the bimetallic nanoparticles. In addition, the relative presence of Pd with respect to Pt in the vicinity of the Pt atoms (N_{pt-Pd}/N_{Pt-Pt}), and the relative presence of Pt in the vicinity of the Pd (N_{Pd-Pt}/N_{Pd-Pd}) tends to decrease after the sulfidation process (Fig. 2). Such trend is more evident for the sample with higher Pd concentration (x = 0.3). In fact, for the Pt_{0.3}Pd_{0.7} nanoparticles, Pd-Pt bonds are no longer observed at the Pd K edge after sulfidation. These observations corroborate the atomic rearrangement, which leads to the formation of a (Pt-rich) core - (Pd-rich) shell structure during thermal treatments. Such structural evolution is a fundamental factor to explain the reactivity behavior of the nanoparticles submitted to sulfidation.



Figure 2. Relative changes in the number of inter-metallic bonds around Pt and Pd atoms before (triangles) and after (circles) the sulfidation: evidences of atomic rearrangement and core-shell structure formation.

ORIGINAL PAPER

F. Bernardi, A. Traverse, L. Olivi, M.C.M. Alves, and J. Morais, *J. Phys. Chem.* C **115**, 12243 (2011)

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Photoemission study of thymidine adsorbed on Au(111) and Cu(110)

sing synchrotron radiation based, high-resolution core level spectroscopies, the electronic structures and adsorption geometries of the DNA nucleoside thymidine on Au(111) and Cu(110) have been studied. All measurements were performed at the Materials Science beamline.

The adsorption of biomolecules on metal surfaces, analyzed by advanced surface science techniques, is an important topic nowadays and relevant to the understanding of interface phenomena in nano-mechanical biosensors, organic semiconductors, biochemistry and pharmacology. The molecular systems studied in the last decade have been continuously growing in complexity. Thymidine (dT) is one of the nucleosides, and is a building block of DNA. Its structure consists of the pyrimidine base thymine bonded to a deoxyribose moiety via a C-N glycosidic bond (Fig. 1).

The experimental C 1s, N 1s, and O 1s photoemission spectra of multilayer and monolayer (ML) coverages of thymidine on Au(111) and Cu(110) crystals are presented in Fig. 1. For comparison, the corresponding spectra of thymine in the gas phase are also shown in the same figure. The gas phase C 1s spectrum of thymine shows four distinct peaks A (C2 carbon), B (C4), D (C6) and E (C5 and C7). Upon bonding of thymine to the deoxyribose ring to form the nucleoside, an additional carbon peak appears in the C 1s spectra due to carbon in the deoxyribose. The peak C in the spectrum we

attribute to the carbon atom of the glycosidic bond. The three carbon atoms bonded to oxygen (alcohol (C–OH) and cyclic ether (C–O–C) in the deoxyribose ring contribute to the feature D, while the hydrocarbon atoms of the sugar ring contribute to peak E. The energy separation of the features in the gas phase thymine spectrum and corresponding peaks in spectra of dT adsorbed on the Au(111) surface are very similar. This suggests that the carbon atoms of dT are not strongly involved in the molecular-surface and/or intermolecular interactions. However, the energy separation between the features related to the thymine moiety



Figure 1. a) C, b) N and c) O 1s core level spectra of thymidine adsorbed on Au(111) and Cu(110), photon energy is 500 eV.

of dT on Cu(110) is significantly smaller than that observed in the thymine gas phase spectrum (see Fig. 1a). These differences suggest that dT is chemisorbed rather than physisorbed on Cu(110). The N 1s spectra of multilayer and ML coverages of dT on Au(111) are shown in Fig. 1b. The peak A at 400.40 eV is attributed to the amino nitrogen atoms of dT species weakly bonded via van der Waals and/or hydrogen bond interactions. The feature B at 399.85 eV is related to the dT molecules lying closer to the surface in the first layer. The N 1s XPS spectrum of dT on Cu(110) shows two features (see Fig. 1b). The chemical shift of ~1.7 eV in the N 1s spectrum (peak C) is clear evidence that nitrogen atom (N3) is bound to the surface.

The effect of adding the deoxyribose ring to the thymine nucleobase is clearly noticeable in the O 1s spectra (see Fig. 1c). The low Binding Energy (BE) peak B is assigned to the carbonyl oxygen atoms of the thymine moiety, while the feature A corresponds to the alcohol and cyclic ether oxygen atoms of the deoxyribose. The energy separation between features A and B in O 1s spectrum of dT adsorbed on Cu(110) surface is 1.8 eV, and is a little larger than the value of 1.6 eV in the O 1s XPS spectrum of a $poly(dT)_{25}$ film. Based on this, we believe that the carbonyl oxygen atoms contribute to the interaction with the copper surface, although the chemical shift is much smaller than for the N 1s core levels. For the ML of dT on the Au(111) surface, the two features A and *B* have a significantly smaller BE difference of ~1.05 eV, which we attribute to intermolecular hydrogen bonding involving the OH and/or ether groups.

The angular dependences of the N

and O NEXAFS spectra show that on the gold substrate the thymine component of adsorbed dT is nearly parallel to the surface, while on the copper surface it is in a nearly perpendicular configuration (see for example Fig. 2).

Overall, the photoelectron spectra show that on Au(111) there is no evidence of chemical interaction with the surface, but instead we find effects due to intermolecular hydrogen bonding. This confirms the conclusions that the process of selfassembly of dT is stabilized mainly by intermolecular hydrogen bonds of the deoxyribose moiety. On the more reactive Cu(110) surface, the molecule-surface interaction dominates and dT chemisorbs on the surface via the deprotonated nitrogen atom of its thymine moiety. Thus the higher reactivity permits dehydrogenation and formation of a Cu-N bond.



Figure 2. N K-edge NEXAFS spectra of thymidine ML adsorbed on Au(111) and Cu(110) surfaces, measured at grazing (GI) and normal incidence (NI).

ORIGINAL PAPER

O. Plekan, V. Feyer, S. Ptasińska, N. Tsud, V. Cháb, V. Matolín, and K.C. Prince, J. Phys. Chem. C, **114** 15036 (2010)

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Molecular orientation in soft matter thin films studied by resonant soft X-ray reflectivity

Where the present a new technique that has the capabilities to study depth profiles of molecular orientation in soft matter thin films. The method combines direct depth-resolving capabilities of angle-resolved X-ray reflectivity with polarization dependent chemical information from resonant absorption of soft X-rays near the carbon K edge. Their interaction with matter is very sensitive to the chemical structure of the studied material and the orientation of specific molecular bonds with respect to the polarization of the soft X-ray beam. This provides a precise tool to detect orientation through anisotropic thin films. Our study on well-aligned liquid crystalline polymer films at the BEAR beamline at Elettra demonstrated the capabilities of this novel technique.

One of the bottlenecks in understanding the properties of polymer thin films is the difficulty to measure spatial profiles of structural properties, such as orientation, across these highly inhomogeneous confined systems. Technologically relevant examples include polymer membranes for novel gas separation technologies where the gas mobility is affected by the chain orientation that can be induced by the free surface and the interface with the membrane support. In organic electronics, an anisotropic distribution of the polymer chain segments is directly related to the anisotropy in the electrical conductivity. Therefore, a detailed knowledge of the depth profile of a laterally-averaged segment orientation is highly desirable. Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy techniques and gracing incidence X-ray diffraction are routinely employed to study structure and molecular orientation near free surfaces. However, these well established methods have only a limited depth profiling capability and are not sensitive to structural changes near buried interfaces. These limitations can be overcome by polarization dependent resonant

soft X-ray reflectivity that carries the

p-pol x-ray s-pol view of the second second

Figure 1. Sketch of the setup for polarization dependent X-ray reflectivity experiments. The reflected X-ray intensities obtained in s and p incidence around the carbon K edge carry information on the side-chain orientation in the liquid crystalline polymer thin film.

full depth dependent information on the orientational profile throughout a whole film. This novel technique exploits changes in the refractive index ellipsoid related to the characteristic absorption spectra of molecular states to get access to element and bond specific information beyond the pure electron density distributions (see Fig. 1). In particular for organic soft matter systems, the orientation of functional groups is encoded in the linear dichroism around the carbon K edge.

The experiments that were carried out at the BEAR beamline at Elettra and at the Advanced Light Source, Berkeley, demonstrated that it is possible to study orientational order in poly(2-{4-[(4-cyanophenoxy)carbonyl] phenoxy}ethyl acrylate) Liquid Crystalline Polymer (LCP) thin films by polarization dependent resonant soft X-ray reflectivity. Fig. 2 shows that reflectivity curves recorded in s and p incidence across the NEXAFS resonances of oriented phenylene and nitrile groups at the carbon K edge exhibit strong linear dichroism. The reflection patterns were quantitatively analyzed using the Berreman matrix formalism for reflection and transmission in anisotropic stratified systems. Comparison of the real and imaginary part of the refractive index ellipsoid of the LCP domains extracted from self-consistent

analysis of the experimental data in s and p incidence with spectroscopic NEXAFS data proved that the values are Kramers-Kronig consistent. Measurements on LCP films of various thicknesses up to 50 nm show that the stiff elongated side-groups tend to align parallel to the surfaces, consistent with the expectations. The degree of orientation was found to be independent of depth and film thickness. This initial demonstration paves the way for studies on a wide class of interesting systems ranging from polymers to biomaterials in which the orientation of functional groups is expected to vary with depth throughout the films.



Figure 2. Experimental (circles) and calculated (solid curves, Berreman formalism) reflectivity for a LCP thin film on silicon in s- (top) and p-incidence (bottom) at 284.8 eV. The Fresnel reflectivity of the substrate (dashed curve) is added for reference.

ORIGINAL PAPER

M. Mezger, B. Jérôme, J.B. Kortright, M. Valvidares, E.M. Gullikson, A. Giglia, N. Mahne, and S. Nannarone, *Phys. Rev. B* **83**, 155406 (2011)

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Phase-contrast mammography with synchrotron radiation: first clinical experience

A ammography with Synchrotron Radiation (MSR) was performed with a phase-detection technique at Elettra on 49 women, between March 2006 and September 2007, after a very long preparation period. These patients were recruited from women undergoing standard mammography, with the purpose to prospectively evaluate the diagnostic contribution of MSR in patients with questionable or suspicious breast abnormalities identified at combined Digital Mammography (DM) and UltraSonography (US). In this sample many healthy patients were considered positive, i.e. were false–positive for DM-US, while MSR had the ability to diagnose them correctly as negative.



Figure 1. Imaging system for mammography with synchrotron radiation. a) Stationary and laminar X-ray beam. b) Movable patient support platform. c) Compression system. d) Holder for screen-film cassette. e) Vertical movement of patient and screen-film system through the beam, which facilitates the acquisition of planar radiographic images. f) Rotational movement of patient, which facilitates the acquisition of craniocaudal and mediolateral oblique views [Castelli E, Tonutti M, Arfelli F, et al. Mammography with synchrotron radiation: first clinical experience with phase-detection technique. Radiology 2011;259:684-694. Copyright 2011 Radiological Society of North America].

Historical introduction: The proposal to build the SYRMEP beamline, already foreseeing the final phase of in vivo mammographic examinations, was presented at the meeting of the Program Advisory Committee of Sincrotrone Trieste (ST) at the National Research Council (CNR) in Rome in September 1991. Elettra began its operations in 1993, and in the same vear the construction of SYRMEP beamline started out. The University of Trieste (UTS) was the major source of funding, with a significant contribution of ST; in addition, the National Intitute of Nuclear Physics supported the development of a new digital detection system. The in vitro experimentation started in 1996 and the results were very promising. In 1998 the international scientific committee of ST approved the next steps of in vivo experimentation, i.e. with patients. In 2000 the beamline upgrade phase started by designing the patient room with the mobile patient support (Fig. 1), the room for medical and technical radiologists, and the control system to comply with all the required safety regulations; the Fondazione CRTrieste financially supported this phase. In July 2004 the Ethical Committee (EC) of the local Hospital authorized the experimentation. In March 2005 an Italian ministerial agency tested out, with positive feedback, the general safety control system. Eventually,

in January 2006, the Ministry of Health gave the ultimate approval and in March the first patients were examined.

The study and the results: 49 patients, who met the inclusion criteria of the protocol authorized by the EC, agreed to enroll and underwent MSR. The final diagnosis, ill or healthy (positive or negative to the disease), was obtained for each patient by means of biopsy or DM-US follow-up at 6 and 12 months. Two patients did not complete the imaging follow-up and thus were excluded from the analysis. Thus, 47 patients, aged 43-78 years, were finally included in the study. At the final diagnosis, 16 were considered ill and 31 healthy. Among the 16 ill, 11 were positive to DM and 13 to MSR; therefore the sensitivity is 0.69 (11/16) for DM and 0.81 (13/16) for MSR. Among the 31 healthy, 17 were negative to DM and 29 to MSR; therefore the specificity is 0.55 (17/31) for DM and 0.94 (29/31) for MSR. Overall, 25 were positive to DM and 15 to MSR; therefore the positive predictive value is 0.44 (11/25) for DM and 0.87 (13/15) for MSR, being 0.34 (16/47) the prevalence of positive finding of the sample. The fact that 0.87 is much larger than 0.34 indicates the efficiency of MSR, mainly due to reduction of positive from 25 in DM to 15 in MSR.

These study results suggest that MSR, as an in-depth examination, can be used to clarify cases of questionable or suspicious breast abnormalities identified at DM-US. As far as the implication for patient care is concerned, MSR has the potential to be a second-level examination after mammography, with the aim of reducing the number of diagnostic biopsies performed. The standard method for diagnosing breast cancer at an early preclinical stage is screen-film mammography or DM, even though these are not perfect imaging tools. The diagnostic performance of these examinations depends on several variables, and they are reported to have a sensitivity of 60%-90% and a specificity of 80%-95%. The reported positive predictive value of screen-film mammography or DM is usually in the order of 10%: this means that for 10 patients positive to the test, luckily only one has breast cancer. US is used as an adjunct to X-ray mammography in patients with dense breasts or to clarify equivocal mammographic findings. At this point there is a strong demand for a second-level test that will help to substantially reduce the high rate of false-positive results. Many methods have been developed over the years to address the perceptual limitations of mammography, with varying levels of success.

ORIGINAL PAPER

E. Castelli, M. Tonutti, F. Arfelli, R. Longo, E. Quaia, L. Rigon, D. Sanabor, F. Zanconati, D. Dreossi, A. Abrami, E. Quai, P. Bregant, K. Casarin, V. Chenda, R.H. Menk, T. Rokvic, A. Vascotto, G. Tromba, and M.A. Cova, *Radiology* **259**, 684 (2011)

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Two-dimensional enzyme diffusion in laterally confined DNA monolayers

A ddressing confinement and crowding on biomolecular function may provide insight into molecular mechanisms within living organisms, and promote the development of novel biotechnology tools. We investigate restriction enzyme reactions with double-stranded (ds) DNA oligomers confined in brushy matrices of monolayer patches of controlled density. We show that enzymes can access the dsDNA matrix only from the matrix sides to diffuse two-dimensionally in the gap between top- and bottom-matrix interfaces. This has important implications on the development of new nanofluidic approaches to the detection of biomolecules.

The immobilization of dense DNA structures on solid supports, obtained by self-assembly and enzymatic manipulations, holds a central role as a tool for developing miniaturized devices with innovative applications in biosensing. In particular, restriction enzymes that cleave dsDNA molecules are widely utilized in cloning as well as in a number of DNA-based assays because they target very specific dsDNA sites. These enzymes have key roles in bacterial cell defence against viruses and other parasitic DNAs, and have the ability to diffuse in one-dimension by sliding on the backbone of long dsDNA filaments during their site-searching process. We use Atomic Force Microscopy (AFM) nanografting to generate monolayer patches of 44-bp dsDNA molecules with variable density (dsDNA matrices), within bioresistant alkylthiol Self-Assembled Monolayers (SAMs), on an ultraflat gold surface. Nanografting is a technique in which the AFM tip induces, at selected locations, a substitutional exchange of the molecules of the original SAM matrix with new molecules present in solution (thiol-DNA in our case). By changing the number of times the tip is overwriting the same area during nanografting, we can fine-tune the molecular density in that area. The topographic height of such dsDNA matrices increases with the dsDNA packing and saturates to the length of dsDNA molecules (~15 nm) as they stand vertically in crowded monolayers. The dsDNA sequences are designed

such that they are cut at half height by a restriction enzyme. We assess the reaction by measuring the dsDNA matrix height before and after enzyme incubation. We tested the action of different restriction enzymes, namely, DpnII, Bfal and BamHI over dsDNA matrices, as a function of their density. Fig. 1 shows that, for patches well below the saturation density (height < 8 nm), the height drops a factor two after incubation with the enzyme, whereas stays constant in control matrices, thus indicating a successful and specific reaction.

Crowder DNA patches are instead not accessed by the enzyme. To understand how restriction enzymes access dsDNA matrices, we generated substrates consisting of adjacent matrices nanografted with different dsDNA densities. The topographic AFM images in Fig. 2a,b show two distinct, identical matrices of low-density DpnII-cleavable dsDNA molecules before and after the enzymatic reaction, respectively. The structure in the top figure is surrounded by a nanografted highdensity barrier. The line profiles in Fig. 2a,b show that the reaction



Figure 1. Dispersion of the absolute height of consensus (blue squares) and control (red circles) dsDNA matrices after reaction with DpnII restriction enzyme (FH) versus the initial height (IH). The black dashed line provides a visual guide for FH=IH (relative to control dsDNA matrices), while two fits are shown for the data relative to consensus matrices. For IH < 12nm, FH ~0.5 indicates these are cleaved. (From doi:10.1038/ncomms1296 NPG copyright permission).

occurs only within the matrix that lacks a surrounding high-density "fence" structure. This indicates that the access of enzyme to the dsDNA matrix, and therefore the progress of the reaction, strictly depends on the packing of dsDNA molecules at the matrix sides. The same result is observed when the high-density barrier is generated with a control dsDNA sequence lacking the DpnII restriction site.

In general, restriction enzymes specifically recognize nucleotides within the consensus palindromic sequences, thereby enabling phosphodiester hydrolysis. One possible interpretation of the enzyme access mechanism shown in Fig. 2a,b could be that consensus restriction sites are directly available at the interface, with the solution only on the sidewalls of the matrix. Therefore, the cleaving reaction would progress from the sidewalls towards the inner matrix. To assess this hypothesis we nanografted a low-density consensus dsDNA matrix within a larger matrix of control DNA sequence with the same density (Fig. 2c) and exposed it to the enzyme (Fig. 2d). Comparing the two line profiles (c1 and d1) we demonstrate that DpnII enzyme molecules can access the consensus dsDNA molecules within the inner

matrix, after having diffused through a non-consensus, low-density, uncleaved dsDNA matrix. These results, confirmed by fluorescence imaging, suggest that the dsDNA density has an important role in the enzyme access mechanism at the matrix sides, and, therefore, in the enzyme 2D diffusion within the matrix. We explain these results by modelling the steric hindrance on the dsDNA matrix-liquid interface, and propose a semiguantitative, steric hindrance-dependent enzyme access mechanism that is inspired by an established model that describes the diffusion of solutes inside polymer matrices.



Figure 2. AFM micrographs and corresponding line profiles for dsDNA matrices before and after restriction reaction. a,b) high density barrier of a consensus dsDNA sequence. c,d) low density barrier of a control dsDNA sequence (c and d). Graphical schemes represent the DNA density underlying topographic profiles. (From doi:10.1038/ ncomms1296 NPG copyright permission).

ORIGINAL PAPER

M. Castronovo, A. Lucesoli, P. Parisse, A. Kournikova, A. Malhotra, M. Grassi, G. Grassi, B. Scaggiante, L. Casalis, and G. Scoles, *Nat. Comm.* **2**, 297 (2011)

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Highly selective vapour sensing by specific molecular recognition of C₁–C₄ alcohols with a fluorescent phosphonate cavitand

olecular-level resolution was achieved for the detection of short-chain alcohols in the vapour phase using a fluorescent phosphonate cavitand sensor. The transduction mechanism, activated exclusively by the complexation mode, is provided by a whole series of crystal structures of C_1-C_4 alcohol-cavitand complexes determined by single crystal diffraction with synchrotron radiation. The solid-state study clearly indicates that the change of the electronic density on the fluorophore is caused by the formation of an intracavity hydrogen bond between the cavitand P=O and the alcohol OH group.

In the last few years there has been a huge demand to monitor different chemical species in the vapour phase, such as environmental pollutants, hazardous chemicals, food aromas, explosives, and volatiles in breath for disease diagnosis. Chemical vapour sensors are among the most promising devices to be exploited for these applications, because they have the great advantage of allowing an online measure suitable for remote control. In this context, the need to develop sensors specific for different classes of analytes is well-recognized and confirmed by the considerable research efforts spent for the preparation of more and more efficient devices. The crucial parameter to define the success of a given sensor is therefore selectivity, and for this reason the strategy to prepare the sensing material following the principle of



Figure 1. Crystal structures of the six cavitand-alcohol complexes. Geometric parameters describing the host-guest interaction, such as the H bond length (O_{alc} ···O=P) and distances of the hydroxyl and methyl groups from the mean plane of O atoms of P=O groups are reported in the top and in the side views, respectively.

supramolecular chemistry has quickly gained increasing importance. We investigated a new solidstate fluorescent sensor based on phosphonate cavitand for detecting short-chain alcohols in the gas phase. At first, a systematic study was undertaken to assess the complexation properties of phosphonate cavitands towards alcohols in the crystalline state. Crystallization trials of this cavitand were performed by the vapour diffusion method with sitting drops in Linbro multiwell plates containing trifluoroethanol (TFE) as solvent. The addition of a short-chain alcohol in the reservoir solution, through vapour diffusion in the drop, allowed the easy and fast growth of monoclinic crystals of the corresponding host-guest complex. A whole series of isomorphic crystal structures of the TFE disolvate of C_1 – C_4 alcohol–cavitand complexes were obtained (Fig. 1) by synchrotron X-ray single-crystal diffraction. All six host-guest complexes present the same interaction pattern: an H-bond between the alcoholic OH group and one of the PO units, and CH– π contacts between the π -rich cavity and one methyl group of the alkyl chain. The relevant geometric parameters describing the hostguest interaction are reported in Fig. 1. In the case of 1-butanol, the contemporary onset of both interactions with the cavitand requires the deep insertion of the methyl group of the guest into the cavity and the weakening of the H-bond. Furtermore, the presence of a single additional methylene unit is sufficient to completely suppress the crystallization process of the 1-pentanol complex. The solid-state study clearly indicates that the two interactions responsible for the high selectivity of phosphonate cavitands towards alcohols occur simultaneously only in the $C_1 - C_4$ alcohol series. Taken

alone, none of them is sufficient to bind alcohols in the solid state. The next step was the selection of a transduction mechanism activated exclusively by this specific complexation mode; we chose to attach a fluorophore to a monophosphonate cavitand. The rationale of this design was based on the belief that the formation of the hydrogen bond between the PO and the alcohol OH group could decrease the electronic density on the phosphorus atom to a such an extent to modify the energy of excited state of the fluorophore covalently linked to the PO group. This design was also conceived to offer a high specificity, as only the formation of a hydrogen bond could cause a specific spectral red-shift. A special designed cell was employed for measuring the fluorescence of the cavitand deposited on glass substrate subject to a continuous gas flow. Upon excitation at 350 nm, the film showed an intense broad and unstructured band emission with a maximum at 414 nm. Upon exposure to different alcohols, the

maximum of this band was redshifted by 5 nm. This difference was sufficient to monitor the concentration of the alcohols in the gas phase. The intensity changes (see Fig. 2) were comparable for the whole C_1-C_4 alcohol series with the exception of 1-butanol, which caused lower responses. This result implies that its H-bond with the PO is less effective, as inferred by the crystal structure.

This work demonstrates that it is possible to achieve high selectivity in chemical vapour sensing by harnessing the binding specificity of a cavitand receptor. The key requirement for transferring the molecular recognition properties from the solid-state to the gas-solid interface is the selection of the transduction mechanism, which must be turned on exclusively by the desired complexation mode with the analyte. The predictive value of solid state crystal structure determination is pivotal to establish type and number of the interactions experienced by the analyte in the receptor layer.



fluorescence intensity changes ($\lambda_{exc} = 350$ nm. $\lambda_{emi} = 460 \text{ nm}$) of PVC films containing the in isomer of the mono-phosphonated receptor (dark grey) or the out isomer as negative control (light grey) exposed to different alcohols in N₂: methanol, ethanol, n-propanol, 2-butanol, 1-butanol, 1-pentanol (500 ppm each).

Figure 2. Relative

ORIGINAL PAPER

F. Maffei, P. Betti, D. Genovese, M. Montalti, L. Prodi, R. De Zorzi, S. Geremia, and E. Dalcanale, *Angew. Chem. Int. Ed.* **50**, 4654 (2011)

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Structural studies of copper complexes as potential bioinorganic target-specific drugs

The knowledge of the local atomic environment of copper in inorganic complexes containing scorpionate-based ligands is essential to study the relationship between cytotoxic activity and structure of the complexes. X-ray Absorption Spectroscopy (XAS) experiments at the XAFS beamline allows to obtain the relevant structural information. The joint XAS and biological data evaluation allows to design new ligands useful for the synthesis of novel copper derivatives to be further evaluated as alternative anticancer drugs.

The well known biochemistry of copper underlines the crucial role played by this metal in different enzymes that catalyze oxidation/ reduction phenomena correlated with the antioxidant systems of living organisms. It has been established that the properties of copper-coordinated compounds are largely determined by the nature of ligands and donor atoms bound to the metal ion. Phosphine complexes of group 11 metals, especially those including the copper(I) and gold(I) ions, have been proposed as alternative anticancer drugs to the cisplatin reference drug. For instance, copper complex with trishydroxymethylphosphine ligand has been shown to be about one order of magnitude more cytotoxic than cisplatin and some less hydrophobic mixed scorpionates-phosphine copper(I) complexes were proved to retain high cytotoxic activity against a panel of human tumor cell lines. Analogously, nitroimidazoles are a class of hypoxia tracer that have been extensively investigated for hypoxia-selective cytotoxicity. The



Figure 1. Artistic artwork showing the interaction of copper scorpionate complexes with a carcinoma cell. The picture also displays the copper coordination resulting by the EXAFS analysis: copper is found to be 6-fold coordinated interacting with 2 units of ligand.

anticancer activity is of outmost interest because these compounds kill cells through parapoptosis, a complex mechanism allowing the organism to get rid of defective cells in a controlled way. The knowledge of the local atomic environment of copper in these inorganic complexes is essential because it can help to understand the cytotoxic activity observed for these complexes. Because these materials are frequently polycrystalline or amorphous and no crystal structure are likely to be obtained using X-ray diffraction, the XAS technique is a good alternative for structural studies. XAS probes the local structure around a selected atomic species and can give information on a range of several angstroms around the selected atom (photoabsorber). We present here the results of copper(II) complexes with two new-synthesized nitroimidazole

and glucosamine conjugated heteroscorpionate ligands, $\{[(L^{MN})_{2}Cu]Cl_{2}\}$ (1), and $\{[(L^{DAC})_{2}Cu]\}$ Cl_{2} (2). The XAS measurements, recorded on solid samples at the XAFS beamline, were successively analyzed taking into account the multiple scattering formalism, allowing the determination of the first shell distances as well as the contribution of the outer shells of copper. Copper is found to be 6-fold coordinated interacting with 2 units of ligand in both complexes. Its local structure is described by four Cu-N and two Cu-O interactions

to form a pseudo-octahedron core. Analysis of the multiple scattering contributions of the outer shells suggests a more structural disorder for complex 2 with respect to 1. The reason lies in the Cu-O interaction which lengthens about 0.14 Å in the case of complex 2 with respect to 1, which may be due to steric hindrance of the substituent. Fig. 2 shows a typical analysis of the experimental EXAFS spectrum which is fitted with a theoretical one. The XANES analysis (not shown) confirms the Cu(II) formal copper oxidation state for both complexes and the local structure rearrangement of the pseudo octahedron. The two copper complexes and the corresponding uncoordinated ligands were evaluated for their cytotoxic activity towards a panel of several human tumour cell lines. In most of the cancer cell lines tested, both Cu(II) complexes display a similar growth inhibitory potency that is in the micromolar range and slightly lower than that shown by cisplatin whereas in colon adenocarcinoma cells, they are about 3-fold more effective. The ultimate goal of the presented studies is to find the relationship between the structure and functionality of novel copper complexes and to design new scorpionate ligands in order to have an increased cytotoxic activity. At the same time these works open up the way for further investigations on biological systems in solution.



Figure 2. Example of EXAFS data analysis. The picture displays the details of the EXAFS best fit for complexes 1 (top) and the corresponding Fourier Transform (FT) curve (at the bottom). As seen, each atomic shell, around the photo-absorber, indicated as 1st, 2nd and 3rd, contributes to the EXAFS signal. The comparison of the total theoretical EXAFS signal (*) with the experimental one (---) is also reported. At the bottom, the corresponding FT theoretical and experimental signal are compared. Three main peaks are found, and they are related to the atomic species belonging to the near imidazole, as indicated by arrows in the figure.

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Advances in understanding of wheat aleurone cell biology using synchrotron soft X-ray microscopy

The complex mechanisms underlying elemental accumulation, distribution and storage within the seeds have received increased attention due to their significance for elemental fortification and benefits for human consumption. Application of Synchrotron Radiation (SR) Full Field Imaging Mode (FFIM) and Low Energy X-ray Fluorescence (LEXRF) microspectroscopy at the TwinMic beamline station to wheat aleurone cells reveal different levels of co-localization of physiologically important metals with phytic acid and pinpoint the globoids in wheat aleurone cells as major structural and functional barrier that affects mineral bioavailability within the mature seeds.

Seeds are designed to provide physiologically important nutrients, primarily carbohydrates, oils and minerals that are mobilized at the onset of germination. The aleurone cell layer is dedicated to storage of minerals. Due to its small volume, total mineral concentrations in seeds are usually low. Wheat (Triticum aestivum) aleurone cells are therefore of significant interest in the studies of elemental concentration, distribution and remobilization, in the challenge to increase seed mineral abundance and reduce the risks related to human mineral malnutrition. Synchrotron radiation X-ray microscopy techniques have the ability to link elemental topographies of biological systems with their structural morphology in situ at impressive spatial resolutions, essential in these studies of complex biological materials. Up to 80% of total seed phosphorus

is stored in the aleurone, the majority in the form of phytic acid. It accumulates in globoids of protein storage vacuoles (Fig. 1, 2). Negatively charged phosphate groups of phytic acid strongly bind accessible metallic cations in aleurone cells, rendering them unavailable for human and animal nutrition. It is therefore of special interest to investigate how detailed spatial elemental distribution maps of physiologically relevant elements (C, N, O, Na, Mg, Si, Zn) relates to phosphorus distribution in order to reveal the level of their colocalization with P. Complementing Low Energy X-ray Fluorescence (LEXRF) cartography maps (acquired at the two different incident photon energies E = 1686 eV for C, O, Fe, Zn and Na, and E = 2172 eV for Mg, Al, Si, and P) with Differential Phase Contrast (DPC) imaging at the TwinMic beamline station at Elettra, we were able to link the predominant elemental distribution to cellular and sub-cellular morphology.

Expectedly, elemental cartographies of Mg, Zn, Fe, Na, Al, and P showed similar repartitions, although with the signals of differing intensities,

Figure 1. Elemental microanalysis of the wheat aleurone cells acquired with the TwinMic X-ray scanning microscope showing structural morphology on DPC image and elemental cartography maps (58 μm x 58 μm). The scale bar is in arbitrary units. From Regvar et al., New insights into globoids of protein storage vacuoles in wheat aleurone using synchrotron soft X-ray microscopy, J. Exp. Bot. **62**, 3929-3939 (2011), courtesy Oxford University Press.



indicating their interconnection (Fig. 1). The distributions of C, N, O, and Si, on the other hand, were more representative of cell wall structural components (predominantly of cellulose, hemicellulose and pectin). The observed repetitive elemental distribution patterns within the aleurone cells indicate their linkage to the sub-cellular structural organization. With the use of high optical resolution images in the Full Field Imaging Mode (FFIM) we were able to portray a plethora of individual globoids inside a single aleurone cell (Fig. 2). In addition, a more in-depth insight in the cellular make-up also revealed more detailed structural organization of the cell wall and prominent cell nuclei, as well as other cellular features at micron and sub-micron resolution. The combination of LEXRF microspectroscopy with FFIM supports different levels of colocalization of physiologically important metals with phytic acid and pinpoint globoids of protein storage vacuoles in wheat aleurone cells as major structural and functional barrier affecting mineral bioavailability in mature wheat seeds. The significance of globoid endomembrane structure organization for mineral immobilization and release at the onset of germination deserves further attention in the future biofortification programmes.

Acknowledgement: Figures from Regvar et al., New insights into globoids of protein storage vacuoles in wheat aleurone using synchrotron soft X-ray microscopy, J. Exp. Bot. **62**, 3929-3939 (2011), courtesy Oxford University Press.



Figure 2. High optical resolution images of wheat aleurone cells acquired in FFIM showing substructural morphology (e = endosome; g = globoids; m = cell plasma membrane; n = cell nucleus; o = oleosome; pr = globoid protrusions; iw = inner cell wall; ow = outer cell wall). From Regvar et al., New insights into globoids of protein storage vacuoles in wheat aleurone using synchrotron soft X-ray microscopy, J. Exp. Bot. **62**, 3929-3939 (2011), courtesy Oxford University Press.

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Wake me up! Anaesthesia, a membrane mediated loss of sensation?

e have studied membrane mediated effects of ketamine in lipid model membranes using high resolution Small Angle X-ray Scattering (SAXS) and molecular dynamics simulations. Our results show that ketamine may affect the opening probability of ion channels of the central nervous system at clinically relevant concentrations by changing the internal pressure field of lipid membranes.

> Most probably everyone reading this article has already encountered several times in his life one of the most important, if not "the" most important drugs of human mankind: Anaesthetics. Without them modern surgery would just not be possible, and even simple medical interventions as those carried out by your dentist would become unbearable. Yet, despite their daily successful application for more than 160 years, we do not know how these drugs act on

the molecular level. The quest for molecular targets boils down to two possibilities. Either anaesthetics directly act on ion channels of the central nervous system, or they change the biophysical properties of nerve membranes such that neurotransmission signals are affected. Arguments can be found in favour of one or the other target and the controversy on this issue is almost as old as the clinical use of anaesthetics.



Figure 1. Lateral pressure profiles of POPC membranes at various concentrations (mol%) of the anaesthetic drug ketamine. The bar plot shows the distribution of ketamine.

We set out to study a mechanism that in a way integrates both views. Membrane proteins such as ion channels are under a constant field of lateral pressure, which is caused by the collective properties of the lipid membrane. When they open up and act as passive channels for the exchange of ions, they have to do this against the lateral pressure field, which costs some work. The idea is simple, yet very powerful. If an anaesthetic drug inserts into the membrane it will change its lateral pressure field, such that the work that the protein needs to perform for opening the channel is different. Thus, it couples via membrane properties mechanically to the opening probability of ion channels. It is very difficult to determine the lateral pressure field experimentally. However, it is possible to measure its integral parameters, such as the membrane thickness, lateral area per lipid or bending rigidity. Because effects

can be expected to be small, in particular at clinically relevant drug concentration, ultra-high structural resolution as provided by the SAXS beamline at Elettra is of need. Nerve membranes were mimicked by vesicles composed of the phospholipid palmitoyl oleoyl phosphatidylcholine (POPC) to which well defined amounts of ketamine was added. Diffraction patterns were analysed in terms of a full q-range model both in terms of the membrane thickness and area per lipid. Interestingly, neither of these parameters showed significant changes in the concentration range of 0-8 mol% ketamine. Therefore, we performed Molecular Dynamics (MD) simulations in order to trace the effects to molecular details. Moreover, MD simulations allow to derive lateral pressure fields in membranes. The MD simulations confirmed our experimental observations. However, at the same time we found significant changes

to the pressure field (Fig. 1). In particular, the results demonstrated that ketamine locates preferentially close to the lipid/water interface and shifts the lateral pressure field toward the centre of the membrane. These results allowed us to calculate the consequent inhibition of ion channels applying simple protein models (Fig. 2). The half value (IC50), where 50% of the ion channels are inhibited, was found to be either at 2 mol% or 18 mol%, respectively, depending on the protein geometry. It can be estimated that this corresponds to ketamine concentrations of 0.08 μ M and 0.9 μ M, respectively, in the blood. These values compare favourably with concentrations of ketamine in clinical applications. Results strongly encourage a further exploitation of membrane mediated effects of anaesthetics, which we think may lead to novel ways for designing membrane active anaesthetic drugs.



Figure 2. Effect of lateral pressure changes on the opening probability of ion channels. Either n-mers of tilted helices or bent helices were used as simple geometric models for the membrane proteins.

ORIGINAL PAPER

H. Jerabek, G. Pabst, M. Rappolt, and T. Stockner, J. Am. Chem. Soc. **132**, 7990 (2010)

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Synchrotron soft X-ray imaging and fluorescence microscopy to study asbestos body morphology and composition in human lung tissues

A sbestos is an established carcinogen and the most aggressive illness associated with this mineral is pleural mesothelioma, a neoplasm that develops in the lining of the lungs. While asbestos exposure has been linked to cancer for quite long time, mechanisms responsible for fiber toxicity and carcinogenic activity are still undefined. In our study, we used synchrotron soft X-ray imaging and X-Ray Fluorescence (XRF) microscopy at TwinMic beamline to examine the chemical makeup of human tissues containing asbestos fibres. We have revealed new details in the chemical mechanisms that lock asbestos fibres in the lung and that provide new insights into the reaction of living tissues to the presence of this foreign material.

Asbestos fibres can enter the body by inhalation and may manifest their toxicity after many years of persistence. Although since 1990 the commercialization and industrial use of asbestos have been limited and it is virtually abolished today, the long latency period (20-40 years) of asbestos makes the asbestosrelated diseases and particularly mesothelioma still an ongoing public health issue. North-eastern Italy (provinces of Trieste and Gorizia), where massive occupational exposure to asbestos occurred in the past, is considered as one of hyperendemic for mesothelioma regions.

When asbestos fibres are inhaled, the mucus is supposed to surround them to facilitate their elimination. However, many fibres get trapped into the lung and remain all life long in the body locked inside biostructures called "asbestos bodies". These formations are the result of the body reaction to the irritation caused by asbestos, which leads to a progressive condition of chronic inflammation (asbestosis) and/or neoplastic transformation. While the cause is known, the real pathogenetic mechanisms of the process are still undefined. The asbestos body consists of an optically transparent asbestos fibre core, surrounded by a golden-brown coat containing iron-rich proteins such as ferritin and hemosiderin. The overall diameter of the body is

usually from 2-5 mm and the length is typically in the range of 20-50 mm. The coating is almost never uniform and may appear segmented along the fibre into spaced spherical or rectangular units that are usually knobbed (as well shown in Fig. 1). Before our study, many authors investigated the chemistry of asbestos bodies to better understand

the mechanism of formation and thus the molecular consequences. The presence of transition metals in the fibres and/or their ability to absorb them is the first mechanism suggested for explaining the toxic and carcinogenic effects of asbestos. The presence of surface redoxactive iron in the fibre as well as iron containing protein aggregation



Figure 1. Soft X-ray microscopy and XRF analyses of an asbestos body in human lung tissue. Panel A: visible light image of the tissue with the asbestos body. Panels B and C: absorption and phase contrast images acquired at a photon energy of 2.018 keV (25 x 40 μ m² size). Panels Fe, Si and Mg: elemental distribution among the area of panels B and C, acquired at 2 keV, (Si and Mg), and at 1.3 keV (Fe).

in tissues is supposed to be greatly responsible for the genotoxic and cytotoxic effects of asbestos by increasing and auto sustaining a continuous Reactive Oxygen Species (ROS) production, thus DNA damage and apoptosis resistance. In our study we applied synchrotronbased techniques to analyze lung samples obtained from patients professionally exposed to asbestos (archives of the hospital of Monfalcone). These are soft X-Ray imaging and XRF microscopy at the TwinMic beamline to specifically study the chemical composition of asbestos bodies and of the surrounding tissues. The goal was to differentiate between the coating and the asbestos fibres in order to understand the net chemical contribution from the tissue to the formation of asbestos bodies. The results of the analyses in two different tissue samples containing asbestos are shown in Fig. 1 and 2. The iron, magnesium and oxygen content that resulted to be abundant constituents of the casing was measured. As expected, the original asbestos fibres were very high in silicon content. It has been found that the tissue surrounding the asbestos contains also significant amount of iron and magnesium, indicating involvement of these elements in the tissue response to asbestos presence and also possibly in the process of oxidative stress leading to cellular damage. The results of this study are an important step towards clarifying the role of specific chemical elements in the development of asbestos related diseases. The information provided by morphology and chemical imaging using X-ray microscopy approach is expected to advance cellular-level investigations,

while the new understanding of the reaction of the human body to asbestos may lead to the development of more effective treatments for asbestos related diseases, particularly mesothelioma.



Figure 2. Soft X-ray microscopy and XRF analyses of an asbestos and other ferruginous formations in human lung tissue. Panel A: visible light image of the analysed asbestos body. Panel B and C: phase contrast (B) and absorption (C) images respectively acquired at photon energy of 1.3 keV (50 x 50 µm² size). Other panels: XRF maps acquired on the region showed in panel C, at 1.3 keV (Fe and O) and at 1.93 keV (Mg and Si). Panel Si-Fe: colocalization of Si (in green) and Fe (in red). Panel Fe-O: colocalization of Fe (in green) and O (in red). Panel D and E: XRF spectra acquired in points a, b and c (see panel B) at 1.3 keV (D) and 2 keV (E).

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Gold nanoparticle labeling of cells is a sensitive method to investigate cell 3-dimensional distribution and migration in animal models of human disease

orking at the biomedical beamline SYRMEP, we have developed an image acquisition method that allows us to track small groups of cells implanted into a host organism with an imaging technique based on synchrotrongenerated X-rays. The cells are loaded with Gold NanoParticles (GNP) prior to implantation, which renders them opaque to X-rays. In combination with a high-resolution detector system this allows us to visualize the migration and proliferation patterns of the implanted cells over a long time.



Figure 1. Coronal slice of rat skull with a malignant brain tumor generated from gold-loaded C6 cells.

In human patients with neurodegenerative diseases or brain tumours, imaging procedures are a staple of the diagnostic process. To conduct preclinical research in diseases of the Central Nervous System (CNS), frequently work in small animal models is required. This confronts researchers with the challenge to identify an imaging technique that allows the visualization of lesions typical for the disease in the small animal brain. Therefore, one of the first requirements for an imaging method used in small animal research would be a high spatial resolution. The world of synchrotron-based imaging would seem like an optimal environment for such a quest. Although the brain structures itself are not identifiable in a synchrotron X-ray Computed Tomography (CT), Gold NanoParticles (GNP)labeled cells have a good contrast. Overlaid or fused with an image acquired with a high-Tesla Magnetic Resonance Imaging (MRI), we would gain highly detailed information about small groups of cells in a background of excellent morphological information. Over the last three decades, cell transplantation therapies have been developed for the therapy of neurodegenerative diseases. Several clinical trials have already been conducted for patients with Parkinson's and Huntington's disease. For studies of this type it would be possible to load the cells to be transplanted with GNP prior to surgery. Since the elemental gold contained in those GNP is biologically inert, i.e. it is not chemically changed once taken up into the cell, it would be stored within small vesicles inside the cell permanently, until the cell dies. Since there is no natural source of gold in either animals or humans,

transplanted cells or their progeny could be easily identified at any time after transplantation.

In order to develop a method that suits those requirements, we have worked in small animal models of malignant tumors. Tumor cells are much easier to grow in culture than the non-malignant cells used for neurotransplantation. We have been able to develop an image acquisition protocol that allows us to visualize primary malignant brain tumors (see Fig. 1) as well as metastatic disease with much smaller foci (see Fig. 2). Thus, the method could be very useful as follow-up tool in research projects where new therapeutic approaches are developed against infiltrating tumors or/and metastatic disease. Our first in vivo experiment was conducted at SYRMEP in October 2010.

An interesting field to test our technique lies in the different models of neurotransplantation, where cells from healthy donor tissue are transplanted into the brain of a host suffering from a neurodegenerative disease. The risks inherent in cell transplantation include the migration of cells to locations other than the intended target location as well as unchecked proliferation and subsequent tumor formation. Loading the cells prior to transplantation with GNP will allow us to track the transplanted cells within the host organism for a long time, possibly for the lifetime of the host. Although it is technically not yet possible at this time, we hope that one day we will be able to introduce our method into the clinical environment. The option to image patients repeatedly after cell transplantation therapy would significantly improve the quality of the follow-up.

With repeated imaging as a followup procedure one would recognize early on small cell groups that proliferate beyond what would be normally expected. In such a case, a minimally invasive procedure would suffice to remove the aberrant cells, rather than being surprised by a tumor that might have destroyed structure and function beyond repair before it becomes symptomatic. Beyond the ability to see very small groups of cells implanted in the host brain, the technique will also allow us to significantly reduce the number of animals required

for some experiments. Rather than killing a larger number of animals at each time point considered crucial in the development of the disease, we can follow one single cohort of animals over a longer time and through the different stages of disease development, imaging them repeatedly.

For this work, our group was awarded the 2010 research award for 'Reduction and Replacement of Animals in Research' by the Ministry of Agriculture and Nutrition of the land Baden-Wuerttemberg in Germany.



Figure 2. Metastasis invading the bone structure of a spinal vertebra (rat).

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Short-term interaction of the human host defence peptide β-Defensin 2 (hBD2) with dendritic cells explored by SR-IRMS

P-Defensins are small proteins that display a broad antimicrobial activity and play a role in both innate and adaptive immunity. They are promising candidates for development of novel multifunctional antibiotics. For this purpose, the understanding of their mode of action is fundamental. In this study we have investigated the interaction of human-beta defensin 2 (hBD2) with a specific class of immune cells by means of flow cytometry and several microscopy techniques, among them Synchrotron Radiation InfraRed MicroSpectroscopy (SR-IRMS) at the SISSI beamline, and we postulated a new mode of action of the peptide, never proposed before.

Mammalian β -defensins are small, cationic host-defence peptides (HDPs) with a characteristic β -sheet fold, which exert their protective functions at the host-environment interface. The overall picture that is emerging on their protective role *in vivo* indicates that they act in an articulated and quite complex manner, by directly contrasting invading microorganisms, by recruiting host immune cells, such as T-cells and immature dendritic cells (iDC), to the site of infection, and as enhancers or regulators of inflammatory and healing responses. It suggests that this class of HDPs may lead to promising leads for the future development of multifunctional anti-infective agents or vaccine adjuvants. We investigated the consequences of short-term (30-60 min) interaction between hBD2 and iDCs. Flow cytometry and confocal microscopy were used to determine whether fluorescently labelled hBD2 localised exclusively at the membrane level or also intracellularly in iDCs, showing that these cells are more efficient in surface binding than in peptideinternalization. In addition, SR-IRMS was employed for typifying cellular samples. Hierarchical Cluster Analysis (HCA) of wholecell microspectra revealed that two subgroups coexist in both control and treated cells, corresponding to the same sub-populations previously observed using flow cytometry (see Fig. 1A).



Figure 1. A) Dendrogram resulting from the HCA on the first derivatives of both control and treated iDCs in the 1755-1475 cm⁻¹ region. Ct-R1 and T-R1 are discriminated into two classes, whereas Ct-R2 and T-R2 are not. Optical images show the typical cell shape of responsive and non-responsive iDCs. B, C) IR average spectra of Ct-R1 (blue line) and T-R1 (red line) and their difference (green area) in the 1760-1480 cm⁻¹ and 3025-2800 cm⁻¹ regions respectively.

Control iDCs non-responsive to peptide treatment (Ct-R2) clustered together with peptide exposed iDCs unaffected by the treatment (T-R2). Spectral differences between control iDCs responsive and non mainly occurred in the 1755-1475 cm⁻¹ region, in bands associated with carbonyl stretching vibrations of DNA, a type of variation that has been assigned to the changes in chromatin structure required for transcription and linked to cell differentiation in hematopoietic cells. A correspondence between those spectral differences and morphological features of iDCs was also successfully established (see Fig. 1A, optical pictures). Responsive iDCs (R1) exhibited distinctive biochemical features before and after the treatment.

Short-term exposure to hBD2 induced striking alterations in the general lipid composition, suggesting a critical role of membranes, and possible effects on lipid bodies (LB), in peptide induced cellular process. In particular, variations in the 1750-1600 cm⁻¹ (Fig. 1B) and 3020-2800 cm⁻¹ (Fig. 1C) spectral regions indicate i) an increased lipid disorder, consistent with an increased membrane fluidity, and *ii*) variations in the CH₂/CH₂ ratio suggesting that exposure to non-toxic concentrations of hBD2 causes significant alterations to the membranes of iDC. Cells from the R1 subgroup were chosen on the basis of cluster analysis of wholecell spectra for IR mapping. Protein (P), lipid (L) and phospholipid (Ph) signals behaved somewhat differently upon treatment (see Fig. 2).

While the overall distribution of proteins and lipids did not alter markedly in treated with respect to the naive cells, the phospholipid map showed a significant relative decrease in the Ph carbonyl ester signal in the cytoplasmic region. This effect was observed for all treated cells that were mapped, regardless of their derivation (3 different donors), and supports a general rearrangement of the endomembrane system upon short exposure to hBD2. These hBD2induced membrane variations could possibly be correlated to increased cellular motility, in line with the reported chemotactic

effect of hBD2 on iDC, which had previously been ascribed to activation of the CCR6 receptor, as well as to specific DCs activities such as the cross-presentation. Accumulation of the peptide in the proximity of membrane-located receptors may favour a receptormediated activation of chemotaxis, while its effects on membrane properties might also assist this process in alternative ways, and cellular motility would in any case benefit from an increased membrane fluidity. This suggests a more complex mode of chemotactic action than was previously supposed.



Figure 2. Chemical maps of control and hBD2-treated iDC. Selected Ct-R1 cell and T-R1 cell, top and bottom rows respectively. Proteins: integral area 1707-1590 cm⁻¹; Lipids: integral area 3000-2800 cm⁻¹; Phospholipids: integral area: 1760-1720 cm⁻¹.

ORIGINAL PAPER

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FERMI@ELETTRA

FERMI@Elettra status report

n December 13th, 2010, that is just a few weeks after completing the installation of the FEL-1 line, the first lasing at the wavelength of 65 nm was observed at FERMI@Elettra. The commissioning went on in the following months gradually improving the performance of the machine; for instance, the measured photon flux at 43 nm increased from less than 10⁹ photons per pulse in December 2010 to more than 10¹³ photons per pulse in July 2011. The commissioning of the beamlines and experimental stations started as well, with two dedicated periods reserved in the operation calendar in March and July 2011.



Figure 1. First lasing on December 13th, 2010.

The seeded Free Electron Laser (FEL) user-facility FERMI@Elettra has entered into an advanced commissioning stage of its first FEL line, FEL-1, which is designed to cover the wavelength range from 100 nm to 20 nm. The FEL-1 line consists of a planar undulator (the "modulator") and six APPLE-II undulators (the "radiators"). The wavelength of the FEL radiation can be varied thanks to the variable undulator gap, which can be closed to a minimum aperture of 10 mm. Furthermore, the use of APPLE II undulators allows control of the FEL polarization that can be varied from linear to circular. The photons generated by FEL-1 are characterized and transported to the beamlines by the Photon Analysis, Delivery and Reduction System (PADReS). The installation started in autumn 2010. The commissioning of the machine started in summer 2009 with the operations on the first part of the machine where electrons are created and accelerated up to 100 MeV. Since then, commissioning runs have been alternating with long shutdown periods to allow machine installation progress. Few weeks after completing FEL-1, with the installation of its seven undulators in November 2010, it was possible to demonstrate first evidence of coherent signal in the range from 60 to 20 nm. Fig. 1 shows the first seeded coherent emission from FEL-1, measured using a fast photodiode on PADReS with undulators tuned at 65 nm. The green trace shows the time profile of a single pulse with the photodiode in saturation. The yellow trace shows a series of seeded FEL pulses, being turned on (left) and off (center-right) by changing the superposition between the seed laser pulses and the electron bunch. The benefit of using external seeding in terms of spectral bandwidth and photon energy stability was evident since the very first days of FEL operation when measurements of the spectrum showed that the width of the produced optical pulses was close to the Fourier limit. During 2011 the FEL-1 performance has improved gradually. In July 2011, after increasing the bunch charge from 250 to 450 pC, with minor other changes in the accelerator and upon optimizing

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the FEL on the TEM₀₀ Gaussian mode, we obtained clear evidence of FEL exponential gain. At 43 nm the measured photon flux increased from less than 10⁹ photons per pulse measured in December 2010 to more than 10¹³ photons per pulse. Similar flux intensities have been measured at 52 nm and at 32.5 nm; Fig. 2 shows the spectrum at 32.5 nm. At the lower wavelength limit of FEL-1, 20 nm, the photon flux achieved was larger than 10¹² photons per pulse. Once the FEL operation is optimized, its stability is quite good over a few hours: the central wavelength jitter is below 10⁻⁴, the spectral bandwidth stability is below the 3% level and the intensity jitter is about 10%. Beamline and end-station commissioning was carried out both in March-April and in July 2011, when FEL light was provided to TIMEX, one of the two end-stations of the Elastic and Inelastic Scattering (EIS) program, to a temporary end-station of the Low Density Matter (LDM) program and to the end-station of the Diffraction and Projection Imaging (DiProl) program. In April, during the LDM period, the FEL polarization was varied for the first time from linear to circular. In July, the wavelength tunability of the FEL has been experimentally demonstrated, when, during the LDM beam time, a small change of the fundamental harmonic of the FEL radiation around 52 nm has been achieved by varying the seeding laser wavelength by approximately 1 nm, corresponding to 0.4% variation of the FEL wavelength. The second FEL line, FEL-2, adopts a high gain harmonic generation double cascade scheme, thus there is a first stage with one modulator and two radiators followed by a second stage with one modulator and six radiators.

The FEL-2 wavelength range will cover in the first harmonic the interval from 20 nm down to 4 nm. The FEL-2 line assembly will be completed within 2011; transport of the electron beam along the FEL-2 line will follow in 2012. The production of the FEL-2 undulators is almost complete; they will be installed later on in 2012.

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In conclusion, the FERMI@Elettra facility will be open to external users in 2012. Commissioning of the FEL-1 line is at a fairly advanced stage and the nominal performance is expected to be attained by the end of 2011. The commissioning of the FEL-2 line will start in 2012, in parallel to the user experimental program which will be launched on FEL-1.



Figure 2. FEL spectrum at 32.5 nm, July 2011.

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Multipurpose modular experimental station for the DiProl beamline of the FERMI@Elettra free electron laser

The end-station that will be operated at the Diffraction and Projection Imaging (DiProI) beamline of the seeded FERMI@Elettra Free Electron Laser (FEL) facility will exploit the full coherence and variable polarization of the FEL pulses with wavelength tunability between 50 and 4 nm in the first harmonics and temporal pulse structure down to a few tens of fs. The instrument is designed to meet the requirements for static and dynamic Coherent Diffraction Imaging (CDI) experiments with diffraction limited resolution and opens new opportunities for time resolved resonant CDI.

X-ray microscopy and imaging have become highly demanded techniques for the characterization of a great variety of morphologically complex materials by nature and design. However, both full-field and scanning microscopes have X-ray optics-limited resolution which has been overcome substantially by applying lensless coherent diffraction and ptychography schemes. In Coherent Diffraction Imaging (CDI) the real-space information of the specimen is extracted from the far-field diffraction pattern using iterative computational algorithms as "virtual lens". The final achievable resolution is governed by the numerical aperture of the detector, the X-ray wavelength, and the coherence, intensity and spectral purity of the beam. The advent of the fully coherent Free Electron Laser (FEL) sources with ultra-short and ultra-bright X-ray pulses has opened

unprecedented opportunities, permitting to collect all speckle information in a single shot coherent imaging mode before the radiation damage manifests itself. This has allowed achieving high spatial and temporal resolution for exploring ultrafast dynamic phenomena in complex functional natural or fabricated materials. The multipurpose end-station that will be operated at the Diffraction and Projection Imaging (DiProl) beamline at FERMI@Elettra has been designed and constructed in partnership with scientists and engineers from Elettra, LLNL, CFEL and Uppsala University, in order to meet the requirements of a modular experimental set up. Several classes of experimental schemes inside the chamber are implemented, such as fix target CDI, injection of nanoparticles or in vitro biological samples, using an aerosol delivery

system, and two color pump and probe capability.

Before implementing the direct detection system, which requires special detector design, an indirect detection set up based on a Charge Coupled Device (CCD) detector and a multilayer mirror with a hole has been realized in order to prevent damage of the CCD chip by the main FEL beam. Fig. 1a shows a cross section of the core part of the instrument in fix target configuration, showing the sample environment, and the detector set-up. The experimental station was first "pre"-commissioned at the Nanospectroscopy beamline of Elettra storage ring, where pilot experiments were performed to exploit the potential of Resonance (R-) CDI, for getting selective chemical and magnetic information. Now it is already installed at the dedicated beamline and is



Figure 1. a) Design of the DiProl indirect acquisition set up using a multilayer deflecting mirror. Propagating from the right, the beam passes through the apertures stage [A], the sample [B] and the multilayer mirror [C], which deflects the diffraction image to the CCD [D], letting the primary beam [E] through a hole. b) DiProl end-station installed on the dedicated Fermi@Elettra FEL beamline.

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undergoing a commissioning period together with the beamline (Fig. 1b). The planned key elements of the DiProl beamline are a soft-X-ray split-delay line dedicated to perform pump and probe experiments, splitting the beam in two parts and introducing a delay between 0.2 and 35 ps, and two custom made active mirrors, mounted in Kirkpatrick-Baez (KB) configuration, providing a variable spot size of few µm² on the sample plane.

Fig. 2 shows one of the first diffraction patterns acquired using the FERMI@Elettra FEL on July 26th, 2011 at 32.5 nm wavelength pulses without adequate focusing and using two beam attenuators. The image was collected in integrative mode averaging several FEL pulses for 10 s. More than six orders of diffraction spots are clearly visible in the recorded data, qualitatively proving the almost full longitudinal coherence of FERMI@Elettra FEL. The installation of a direct detection system set-up, consisting of two CCD planes, is planned: one placed close to the sample to collect the high angle scattered photons and a rear one. The installation of this sophisticated detector in combination with the wavelength tunability and variable photon polarization of the FERMI@Elettra FEL source will allow R-CDI experiments across the absorption edges of elements in a single shot mode.



Figure 2. Far field diffraction pattern of a bi-dimensional array of holes (600 nm diameter, 1.8 µm pitch) acquired at 32.5 nm wavelength.

ORIGINAL PAPER

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All-reflective femtosecond optical pump–probe setup for transient grating spectroscopy

e develop a chirp-free pump-probe Transient Grating (TG) setup without transmission optical elements exploitable in FEL-based experiments. The measurements successfully carried out using different samples and experimental geometries make us confident about the applicability of a FEL-based TG technique to study the dynamics in the mesoscopic region.



Figure 1. a) Sketch of the experimental setup; Pb, Brewster polarizer; $\lambda/2$, half wave plate; EBS, knife-edged beam splitter; SHG, second-harmonic generation crystal; DM, dichroic mirror; IF, interferential filter; FM, focalizing mirror; Oc, UV focusing objective; PD, photodiode detector. All other optical elements are mirrors. b) Knife-edged beam splitter for pump/probe and pump/ pump splitting.

The actual development of Free Electron Laser (FEL) sources is opening up the capability of performing pump-probe experiments in the femtosecond/nanometer time/length scales. Among various pump-probe techniques, Four-Wave Mixing (FWM) spectroscopy in the Extreme Ultraviolet (EUV) range surely represents a challenge. Four-wave mixing techniques are based on the optical mixing of three incident fields, two pumps, and one probe, which, by interaction with the medium, give a nonlinear polarization that becomes the source of the signal field. One of the most interesting applications of this technique is the study of dynamics in disordered systems at mesoscopic (10-100 nm) length scales. This point can be used to stress the importance of FELbased FWM experiments in the EUV range. The characterization of mesoscopic dynamics in disordered systems is actually carried out with energy-resolved inelastic scattering techniques, which are limited by the energy resolution. In principle, by exploiting time-resolved FWM techniques it is possible to overcome any restriction related to the energy resolution. Transient Grating (TG) is a particular kind of time resolved

FWM spectroscopy, actually based on conventional laser sources, which limits the accessible range to the long length-scale region. Such range can be straightforwardly extended using FEL sources. In particular, the FERMI@Elettra seeded FEL permits exploitation of the EUV region, thus allowing performance of TG experiments in the mesoscopic region. A FEL-based FWM instrument (TIMER) is presently in development at the FERMI@Elettra facility. The main issue related with the development of the EUV optical layout is the absence of efficient transmission optical elements. The choice for beam-splitting and focusing is then restricted to reflective and/or diffractive devices. In our laser laboratory, we create a possible TG setup based only on reflection optics, which represents a testing bench for the FEL-based FWM instrument and a possible

solution for the pulse chirping in pump-probe FEL-based experiments, introduced by diffractive devices. Fig. 1a displays the setup used for the present experiments. The main differences with respect to the more recent TG setup are the absence of lenses and diffractive optical elements, as well as a simple plane mirror as beam splitter. The actually existing devices that may act as beam splitters in the EUV region cannot operate in a large wavelength range and cannot provide the required photon throughput and radiation hardness.

A simple way to overcome these limits is to use a knife-edged beam splitter (see Fig. 1b), consisting of a plane mirror that "cuts" the incident beam into two halves. Since the beam centre impinges on the mirror edge instead of on the middle, half of the beam is reflected (probe) while the other half

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propagates freely. The latter impinges on a second mirror, which further cuts the beam along the direction orthogonal with respect to the previous cut, creating the two pump pulses. In order to understand if the TG signals maintain their properties also using only reflective optics, TG spectra from a neutral density filter and dimethyl sulfoxide (DMSO) have been collected in transmission geometry. The recorded spectra are reported in Fig. 2 (a1 and a2). The high quality of the data shows how the use of only reflective optical elements does not affect significantly the measures. The application of a TG experiment in the EUV range, where most materials are not transparent, drove us to test the TG setup also in reflection geometry. Specifically, we probed a 100 nm thick gold layer on a silicon substrate (Fig. 2b). Also in this case, a very good quality of the data is obtained.



Figure 2. a) TG signal in transmission geometry from neutral density filter (a1) and DMSO (a2). Insets show the fast relaxation features on an expanded time scale. b) TG signal in reflection geometry from 100 nm thick gold layer on a silicon substrate.

ORIGINAL PAPER

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A velocity map imaging apparatus for gas phase studies at FERMI@Elettra

A velocity map imaging spectrometer specifically optimised for experiments at the FERMI free electron laser source has been designed and tested using synchrotron light at the Gas Phase beamline at Elettra. Optimisation of the set-up for the detection of high energy electrons (calibrated up to 45 eV), reduction of scattered light and characterisation of the pulsed gas source are outlined.

The advent of Free Electron Lasers (FELs) with extremely intense and short pulses in the VUV/Soft X-ray region, is opening up a wide range of opportunities not available from present sources and calls for the development of appropriate instrumentation. Velocity Map Imaging (VMI) spectrometers with their high detection efficiency and flexibility are suitable candidates for the latter, as they can be used either for electron or ion imaging as well as ion Time Of Flight (TOF) spectrometers, and have the possibility to measure angular and kinetic energy distributions simultaneously. A VMI spectrometer works by projecting the expanding 3D photoelectron distribution onto a 2D position sensitive detector (see Fig. 1 for schematic representation). The photoelectron angular and kinetic energy distributions can be extracted from the resulting



Figure 1. Schematic representation of how VMI works. Rep: repeller electrode, Ext: extractor electrode; Grd: ground electrode. The electrons produced by the interaction of the light with the atom beam expand on the surface of a sphere due to the kinetic energy given to them by the photoionisation event. The electrostatic field generated by the electrodes projects this sphere onto a position sensitive detector where a 2D projection is recorded.

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image following a mathematical transformation provided the original 3D distribution has cylindrical symmetry. The instrument constructed for use at FERMI is based on the VMI spectrometer built for laser-synchrotron experiments at the Gas Phase beamline. To extend the kinetic energy range of the detected electrons the size of the electrodes and of the Position Sensitive Detector (PSD) increased. The PSD consists of a pair of Micro Channel Plates (MCPs) (77 mm active area) coupled to a phosphor screen. The electrons arriving on the phosphor screen are imaged using a lens plus CCD camera system. Due to the "open" geometry of imaging-type detectors scattered light becomes a significant problem. This can be significantly reduced by the use of light baffles in the FEL beam and the introduction of a new, so called "third electrode" between the extractor and the time of flight tube of the VMI. The baffles act directly by shielding the interaction region from stray photons from the FEL source while the additional electrode (not shown in Fig. 1) deviates the secondary electrons without noticeably modifying the trajectories of the electrons produced in the interaction region of the spectrometer. Finally, a pulsed gas source which could be adapted to the repetition rate of the

FERMI@Elettra free electron laser source was installed. This novel instrument has been tested at the Gas Phase beamline, where we have been able to measure the images of electrons with Kinetic Energy (KE) up to 45 eV. An example image is shown in Fig. 2a for electrons of KE = 35 eV, while in Fig. 2 b the ray tracing to study the effect of the additional electrode is shown. Further simulations show that by increasing the repeller voltage it will be possible to analyse electrons of up to 100 eV. The characterization of the gas pulse envelope proved that it is possible to vary the gas density in the interaction region by two orders of magnitude by simply changing the delay between the light pulse and the gas nozzle opening time. This provision is quite important to avoid saturation of the detector at FEL intensities.



Figure 2. a) A raw image recorded following Ne photoionisation with synchrotron radiation at hv = 56.6 eV. The two circles correspond to ionisation of the 2p (outer circle) and the 2s electrons (inner circle) of Ne. b) Simulations of the trajectories of 5 eV photoelectrons with $V_{rep} = -2.0$ kV and $V_{3rd electrode} = 0$ V (top panel) and $V_{3rd electrode} = +2.0$ kV (bottom panel). Electrons produced at the repeller are clearly seen on the edge of the detector in the top panel while they are deflected off the detector in the bottom one.

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FACILITY DEVELOPMENTS

Elettra status report

Since May 2010 Elettra operates in top-up at both 2 and 2.4 GeV. In this report the experience during more than a year of operation in top-up is discussed and the machine uptime statistics are presented and compared with the period before top-up.



Figure 1. Availability of Elettra since 2004.

Since May 2010 Elettra successfully operates fully in the top-up mode in which frequent beam injections maintain a constant beam current in the storage ring during user operations *i.e.*, while experimenters take data.

After more than a year of operations in top-up the machine shows high stability and reliability. The radiation levels at all beamlines remain below 1 μ Sv/h for the high injection efficiencies established at both user operating energies. The storage ring beam current at 2 GeV remains as set by the users to 310 mA (270 nC) and top-up occurs every 6 minutes by injecting 1 mA for 4 s, thus keeping the current level constant within 3‰. At 2.4 GeV the stored beam current is set at 150 mA and top-up occurs every 20 minutes, injecting 1 mA for 4 s to maintain the current level constant within 7‰. The gating signal provided is acquired currently by just two beamlines. The injection chain consists of a 100 MeV linear accelerator and a 2.5 GeV 3 Hz booster. The booster successfully operates in the on-the-fly mode whereby the required energy is obtained by adjusting the extraction time while the booster itself is always performing the full cycle, *i.e.*, 100 MeV to 2.5 GeV. The booster can provide any energy from 0.1 to 2.5 GeV but the energies used in the storage ring are 1.0 and 1.5 GeV for THz,

1.8 GeV for the SR-FEL, 2 and 2.4 GeV for main users.

The percentage of top-up compared to the total beam time delivered for users is partly a measure of the availability of the injector and for 2011 is currently at 98.7%. The control system monitors the balance of the net charge extracted from the booster and the charge effectively injected in the storage ring and the current loss budget set, that should not exceed 10 mA/h at 2 GeV and 5 mA/h at 2.4 GeV. When the budget is exceeded the top-up process stops for the rest of the hour. This mechanism sets the lower limit of injection tolerable efficiency to 60% and only very few times within the year the top-up process stopped due to this reason. At the same time the radiation budget, set for each beam line of

 0.4μ Sv for a four hour time interval (if this budget is exceeded, the shutters of the beamline remain shut for the following four hours), was up to now never exceeded. It was expected that top-up would improve the availability of Elettra. In Fig. 1 one can see the availability during the 3 phases of operations of Elettra. Before 2008 the storage ring was energy ramping, whereas since 2008 it is operated with a full energy injector and since 2010 functioned in top-up. Another important number for the reliability of a light source is the Mean Time Between Failures (MTBF), i.e., the average time the machine runs without interruption. Also in this case (see Fig. 2) a clear

improvement can be observed after 2008. The tendency for 2011 is for higher MTBF and for the two first runs of 2011 the machine had 130 hours of MTBF. At the same time the longest top-up duration between failures has been 200 hours. Stability of the electron orbit is also excellent and over a long period of time, i.e., 100 hours with the machine in top-up, only a 4 µm horizontal and 1.5 µm vertical shift was measured. Occasionally when a large temperature gradient between day and night exists the electron orbit follows a day night thermal pattern. The mean orbit feedback changes the radio frequency by about 50 Hz that corresponds to 26 µm

FACILITY DEVELOPMENTS

in circumference in order to keep the mean horizontal orbit at zero. The orbit reproducibility depends mainly on the thermal equilibrium and it needs some time after refill following a beam dump to arrive at the previous position settings due to the vacuum chamber heating. It was found that 20 °C difference (about 10 minutes after the beam dump) shifts 90 µm rms the horizontal and only 4 µm rms the vertical orbit. When re-injecting from zero to full intensity after a typical mean failure duration (which at present is about 0.8 h), about 1.5 hours are needed for the machine to reach thermal equilibrium and therefore for the orbit to get back to its previous "golden orbit" values.



Figure 2. Mean time between failures since 2004.

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Simultaneous determination of the X-ray refractive index and the attenuation length from single radiographs of rectangular prisms

t is shown that a single radiograph, which is taken with X-rays from a small prism at rather grazing angle of incidence, contains already all information, which allows one to determine both optical constants (refractive index and attenuation length) of the prism material without any need for a data normalisation. The technique is thus well adapted for unstable or single shot sources. Moreover it can provide rather accurate data, even when the incident beam contains a significant amount of different harmonics of a fundamental photon energy.

When Roentgen had discovered the X-rays in 1895, he immediately started to investigate their interaction with matter, i.e. their absorption and successively their refraction in prisms, however, unsuccessfully. His result meant that the refractive index n of matter for X-rays can be only slightly different from unity. Finally, more than 25 years later, Larsson et al. [A. Larsson, M. Siegbahn, and I. Waller, Die Naturwissenschaften 12 1212 (1924)] operated a prism at grazing incidence (upper configuration in Fig. 1), when it will provide maximum, and thus detectable, beam deflection. They limited the beam in a small slit and calculate the refractive index n from the beam deflection Δ to be n =1- δ < 1, with small though accurately derivable numbers for δ . Obviously the prism transmission function modulates locally the intensity of the refracted rays. Davis and Slack [G. Davis and C.M. Slack, Phys. Rev. 25, 881 (1925)] observe that this disturbs as "the maxima ... are shifted not only by refraction but by the unsymmetrical absorption of the beam in the prism." With the availability of digital devices for X-ray radiograph registration it is worth to investigate whether the "disturbance" eventually contains useful data. Larsson et al. used the upper configuration in Fig. 1, as it provides also a beam, which is specularly reflected and deflected upwards by 26. The lower configuration will refract the beam at grazing internal

incidence, while the downwards specularly reflected beam is likely to be re-absorbed in the prism. Snell's refraction law reads here $\cos\phi = n \cos\theta$

or for small angles $\phi^2 = \theta^2 + 2\delta$ (1).

The incident beam is simply deflected by $\Delta = \phi - \theta$. These two equations immediately lead to some limitations: a) $\Delta \le \sqrt{2\delta}$, where $\sqrt{2\delta}$ is the critical angle for total reflection of the prism material; b) refraction is observed only with $\phi \ge \sqrt{2\delta}$, while θ can be chosen freely. Upon refraction the beam crosssection for an incident plane wave changes as shown in Fig. 1 More importantly Fig. 1 shows that the beam path in material is linearly increasing with the distance y of a ray from the prism tip in the direction orthogonal to its trajectory. The transmission function of the prism is then simply a decay function. For the calculation of the intensity distribution at a detector downstream of the prism, the transmission function needs to be corrected for the beam crosssection change, for the intensity distribution in the incident beam and for the intensity losses due to reflection at the refracting interface.



Figure 1. Refraction of X-rays at prisms at grazing angle of incidence. Internal rays hit the refracting interface with an angle θ , while ϕ is counted between the interface and the external ray trajectories. The incident beam is deflected by an angle Δ .

For uniform incident intensity in a well collimated beam the latter two corrections are position independent. In this condition the derivative $\partial/\partial y'$ of the natural logarithm In of the transmitted refracted flux density distribution $\partial(\ln\{y'\})/\partial y'$ contains only a constant term. For the operated configuration B, which provides a widened refracted beam, the latter is $-(\phi AL\{Z,E\})^{-1}$, where $AL\{Z,E\}$ is the X-ray attenuation length depending on the atomic number Z of the prism material and on the photon energy E. In other words the attenuation length AL for the prism material is obtained from the slope of the measured distribution $\partial ln \{y'\}$, i.e. formally via

$$AL = -\frac{1}{\phi \frac{\partial}{\partial y'} (\ln I \{y'\})}$$

Fig. 2 presents a single radiograph, in which the prism (dark shadow) refracts the beam rather uniformly to the right at a 2 mm long edge. In the same radiograph for a known angle θ one can also deduce the angle Δ , which provides directly the angle ϕ for the calculation of AL. The refractive index decrement δ can be obtained from (1). Which are the advantageous features in this technique? First of all, the refractive index and the attenuation length are obtained from the same single radiograph with no need for data normalisation. The dispersion in the prism is strongly photon energy dependent with larger photon energies being less refracted. Consequently, the transmitted intensity distributions for different harmonics of a given photon energy can easily be separated in the radiograph, which eliminates any systematic error, which arises usually when transmission data are normalised with a "dirty" reference spectrum.

FACILITY DEVELOPMENTS



Figure 2. X-ray radiograph of an inclined prism. Data were analysed in the area surrounded by a square. The natural logarithm of the measured intensity distribution, after appropriate subtraction of the incident intensity, is plotted depending on the deflection y' from the projected position of the prism tip. The circled data points line up on a straight line.

ORIGINAL PAPER

W. Jark, L. Rigon, and K. Oliver, Opt. Commun. 284, 4525(2011)

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Spectral analysis in scanning spectromicroscopy

rom an information theory standpoint, the amount of scientific data is growing so fast that novel techniques for their management and treatment are necessary. Such techniques intend to provide solutions for data storage, processing, sharing and provenance. Focused on the scanning spectromicroscopy requirements of the TwinMic beamline, we deployed a specialized data structure based on the HDF5 format. The advantages of this deployment inspired and permitted new developments on spectral data processing that collectively form the *spectrαrithmetics* platform of algorithms and methods.



Figure 1. Spectrarithmetics' pre & post processing (i.e. energy calibration, topography reconstruction) and visualization features rely on advanced data structures and formats (HDF5).

The way of storing and organising data is of high importance as it affects their later use. This may be valid for handwritten lecture notes to large and complex datasets in experimental physics. In the context of computer science a data structure provides such an organisation and arrangement that promote the efficient use of the data. Factors that this may impact include the data size, the access speed, and the way of I/O (parallel/sequential). The scientific computing team and the TwinMic beamline have developed a data pipeline based on novel data structures specialised for scanning spectromicroscopy. The data format that has been used as container is HDF5. A typical TwinMic LEXRF dataset stores in such a single HDF5 file heterogeneous information like metadata for the experiment, individual X-ray fluorescence spectra for thousands of scan points, calibration coefficients and other relevant parameters; reducing the final size and improving the access speed. The data structure has been designed in a way that makes possible its expansion to other scanning spectromicroscopy applications beyond TwinMic. The new HDF5-based data structure for TwinMic enables a better insight to the data. The microscope has a unique 8 MCA/SDDs setup and now the users can easily and efficiently access and evaluate the maps of the individual detectors plus derivatives of them (e.g. calibrated sum, standard deviation, eigenvectors). A collection of data analysis algorithms and procedures for processing the contained spectra is in development - named Spectr α rithmetics. The Spectr α rithmetics platform makes full use of the above mentioned data structures in order to provide efficient performance and data analysis techniques on datasets of large dimensions. In terms of

traditional information theoretic imaging a typical XRF TwinMic 80x80 scan has more than 419 MegaPixel of 16bit information. Spectr α rithmetics aims to be complementary to software like PyMCA, GeoPIXE, and MantiS, and customised for TwinMic purposes (i.e. multiple MCAs). Spectr α rithmetics has been developed in a modular way that allows its easy expansion. The implementation of existing or new algorithms is compatible with the backbone of the system and the way it stores the data. It has been developed in Python while the computationally demanding parts are in C. It is platform independent as it runs both on Linux and Windows, and experimentally on MacOSX. Due to the memory requirements for certain classes of computations 64bit operating systems are recommended. The current deployment of Spectrarithmetics in Elettra is on a CentoOS 5.4 64bit cluster with suitable setup that permits access to on-site supercomputing resources through the Oracle Grid Engine. The computationally intensive tasks of the platform make full use of modern multi-core architectures and distributed computing infrastructures. Eventually the enduser/scientist may expand the system by adding new methods without worrying about technicalities like data access, format parsing and computational resources. These are handled transparently from the *core* modules of the platform. Interoperability and connectivity with existing control solutions like LabView and Tango is feasible. The current version of Spectr α rithmetics consists of four main families of modules that can be summarized as follows: Core modules: These handle the reading and writing of TwinMic LEXRF data and metadata on

FACILITY DEVELOPMENTS

suitable HDF5 files containers, while provide fast and secure archiving on the Elettra network storage systems. The module family also provides the various methods of access to computational resources.

Preprocessing modules: These operate directly on the raw data during the acquisition or after. One of the implemented methods aligns (energy calibration) the individual detectors (SSD) and sums the counts of the selected ones (Fig. 1). Another module in development handles the dead time effect aiming at its correction. Functionalities like scan cropping and detector exclusion are implemented in these modules. Planned expansions will assist the quantification of the acquired data. This family should perform various arithmetics that should result to data that can be further processed on software like PyMCA and Igor Pro.

Visualization modules: Various ways of visualization of the XRF data have been implemented. These can be useful for fast assessment and preview of the scans by allowing plotting of individual detectors prior to or after their alignment. The plotting facility is interactive (zooms, ROIs, SSD selection) and can export publication quality illustrations (vector graphics).

Methods modules: In order to cover post-processing requirements the methods modules is an umbrella family that consists of implementations of new algorithms and techniques. Contrary to the preprocessing modules which are a preparation stage, these aim at final data analysis. A recent imitative aims at the generation of 3D bump maps for representation of topographical information of the scanned sample (Fig. 1). Relevant actions and projects that have partially supported this work include ColorMic, I-SOI, and PanData.

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The SGS project: managing the scientific business

The SGS project initiated few years ago is now starting to produce important results. From the analysis of the matrix organizational structure and of the underlying processes and workflows a new set of tools has been implemented and introduced gradually. In this contribution we will briefly pinpoint the achieved results, the systems involved and the innovation already in place and we will provide a perspective on innovations under development.

The SGS (Sistema Gestionale Sincrotrone) project, structured in four work packages: *Laboratory organisation*, *Operating procedures*, *Management control* and *Information systems*, has the objective to analyze and enhance the operating systems that are the backbone of the activity of the research laboratory. Starting from the analysis of the matrix organizational structure and of the underlying processes and workflows, the SGS project has produced in the last year important results: a sort of a silent revolution that enables the management to take informed decisions.



Figure 1. Architecture of the Information systems involved in the project.

From the technical point of view, the operating system is the result of the orchestration of a set of integrated components like the anagraphic information database, a document management system, the human resources management system, the ERP system allowing managing the passive cycle (purchases, accountability, warehouse), the active cycle (sells) and providing advanced analytical accountability functionalities. This system works in synergy with the well known system for the management of the scientific business, the Virtual Unified Office (VUO), that provides support to the management of the different initiatives of the laboratory (like projects, industrial orders and structural activities) and an advanced support for co-funded project reporting. The whole architecture is described in Fig. 1.

Most of the web based management applications have been developed in the VUO that is becoming a sort of reference platform. During the last year, a new system for digitalisation of the letters of appointment has been developed and a new system for the digitalisation of the human resources evaluation process is under development. In a similar way, a Customer Relationship Management system to support the Industrial Liaison Office (ILO) and a document management system to store digitally relevant documents have been implemented and deployed. All these systems have been delivered according to the scheduled time without interfering with the normal operations of the laboratory. In the near future on top of these databases and systems the digitalisation effort will proceed

FACILITY DEVELOPMENTS

with the setting of the management and strategic management control systems based on a new project management, planning and supervision system and on a new system to manage a set of company wide key performance indicators. Fig. 2 reports a simplified workflow of the company initiatives in the business process modelling notation, which was chosen as the standard notation to represent the operating procedures of the laboratory. The new management system for the company initiatives will allow us to track the effective involvement of the personnel in the many company initiatives. This, coupled with a system to manage the skill and competences of the personnel, will give us a better capacity to evaluate the real feasibility of specific initiatives and a better capacity to forecast cost and delivery times.



Figure 2. Simplified workflow of the company initiatives including planning and execution phases.

Life science booster: the new structural biology laboratory at Elettra

ver the last three years Elettra has heavily invested in setting up a new structural biology laboratory providing state-of-the-art facilities for cloning, expression, purification and characterization of proteins, with the aim of supporting the local structural biology group as well as providing facilities for other Elettra scientists, external collaborators and users. A thriving program of in-house research is being developed, focused on proteins involved in fundamental biological processes with a strong relevance for tumor biology.

A new laboratory has been activated in 2010 at Elettra to provide stateof-the-art facilities to the in-house structural biology community, as well as other Elettra scientists or users interested in biological research and its applications. The laboratory is located in close proximity to the Elettra beamlines, occupies a large area (270 m²) and is equipped with most modern instrumentations for molecular biology, biochemistry, biophysics and crystallization experiments. Although the final goal of the projects is the determination of atomic structures by macromolecular crystallography, samples will also be used for other structural and biophysical studies using techniques available at Elettra, such as EXAFS, SAXS and AFM.

The laboratory is set up for highthroughput cloning, large-scale expression and purification of recombinant proteins. A robotized liquid-handling workstation (Tecan Freedom Evo 150) has been designed to support both crystallization experiments and parallel cloning/expression of protein targets. The lab can support different expression hosts, such as prokaryotic *E. coli* systems or baculovirus-infected insect cells. Scale up of cultures can easily be done using either shaking flasks or bioreactors systems, as the laboratory is equipped with four Sartorius fermentors with capacities ranging from 1 to 10 liters of culture.

A new automated crystallization facility is being implemented, including a Tecan liquid handler to set up crystallization screens and a Mosquito crystallization robot (both routinely used), as well as an Explora Nova Xtal Focus Storage and Imaging system, soon to be installed. A highly automated crystallization



Figure 1. Bioinformatic analysis has identified an intriguing evolutionary relationship between the human Cdc45 replication factor and a family of bacterial and archaeal proteins called RecJ. Small-angle X-ray scattering data (collected at Elettra in collaboration with H. Amenitsch) represent the first structural information on this important protein and confirmed that the 3D structure of Cdc45 is compatible with the bioinformatic analysis (Krastanova et al., submitted).

platform is therefore now available for the scientific community The lab, coordinated by Paola Storici, is primarily designed to support the internal structural biology research activities but is also opened for access to beamline scientists, external collaborators or synchrotron users. Moreover, the lab space is shared with the research groups of the International School for Advanced Studies (SISSA) and the Institute of Crystallography of the National Research Council (CNR). A collaboration agreement has been signed between these two institutes and Sincrotrone Trieste with the aim to create a task force for structural biology by sharing expertise, skills and equipments.

The research activity of the Elettra structural biology group is under the direction of Silvia Onesti and focuses on the understanding of the molecular mechanisms of eukaryotic DNA replication, using both biochemical and structural approaches. We are currently studying a number of human proteins involved in DNA replication and repair, including various MCM proteins, the GINS complex, Cdc45, the human primase heterodimer and RecQ helicases (in collaboration with A. Vindigni). Most of these proteins are expressed only in proliferating cells and are therefore good candidates for novel cancer biomarkers and/or putative targets for drug design against tumors. The research is partly funded by the Associazione Italiana per la Ricerca sul Cancro (AIRC). Alessandro Vindigni, currently

at Saint Louis University School of Medicine, is associated with Sincrotrone Trieste as distinguished fellow. In the lab he is leading a project to study the biochemical and cellular roles of the human RecQ helicases, a family of enzymes that are key players in the maintenance of genome integrity. This research is also funded by AIRC. A specific effort is ongoing to implement a high-throughput protein production platform,

exploiting the Tecan liquid handler workstation, to support both internal research and external users. Paola Storici, responsible for this activity, is focusing on two projects that will serve as test cases: (i) the structural characterisation of human ULK1 (a

FACILITY DEVELOPMENTS

Ser/Thr protein kinase relevant in autophagic cell response); (ii) the structural study of post-translational modification of human VEGFR2 (collaboration with M. Giacca, ICGEB-Trieste).

The SISSA group, directed by Giuseppe Legname is centered on biophysical studies of prion proteins, in order to understand the conformational transitions that leads to prion diseases.

The IC-CNR group, directed by Doriano Lamba is focused on structural studies of protein drug targets of neurodegenerative diseases, including structurebased drug design of inhibitors of acetylcholinesterases as anti-Alzheimer therapy and neutralizing antibodies targeting NGF-mediated neuropathic pain.

Sincrotrone Trieste has thus successfully managed to create a well equipped and effective structural biology laboratory that can act in synergy with the beamlines for biological experiments at Elettra. Scientific competences and infrastructures are now in place to ensure the laboratory can act as a hub for structural biology research.



Figure 2. The TECAN Freedom EVO150 installed at Elettra is a versatile liquid handler workstation used for two distinct applications: parallel cloning/protein expression and set up of crystallization screens. The workstation is equipped with two robotic arms (a robotic manipulator arm and a high precision liquid-handling arm with 8 pipetting channels), a vacuum separation module, a thermostated shaker and a barcode reader.

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FACTS & FIGURES

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EVENTS

4

Gelettr

The Company

Sincrotrone Trieste S.C.p.A. began operations in 1987: it is a non-profit Share Company (Società Consortile per Azioni) recognised as being of national interest by a State Law, which manages the **Elettra Laboratory**. Elettra continues to update itself and grow. In addition to significant modernisation projects relating to beamline sources and other components, a new fourth generation light source, **FERMI@Elettra**, has been built alongside the original one.

The centre is one of the laboratories associated with the **IAEA**, the **International Atomic Energy Agency** (founded in 1957 under the auspices of the United Nations for the peaceful use of nuclear technology) and is part of the primary network for science and technology of the **CEI**, the **Central European Initiative**. It is also the coordinator of the network of all of the synchrotron and free electron lasers facilities in Europe, promoting transnational access to the laboratories and joint research activities in their field.

On its site Elettra hosts the **National TASC Laboratory** (IOM-CNR), a facility for micromanufacturing and nanoscience. It has also established enduring working relationships with important Italian and foreign institutions, including various **Italian National Research Council Institutes**, the **Academies of Science of Austria** and the **Czech Republic**, UNESCO's International Centre for Theoretical Physics (**ICTP**), the International School of Advanced Studies (**ISAS/SISSA**), The **Indian Institute of Science** and the **Universities** of Milan, Nova Gorica, Trento, Trieste and Udine. These partners are actively contributing to the construction and operation of beamlines and support laboratories.

Elettra's scientific and technical quality and developments are constantly monitored by board-appointed international Committees, which advise on all relevant aspects of the general and development policy, scientific programs, accelerator development, technology transfer and industrial applications.

SHAREHOLDERS

- AREA Science Park Consortium (51%)
- Autonomous Region of Friuli Venezia Giulia (40%)
- Italian National Research Council (5%)
- The national Agency for inward investment promotion and enterprise development (4%)

ALLIANCES AND PARTNERSHIPS

- IAEA (International Atomic Energy Agency)
- CEI (Central European Initiative)
- IRUVX (European Consortium for FELs up to the UV/softXray)
- Austrian Academy of Sciences
- Academy of Sciences of the Czech Republic
- CNR (Consiglio Nazionale delle Ricerche Italian National Research Council)
- CNRS (Centre National de la Recherche Scientifique French National Research Council)
- ICTP UNESCO (International Centre for Theoretical Physics)
- Indian Institute of Science, Bangalore
- Institut für Festkorperforschung Forschungzentrum Jülich
- INSTM (Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali – National Inter-University Consortium for Materials Science and Technology)
- INFN (Istituto Nazionale di Fisica Nucleare National Institute of Nuclear Physics)
- ISAS/SISSA (International School of Advanced Studies)
- Charles University, Prague
- University of Nova Gorica
- University of Milan Bicocca
- University of Trento
- University of Trieste
- University of Udine

Sincrotrone Trieste S.C.p.A. is managed by a Board of Directors, assisted by a Board of Auditors, and advised by board-appointed international committees such as the Council of Partners for general and development policy, the Scientific Advisory Council for scientific programs, the Machine Advisory Committee for accelerator development, and the Industrial Advisory Panel for technology transfer and industrial applications are concerned.

BOARD OF DIRECTORS

President: Carlo Rizzuto

Vice President: Giovanni Comelli Chief Executive Officer: Alfonso Franciosi Marcello Fontanesi Gemma Luisa Ravizza



| MAC Machine Advisory Committee | SAC Scientific Advisory Council | IAP Industrial Advisory Panel |
|-----------------------------------|------------------------------------|---|
| Chairman: Richard P. Walker | Chairman: Ingolf Lindau | Chairman: Alberto Sangiovanni-Vincentelli |
| Paul J. Emma | David Attwood | Carlo Castellano |
| Mikael Eriksson | Gordon Brown | Enrico Albizzati |
| Jerome Hastings | Charles S. Fadley | Maurizio Arienzo |
| Carlo Pagani | Robert Huber | Mauro Ferrari |
| Claudio Pellegrini | Sine Larsen | |
| Mike Poole | Dietrich Menzel | |
| Robert W. Schoenlein | Charles V. Shank | |

Beamlines and users



OPERATING BEAMLINES

FUTURE DEVELOPMENTS

| exit | BEAMLINES | | source * | energy range (eV) | partner institutions |
|-------|-------------------------|---|----------|----------------------|---|
| 1.1L | TWINMIC | A multipurpose twin X-ray microscopy beamline for improving life conditions and human health | short id | 250 - 2000 | |
| 1.2L | Nanospectroscopy | SPELEEM and LEEM-PEEM end-station | id | 50-1000 | IFF Jülich (from 2011) |
| 1.2R | FEL | European Free-Electron Laser project | id | 1,8 - 9,5 | |
| 2.2L | ESCA Microscopy | Scanning PhotoElectron Microscopy (SPEM) | id | 200-1400 | |
| 2.2R | SuperESCA | Fast and High Energy Resolution Photoemission and Absorption Spectroscopy | id | 85 - 1500 | |
| 3.2L | Spectro Microscopy | Angle-Resolved Photoemission microscope | id | 27 - 95 | |
| 3.2R | VUV Photoemission | Angle-Resolved PhotoElectron Spectroscopy (ARPES) in the VUV range | id | 16 - 1000 | ISM-CNR |
| 4.2 | Circular Polarization | Dichroic measurements on chiral systems | id | 5 - 1000 | ISM-CNR |
| 5.2L | SAXS | Small Angle X-Ray Scattering | id | 8000 16000 | IBM-ÖAW (A) |
| 5.2R | XRD1 | X-ray Diffraction | id | 4000 - 22000 | IC-CNR |
| 6.1L | Materials science | Photoemission and X-ray absorption | bm | 40 - 800 | ASCR, Charles University of Prague (CZ) |
| 6.1R | SYRMEP | SYnchrotron Radiation for MEdical Physics | bm | 8000 - 35000 | UNITS |
| 6.2R | Gas Phase | Research on gaseous systems | id | 14 - 1000 | IMIP-CNR, IOM-CNR |
| 7.1 | МСХ | Powder Diffraction Beamline | bm | 2100 - 23000 | UNITN, INSTM |
| 7.2 | ALOISA | Advanced Line for Overlayer, Interface and Surface Analysis | id | 120 - 8000 | IOM-CNR |
| 8.1L | BEAR | Bending magnet for Emission Absorption and Reflectivity | bm | 4 - 1400 | IOM-CNR |
| 8.1R | LILIT | Laboratory for Interdisciplinary LIThography | bm | 1000 - 5000 | IFN-CNR, IOM-CNR |
| 8.2 | BACH | Beamline for Advanced DiCHroism | id | 35 - 1600 | IOM-CNR |
| 9.1 | SISSI | Synchrotron Infrared Source for Spectroscopy and Imaging | bm | 0,001 - 3 | |
| 9.2 | APE | Advanced Photoelectric Effect experiments | id | 10-2000 | IOM-CNR |
| 10.1L | X-ray microfluorescence | X-ray microfluorescence | bm | 4000 - 20000 | |
| 10.1R | DXRL | Deep-etch Lithography | bm | 2000 - 20000 | |
| 10.2L | IUVS | Inelastic Ultra Violet Scattering | id | 11-2008 | |
| 10.2R | BAD Elph | Low-energy Angle-Resolved PhotoEmission Spectroscopy (ARPES) | id | 4 - 25 | |
| 11.1R | XAFS | X-ray Absorption Fine Structure | bm | 2400 - 25000 | ICTP |
| 11.2 | XRD2 | X-ray Diffraction | id | | IIS Bangalore (IN) |

Elettra Highlights 2010-2011

source* id = Insertion Device (wiggler or undulator) bm = bending magnet The **Proposal Review Panel** is a panel composed of senior scientists active in different scientific fields and appointed by the Elettra laboratory management with the aim of evaluating the general User's proposals.

The panel is divided into seven subcommittees.

The Proposal Review Panel meets twice a year, gives a written report for each proposal submitted for the ongoing semester and gives suggestions for beamtime allocation at the beamlines open to the users.

ELETTRA PROPOSAL REVIEW PANEL

Proposal Review Panel Chairman Carlo MARIANI

SUB COMMITTEES

A - Atoms Molecules and Plasmas

Svante SVENSSON (Chairman) Vincenzo AQUILANTI Uwe Yu Eugen BECKER John Malcolm DYKE

C - Catalytic Materials/Surface Science

Carlo MARIANI (Chairman) Maria Carmen ASENSIO Karol HRICOVINI Adam Fraser LEE Falko NETZER Luca OTTAVIANO Michele Rose SAUVAGE SIMKIN

H - Condensed matter - Electronic and Magnetic Structure

Maurizio SACCHI (Chairman) Mark GOLDEN Giorgio MARGARITONDO Danilo PESCIA Maurizio SACCHI Jan VOGEL

ILP - Instrumentation and Technological materials - Life and Medical Sciences (excluding Crystallography) - Polymers and Soft Matter

Graeme Rennie MORRISON (Chairman) Alberto BRAVIN Gianfelice CINQUE Paul DUMAS Christopher John HALL Lisa MILLER Gunter SCHMAHL Andrew Duncan SMITH Mark TOBIN

Stephen William WILKINS

M - Protein and Macromolecular Crystallography

Giuseppe ZANOTTI (Chairman) Peter BRICK Dusan TURK Luigi VITAGLIANO

S - Hard condensed matter - Structures

Maurizio BENFATTO (Chairman) Robert Joseph CERNIK Paola D'ANGELO Marco MILANESIO Maria Grazia PROIETTI

T - Scattering

Paolo MARIANI (Chairman) Stephanie Brigitte FINET Daniele FIORETTO Hermann FRANZ Giulio MONACO

USERS AT ELETTRA (July 2010 – June 2011)

| EU funded users | 107 | | European Union | 825 |
|-----------------------------|----------|--|--|-----------|
| Italian funded users | 231 | | CROATIA | 5 |
| General users (not founded) | 645 | | HONG KONG | 2 |
| | | | INDIA | 60 |
| | | | ISRAEL | 2 |
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| 25 | | | THAILAND | 4 |
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| 255 | | ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ | UNITED STATES | 27 |
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ALLOCATED PROPOSALS BY RESEARCH AREA: TOTAL = 421 (July 2010 – June 2011)



2004-2012 SUBMITTED PROPOSALS BY SEMESTER



From October 1st, 2007 to March 2nd, 2008 the Elettra light source was closed due to the booster installation.

rincrotrone Trieste has adopted a matrix-type of organization. The four Strategic Initiatives correspond to and are Jimplemented through four Clusters of different Projects, grouped together based on the complementarity of the different project goals. The human and instrumental resources required by the different projects are managed within Groups of staff members with similar or related expertise.



* including personnel, legal, industral liaison, users office, etc.

August 31th, 2011

Financial figures

BUDGET ALLOCATION FOR 2011

| RUNNING COSTS | |
|--|--------------|
| General costs | € 8.779.700 |
| Personnel | € 11.500.000 |
| Utilities | € 5.000.000 |
| Accelerator Group | € 50.000 |
| Administration Group | € 283.000 |
| Beamlines Group | € 925.000 |
| General services Group | € 1.134.274 |
| Electromagnetism Group | € 161.388 |
| IT Group | € 260.300 |
| Infrastructure Group | € 1.031.909 |
| Mechanical, Vacuum and Optical engineering Group | € 302.711 |
| Industrial Liason Office operation | € 689.500 |
| Scientific partnerships | € 700.000 |
| OPAC | € 892.763 |
| Development projects | € 1.643.500 |
| TOTAL ORDINARY OPERATION | € 33.354.045 |
| Special projects | |
| FERMI | € 19.587.031 |
| Total special projects | € 19.587.031 |
| GENERAL TOTAL | € 52.941.076 |

Projects/Sponsored research

The last two calendar years, 2010 and 2011 (not yet concluded), were extremely successful in attracting resources from external funding institutions: the contributions acquired through research contracts amount to more than 3.2 million Euro in 2010 and about 2.3 million Euro in the first nine months of 2011. A reason of concern is the reduction in the support available to European users following the conclusion of the I3 project ELISA (http://www.elettra.eu/ELISA/) on August 31st, 2011: the follow-up I3 project, submitted to the European Commission in November 2010, was not selected for funding.

During the last ELISA Council Meeting, held in Trieste on June 9th-10th, 2011, several possible future perspectives were examined, in agreement with the European Synchrotron Users Organisation – ESUO (http://www.esuo.org/).

At the time of this writing, a new proposal (Coordinated Access to Lightsources to Promote Standards and Optimization – CALIPSO) is in preparation for submission under call FP7-INFRASTRUC-TURES-2012-1 and a new portal for European users is being created (http://www.waytolight.eu). For the said application, Elettra proposed to the partners an innovative project aimed at an increased integration among the individual laboratories and at an increased support to new users. For this reason, and in recognition of the competency achieved by our team in the management of the previous I3 projects, the future project partners unanimously selected Elettra as coordinator of the new proposal.

During the last 12 months, Elettra participated in 36 research contracts (see table) funded by the following external agencies: European Commission, European Science Foundation, Italian Ministry of Research, Italian Ministry of Economic Development, Italian Ministry of Foreign Affairs, Italian Association for Cancer Research, Regional Government of Friuli Venezia Giulia, International Centre for Theoretical Physics, Indian Department of Science and Technology.

RUNNING RESEARCH CONTRACTS:

| EUROPEAN/INTERNATIONAL RESEARCH CONTRACTS | | |
|--|--------------------|--|
| Name | SHORT NAME | COORDINATOR |
| ICTP-Elettra Users Programme | | Elettra |
| Transnational access of the Indian scientists to the Elettra beamlines | | Elettra |
| Preparatory Phase of the IRUVX-FEL Consortium | IRUVX-PP | DESY, Germany |
| TIME-Resolved Spectroscopy of Nanoscale Dynamics in Condensed Matter Physics | Timer | Elettra |
| Maximizing Synergies for Central European Biotech Research Infrastructures | SynBlOsis | JIC, z.s.p.o., Czech Republic |
| CEI Research Fellowship Programme | CERES | INCE - Central European Initiative, Italy |
| PaN-data Europe Strategic Working Group | PaN-data Europe | STFC, United Kingdom |
| Science in Trieste And Researchers 2011 | STAR2011 | University of Trieste, Italy |
| Realising and Managing International Research Infrastructures 2 | RAMIRI 2 | Elettra |
| Understanding and Manipulating Enzymatic and Proteomic Processes in Biomineralization | COST ACTION TD0903 | Elettra |
| Synchrotron X-ray μ -Tomography with rare earth based nanoparticles as contrast agents for enhanced biomedical imaging; MicroCT with nanoparticle-based contrast agents for biomedical imaging - Joint project: Italy-Sweden | NP-based-MicroCT | Elettra |
| Transnational access and enhancement of integrated Biological Structure determination at synchrotron X-ray facilities | BioStruct-X | EMBL, Germany |
| NATIONAL RESEARCH CONTRACTS | | |
| High efficiency innovative light sources for solid state illumination devices with civil and automotive applications | LUCI | CNR, Italy |
| FERMI@Elettra - Phase II | | Elettra |
| Development and production of high performance biocompatible and multifunctional innovative materials | PROCERPOL | Lima Lto. Spa, Italy |
| Elucidation of the structure and function of MCM Helicases | AIRC-MCM | Elettra |
| Production, management and distribution systems for photovoltaic electric power | ERG | STMicroelectronics Srl, Italy |
| Executive programme of scientific and technological co-operation between the Italian Republic and Republic of South Africa for the year 2011-2013 | SISTER-MAE | Elettra |
| Analysis of the human RECQ1 helicase function in DNA replication and repair | AIRC-RECQ1 | Elettra |
| REGIONAL/CROSS BORDER RESEARCH CONTRACTS | | |
| Realization of a technological platform for the crystallographic analysis of biological macromolecules of biomedical interest for the industrial research | DAGEAS | Elettra |
| Development and realization of solid state ultrafast laser amplifiers optimized for FEL applications | FEMTOREG | Elettra |
| Distributed environment monitoring based on Grid | MADBAG | Elettra |
| Development of chemical sensors for environmental and biological diagnosis based on nanowires and nanotubes | AMBIOSEN | Elettra |
| Studies on the decay mechanisms of nanomaterials and their potential dangers in biological systems | NANOTOX | Elettra |
| Studies and characterization of high power X-band (12 GHz) radiofrequency devices | X-BAND | Elettra |
| Study of a femtosecond timing system for new synchrotron light sources | SYRATIM@FS | Elettra |
| Dynamics of macromolecular and biological systems via Raman spectroscopywith ultrashort pulses | MASPERA | Elettra |
| Study for a photoinjector capable of supplying a 50Hz pulsed beam with very high brilliance | HiBEGuS | Elettra |
| Interregional Centre of Ultrafast Photonic Technologies for Spectroscopy | CITIUS | University of Nova Gorica, Slovenia |
| Definition of protocols for the production of inks based on the technology "Invisible" | Sister LiF | AREA Science Park, Italy |
| Development of a digital Direct Current Current Transformer (DCCT) system for the measurement of direct current with a resolution, accuracy and stability of few parts per million | Sister DCCT | AREA Science Park, Italy |
| Imaging - Service Oriented Infrastructure | I-SOI | Elettra |
| User-friendly domotic systems based on smart lighting devices | EASYHOME | Centro Ricerche Plast-optica S.p.A., Italy |
| Experimentation of an extra-fine thermostating system for particle accelerators | TEXA | Elettra |
| Free-electron-laser based analysis of nanostructures in supersonic beams | ANGEL | Elettra |
| Identification of new cancer stem cell markers for diagnostic and therapeutic purposes | GLIOMA | National Institute of Biology, Slovenia |

Technology transfer @ Elettra

he Industrial Liaison Office (ILO) was set-up in 2004 to promote the exceptional body of skills and technical expertise resulting from the experience accumulated in the construction and operations of the Elettra facilities. In addition, the "Free Electron Laser" (FERMI@Elettra), recently commissioned, contributed to the development of new devices and technologies whose benefits are offered in support of industry R&D activities and other research Laboratories. The Industrial Liaison Office supplies advanced instrumentation to other Synchrotron Facilities and Research Laboratories and provides products and services to private companies operating in different fields: mechanics, optics, pharmaceutical, microelectronics, energy, chemistry, agri-foodstuffs etc. Collaboration with Industry mainly concerns:

- Analytical and metrological services on the micro-nanoscale for characterization of the chemical-physical and electronic structure of materials and devices: industry pays the laboratory to provide dedicated measurements selected among the available technologies, granting confidentiality of results and support in problem solving activities;
- Research and Development Projects: the Elettra staff work with the industry using their knowledge and the facilities for products and process co-development;
- Micro Fabrication: Photolithographic fabrication of microelectronic, optoelectronic, micromechanic and microfluidic devices;
- Design and Development of advanced scientific instrumentation for the construction of new facilities or laboratory improvements such as: accelerator components, scientific instrumentation, customized software etc..;
- Spin Offs and New Business Development to promote the use of patented scientific results;
- Consulting and Training of industry personnel.

Some examples of recent activities are the development of new technology for the production of OLED Monitors; the collaboration with textile industry for the optimization of the production process and improvements of quality; the collaboration with pharma industry for better process control; the development of an anti counterfeiting methodology for museums and fine arts. It is also worth mentioning the contract with ESA (European Space Agency) to develop a biometric adhesive, inspired by Gecko feet.

These services, among other analysis and measurements performed at Elettra, are illustrated in our catalogue, available upon request, in our promotional video available on You Tube and, finally, in our web site (services section).

The same web site (products section) presents the main groups of devices designed at Elettra and sold throughout the world:

Power Supplies

New families of intelligent (DSP or PC embedded) power supplies, that cover many features (high voltage/current, four-quadrant etc.) with several configurations available. Epics or Tango interface are often already included and custom-built solutions are possible.

Detectors

Photons and charged particles detectors, based on cross delay anodes, multi anodes and centroid finding techniques. 3D information (x,y,time) with spatial and time resolutions in the order of tens of microns and picoseconds are available through many custom-built solutions.

Laboratory Instrumentation

Several instruments necessary for typical or extreme applications are available: fast picoammeters, multi-point strain gauge, charge pulse amplifiers, ion chambers, pulse generators, RF filters etc. Every tool is intelligent and in some cases "Epics/Tango interface" is already provided.

Accelerator Components

Elettra, over the years, has acquired wide-ranging experience in developing and realizing accelerators components, including undulators, resonant cavities etc. For the production of Insertion Devices, a spin-off company (Kyma S.r.l.) has been set-up.

This year a new **Picoammeter** version has been developed. The AH-501B version incorporates 4 analog outputs +/- 5 Volts - for direct measurement of the currents (in addition to the TCP/IP data transfer, still available) - and one 0 - 30 Volt output for detector polarization.

(See next page for a technical description)

Moreover, thanks to the construction of the new fourth generation light source, FERMI@Elettra, a new **lonization chamber**, developed for beam loss monitoring along the undulators of FEL, is available. The chamber is controlled through a new 4-channel electronic frontend - XPi rack module - that embodies +/-2kVolt and digital trigger input/ output, charge integration amplifiers and microprocessor controlled Ethernet interface.

(See next page for a technical description)

For more information concerning our products please see our product catalogue, that is available upon request, and on our web site, ilo.elettra.trieste.it, product section.



ph. Massimo Belluz

How to contact us:

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AH501B Fast High Resolution Bipolar Digital Picoammeter

The AH501B is a compact, fast and high resolution, wide-bandwidth, ultra-wide dynamic range picoammeter with 4-channel simultaneous sampling inputs.

It is composed by a specially designed transimpedance input stage for current sensing combined with several analog signal conditioning and filtering stages with state of the art electronics.

This device performs bipolar current measurements from ± 2.5 nA (with a resolution of 298 aA) up to ± 2.5 mA (resolution of 298 nA) with sampling frequencies up to 26 kHz (for 1 channel and a 16-bit resolution) and 6.5 kHz (4 channels, 16 bit/sample).

The simultaneous sampling of the 4 independent channels makes this instrument ideal for beam position monitor applications or multichannel acquisition.

The AH501B is housed in a light and extremely compact box that can be placed close to the signal sources in order to reduce cable lengths and minimize possible noise pick-up.

The picoammeter can be remotely controlled via a TCP/IP communication interface: range, data format and a lot of other parameters can be easily set and checked through SCPI commands (LabVIEW VIs are available, if required).

The AH501B has an external TRIGGER/GATE input signal to synchronize the acquisition of the picoammeter with external events (e.g. laser triggering).

Data are transferred through TCP/IP or UDP communication; moreover 4 analog output +/- 5 Volts are incorporated for current analogue measurements and one 0 - 30 Volt output is available for detector polarization.



| FEATURES | APPLICATIONS |
|--|----------------------------------|
| From ± 2.5 nA up to ± 2.5 mA current range | Fast Feedback applications |
| Up to 26 kHz sampling frequencies | 4-quadrant beam position monitor |
| 24 bit ADC converter | Ion Chamber flux monitoring |
| less than 140fA @RNG2 full scale range noise | Photodiode acquisition |
| 4-channel simultaneous sampling | Precision process control |
| Lightweight and compact design | Multichannel current acquisition |
| Ethernet 10/100 communication interface | |
| 4 analog output +/- 5 Volts | Direct measure of currents |
| 1 bias voltage output 0 20 Volt | Detector polarization |
BLM-IC02 Ionization Chamber Beam Loss Monitor

The BLM-IC02 ionization chamber, developed for the FERMI@Elettra project, is an instrument particularly suited for beam loss monitoring in high energy particle accelerators.

It consists of three plane electrodes mounted inside a rugged aluminum enclosure containing a gas volume of 1.3 litres. An externally supplied high voltage of up to 1000 V is applied between the outer electrodes and the central one. The chamber has a gas inlet and outlet to allow the operation with a constant gas flux of typical detector gases like Argon or Nitrogen. Alternatively, it can work in air without need of an external gas supply.

Filled with air at standard atmospheric pressure, the sensitivity of the chamber amounts to 46 μ C/Gy (in terms of generated charge per absorbed dose).

The BLM-IC02 can be easily interfaced with the XPi data acquisition system or with the AH401B, AH501B picoammeters.



| BLM - IC02 SPECIFICATIONS | APPLICATIONS |
|---|--------------------------------|
| Sensitivity (in air) 46 µC/Gy | Beam Loss Monitoring |
| Maximum Voltage 1000 V | Machine Protection |
| Gas volume 1.3 l | Insertion Device Protection |
| Output connector BNC | Radiation Dose Measurement 100 |
| HV connector SHV | |
| Gas Inlet/Outlet 6 mm Swagelok® tube fittings | |

XPi Data Acquisition System

The XPi data acquisition system, conceived for the FERMI@Elettra project, is a new modular controller particularly suited for beam diagnostic devices like ion-chambers and beam position monitors. It is a system that can be equipped with *ad-hoc* modules according to the device controlled.

Currently available modules are a fast 4-channel, low noise charge integration picoammeter and an ultra low noise high-voltage module. The picoammeter module performs triggerable charge measurement ranging from 50pC (with a resolution of 50aC) up to 1.8nC (with a resolution of 1.8fC). With a software programmable integration-time starting from 500µs up to 1s, a current measurement ranging from 50pA (resolution of 50 aA) up to 3.6µA (resolution of 3.6 pA) is achievable. The ultra-low noise, high-stability, 16-bit resolution, high-voltage module can be selected from +/-200V (with a minimum step increment of 3 mV) up to +/-2000V (with a minimum step increment of 30.5mV) and it is especially suited for ion-chambers or other detectors' polarization.

The controller has several external input/output optical TRIGGER and CONVERSION signals useful for data acquisition synchronization with external events like Lasers or FEL pulses. The system is also equipped with an output switch contact for interlock systems.

The XPi device includes an LCD display for direct data readings and a manual control to configure the main device parameters. Moreover, the system can be remotely controlled through the installed standard 10/100 Ethernet interface. Instrument communication TCP/IP or UDP protocols can be selected (TANGO device driver and LabVIEW VIs are available on request).

The whole system is housed in a compact 1U 19" standard rack and is directly powered from the 110/220V main supply.



| FEATURES | APPLICATIONS | | |
|---|---|--|--|
| From 50pC up to 1.8nC charge integration range | Fast Feedback applications | | |
| From 500µs up to 1s programmable integration time | 4-quadrant beam position monitor | | |
| 20 bit ADC converter | Ion Chamber flux monitoring | | |
| From 50pA up to 3.6µA current measurement | Photodiode acquisition | | |
| 4-channel simultaneous sampling | Precision process control | | |
| 1U 19″ Standard Rack | Multichannel charge/current acquisition | | |
| Ethernet 10/100 communication interface | | | |
| TCP/IP or UDP selectable protocol | | | |
| HV output from +/-100V up to +/-2000V | Direct measure of currents | | |
| LCD Front Panel display | Detector polarization | | |

Insertion device design and manufacturing @ KYMA srl

Kyma Srl was established in 2007 as a joint venture between Sincrotrone Trieste SCpA and the industrial companies Cosylab d.d. (Ljubljana) and Euromisure SpA (Cremona).

Kyma activities focus on accelerator technology, with specific regard to the development and realization of insertion devices for light sources.

More than twenty years of experience in design, assembling, characterization and operation of insertion devices at Sincrotrone Trieste, have been put together with the manufacturing capabilities of the industrial partners, to build a world-class company for IDs realization and application.

Since 2008 a daughter company, Kyma Tehnologija d.o.o., has been established in Sežana, just 10 km from the Elettra site, where all the activities connected with magnetic assembling and characterization are carried out.

The original purpose of Kyma was the realization of the undulators for the FERMI@Elettra project.

By summer 2010 all the undulators for the FEL-1 free-electron laser have been realized and subsequently installed and commissioned. The undulators for the first and second stage of FEL-2 have been completed and the remaining undulators are scheduled to be delivered by the end of August 2011.

Next table summarizes the undulators for the FERMI@Elettra project.

| F | UNCTION | ТҮРЕ | LENGHT | PERIOD |
|--------------------------------|-------------|---------|--------|--------|
| L | aser heater | LPU | 540 | 40.36 |
| FEL1 | Modulator | LPU | 3220 | 100.0 |
| | Radiator | 6 x EPU | 2415 | 55.2 |
| FEL 2 1 st stage | Modulator | LPU | 3220 | 100.0 |
| | Radiator | 2 x EPU | 2415 | 55.2 |
| FEL 2 2 nd stage | Modulator | EPU | 2415 | 55.2 |
| | Radiator | 6 x EPU | 2400 | 34.8 |

Further to the realization of the undulators for FERMI@Elettra, Kyma is now developing its business on the world market. A number of contracts have been already awarded:

- one hybrid wiggler for Canadian Light Source, Saskatoon (Canada);
- one Linearly Polarized Undulator for Raja Ramanna Centre for Advanced Technology, Indore (India);
- two Elliptically Polarized Undulators for Pohang Light Source, Pohang (Korea).
- two EPUs (4 movable quadrant Elliptically Polarized Undulators) for Brookhaven National Laboratory (USA)
- Development of innovative prototype undulators for SPARX with ENEA (Italia)



The seven undulators of the FEL-1 chain installed in the FERMI@Elettra tunnel

How to contact us:

Kyma Srl

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Undulators under magnetic characterization at the Kyma Tehnologija laboratory in Sežana

Institutional events



MEETING OF CEI MINISTERS FOR SCIENCE AND TECHNOLOGY

(Trieste, October 19, 2011)

The Ministerial Meeting on Science and Technology of the Central European Initiative (CEI) took place in Trieste, under the Serbian Presidency. Delegations from Member States attended the meeting, including 3 Ministers and 6 Deputy Ministers and/or High Officials, as well as a Representative of the European Commission (Directorate General for Research and Innovation) and other guests. Sincrotrone Trieste hosted the opening session.

Workshop







WIRMS

(Trieste, September 4-8, 2011) The 6th Workshop on Infrared Microscopy and Spectroscopy with Accelerator-Based Sources brought together SR & FEL scientists and synchrotron-IR and FEL-IR users. They discussed the latest developments and trends, as well as the future directions of the field, and promote even more promising applications.

ph. Roberto Barnabà









The Researchers' Night



(*Trieste, September 23, 2011*) The Researchers' Night is a Europewide event bringing together the public at large with researchers once a year on the fourth Friday of September. In 2011 it took place in over 800 venues of 320 European cities in 32 countries.









In Trieste the event, named STAR (Star in Trieste And Researchers), was held within the suggestive backdrop of Piazza Unità d'Italia and its surroundings.

At the Elettra "kitchen", the chefresearchers "cooked" solar cells with food and home products.

ph. Roberto Barnabà

EVENTS











School



XI SCHOOL ON SYNCHROTRON RADIATION: FUNDAMENTALS, METHODS AND APPLICATIONS

(Trieste, September 5-16, 2011)

The School was organized by SILS (Italian Society of Synchrotron Radiation) in collaboration with Sincrotrone Trieste, in the setting of the Castle of Duino.

The School gave a general overview of the characteristics and potentiality of synchrotron radiation to graduated students and young researchers interested in its use. Data analysis sessions, as well as experimental training on some of the Elettra beamlines, were also held.

ph. Roberto Barnabà







EVENTS

| WORKSHOPS, CONFERENCES, MEETINGS AND SCHOOLS | | November 2010 - September 2011 |
|---|-------------------------|---|
| Event | Place / Date | Organisers / Collaborators |
| ESLS XVIII - European Synchrotron Light Source workshop | Trieste, 25-26/11, 2010 | Sincrotrone Trieste |
| LabVIEW 2010 Tour | Trieste, 30/11, 2010 | Sincrotrone Trieste / National Instruments |
| SPEM 2010 - Present and future of the scanning photoelectron microscopy | Trieste, 13-14/12, 2010 | Sincrotrone Trieste |
| Users' Assembly | Trieste, 14/12, 2010 | Sincrotrone Trieste |
| SESTRE - Seed FEL sources and Time-resolved experiments | Trieste, 14-15/12, 2010 | Sincrotrone Trieste |
| International Workshop on the Soft X-Ray Science and Instrumentation at the European XFEL | Trieste, 16-17/12, 2010 | Sincrotrone Trieste and European XFEL |
| 1ª Conferenza dei Servizi | Trieste, 14/04, 2011 | Comune di Trieste / Sincrotrone Trieste |
| 24th TANGO Collaboration Meeting | Trieste, 26-27/05, 2011 | Sincrotrone Trieste |
| Secondo Convegno congiunto SILS-SINS | Trieste, 01-03/09, 2011 | SILS / SINS / UniTS / Sincrotrone Trieste |
| WIRMS 2011 - 6th International Workshop on Infrared Spectroscopy and Microscopy with Accelerator-Based Sources | Trieste, 27-28/09, 2011 | Sincrotrone Trieste / Università di Roma "La Sapienza" |
| XI School on Synchrotron Radiation: Fundamentals, Methods and Applications | Trieste, 05-16/09, 2011 | Sincrotrone Trieste / SILS |

VISITOR DISTRIBUTION: TYPE OF INSTITUTION



VISITOR DISTRIBUTION: GEOGRAPHICAL BREAKDOWN

(August 2010 - September 2011)

VISITORS - PERIOD 2006 - 2011

* estimated visitors at December 2011



Visits

*2011



Sincrotrone Trieste

Elettra Laboratory

PRODUCTS FOR RESEARCH LABS AND SYNCHTROTRONS

Power Supply Equipment

New families of intelligent (DSP or PC embedded) power supplies, that cover many typologies (high voltage/current, four-quadrant etc.) and configurations are forthcoming. Epics or Tango interface are often already present and custom-built solutions are possible.

Detectors

Photons and charged particles detectors, based on cross delay anodes, multi anodes and centroid finding techniques are steadily developed. 3D information (x,y,time) with spatial and time resolutions in the order of tens of microns and picoseconds are available through many custom-built solutions.

Lab Instruments

Several instruments necessary for typical or extreme applications are available: fast picoammeters, multi-point strain gauge, charge pulse amplifiers, ion chambers, pulse generators, RF filters etc. Every tool is intelligent and in some cases "Epics/ Tango interface" is already provided.

Accelerator Parts

Elettra, over the years, has acquired great experience in developing and realizing accelerators components i.e undulators, resonant cavities etc. While for the production of Insertion Devices, a specific spin-off company has been set-up, for all the other components Elettra will provide them on request.

Sincrotrone Trieste S.C.p.A.

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...riding the wave



- PPM insertion devices (planar, APPLE-II, APPLE-III, etc.)
- Hybrid insertion device
- In-vacuum insertion devices
- Co-design and co-development
- Consultancy services
- Supply of mechanical structures and components
- Refurbishment and upgrade of existing insertion devices
- Magnetic measurement and magnet characterization
- Equipment for magnet measurements

KYMA lab for magnetic assembly and characlestation

Kyma is the only company worldwide completely focused on the design and production of customized insertion devices.

Kyma's qualified team provide in-house design and manufacturing capabilities through the entire project, from the Research & Development and design stage, to mechanical engineering and construction, and control system implementation, as well as installation and after-sale support.

Kyma has developed original software and hardware solutions for magnetic design, assembly, and characterization of insertion devices.





KYMA SRL

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EVALVE Filly simply Providency Alog wells are built of all PATENDERS Part house



La vision:

essere riferimento internazionale del trasferimento tecnologico e dell'innovazione organizzativa per la gestione strategica e operativa di ricerca e impresa.

La mission:

accrescere la competitività e l'attrattività dei territori di riferimento mediante:

- la valorizzazione di ricerca e impresa
- la formazione per lo sviluppo d'impresa e per la gestione di ricerca e innovazione
- la promozione, a livello internazionale, di reti di eccellenza scientifiche e imprenditoriali.

Le strategie:

- sviluppo dell'Ente nel Mezzogiorno e nell'Est europeo (la nuova Europa) per il trasferimento delle metodologie di formazione e governo di nuovi poli scientifico tecnologici e distretti
- stimolare l'innovazione di prodotti e processi energetici e un uso più sostenibile dell'energia attraverso le fonti rinnovabili e il miglioramento dell'efficienza energetica
- promuovere l'insediamento di laboratori di ricerca (pubblici e privati) e di imprese ad alta intensità di conoscenza, anche di nuova costituzione.

Gli scenari futuri:

- sviluppo di AREA nel Mezzogiorno, soprattutto con la formazione di broker tecnologici
- selezione e valorizzazione di idee e imprese innovative nel settore dell'energia e del risparmio energetico
- crescita continua e diffusione, anche con partnership qualificate, delle competenze interne trasformate in metodologie distintive a livello internazionale.

The vision:

to be an international reference for technological transfer and organisational innovation for strategic and operative management of research and enterprise.

The mission:

to competitively increase attractiveness in reference areas by means of:

- the enhancement of research and development
- training for company development and for research and innovation management
- promotion, on an international level, of a scientific and entrepreneurial excellence network.

The strategies:

- promote the development of AREA Science Park, with particular regard to the South of Italy and to Eastern Europe (the New Europe) for the transfer of training methodologies and management of new science centersand technology districts
- stimulate innovation in products and energy processes and a more sustainable use of energy through renewable sources and improving energy efficiency
- promote the establishment of research laboratories (public and private) and knowledge-intensive firms, including start-ups.

The future scenarios:

- development of AREA in the South of Italy, particularly with the creation of technology brokers
- selection and enhancement of ideas and innovative enterprise in the energy and energy saving sectors
- continuous growth and circulation, with qualified partners as well, for internal proficiency that is transformed into distinct methods at an international level.











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