TERS IV

4th International Conference on Tip Enhanced Raman Spectroscopy

RIO DE JANEIRO, BRAZIL

SEPTEMBER 8 & 9, 2014

TERS IV

4th International Conference on Tip Enhanced Raman Spectroscopy

RIO DE JANEIRO, BRAZIL

SEPTEMBER 8 & 9, 2014

WELCOME TO THE 4TH INTERNATIONAL CONFERENCE ON TIP ENHANCED RAMAN SPECTROSCOPY

The International Conference on Tip Enhanced Raman Spectroscopy (the TERS series) brings together academic and industrial researchers interested in the latest developments in the field of Tip Enhanced Raman Spectroscopy (TERS).

The meeting addresses the fundamentals and applications of TERS, with special emphasis on improvements in reliability, comparability, robustness, spatial resolution, enhancement and methodology. The scientific program includes invited and contributed talks, industry presentations and a poster session.

The TERS series had its first edition in 2009, and since then it has been gathering a growing number of scientists from around the world.

This 4th edition will take place in Rio de Janeiro, Brazil on September 8 & 9, 2014. Many groups have now achieved the impressive spacial resolutions of 1 nanometer and below, and the TERS4 meeting will have a special discussion on this this ultra-high resolution.

The conference will bring together leading academic scientists, researchers and scholars in the domain of interest from around the world. Topics of interest include:

- TER SPECTROSCOPY
- TERS IMAGING
- TERS ENHANCEMENT
- REFERENCE SAMPLE FOR TERS
- TIP FABRICATION
- SPATIAL RESOLUTION WITH TERS
- SINGLE-MOLECULE DETECTION
- APPLICATIONS
- COMMERCIALIZATION

We welcome and wish you a productive and memorable conference.

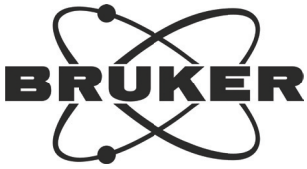
Rio de Janeiro, September 7, 2014

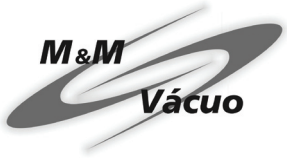
STEERING COMMITTEE

EXHIBITORS


altmann
altmann s.a. importação e comércio


IOP
Institute of Physics


BRUKER


M&M
Vácuo


EDWARDS


QuantumDesign


FEI™


SPECS™


HORIBA


ZEISS

SCIENTIFIC PROGRAM

SEPTEMBER 8 . MONDAY

SEPTEMBER 9 . TUESDAY

PROGRAM TABLE

SEPTEMBER 7 . SUNDAY

16:30 – 18:00	Welcome Cocktail

SEPTEMBER 8 . MONDAY

08:00 – 08:45	Registration
08:45 – 09:15	Opening session
09:15 – 10:15	*Plenary 1:* Hong-Jun Gao
10:15 – 10:35	Coffee break
10:35 – 11:20	*Invited 1:* Renato Zenobi
11:20 – 11:40	*Contributed 1:* Razvigor Ossikovski
11:40 – 12:00	*Contributed 2:* Sergey Kharintsev
12:00 – 12:20	*Contributed 3:* Debdulal Roy
12:20 – 13:05	*Invited 2:* Luiz Gustavo Cançado
13:05 – 14:30	Break for lunch
14:30 – 15:15	*Invited 3:* Volker Deckert
15:15 – 16:00	*Invited 4:* Satoshi Kawata
16:00 – 16:15	Coffee break
16:15 – 17:00	*Invited 5:* Zhenchao Dong
17:00 – 18:00	Discussion
18:00 – 19:00	Poster session

SEPTEMBER 9 . TUESDAY

09:00 – 10:00	*Plenary 2:* Lukas Novotny
10:00 – 10:05	Transfer to TERS room
10:05 – 10:25	*Contributed 4:* Thiago L. Vasconcelos
10:25 – 10:45	*Contributed 5:* Tyler J. Dill
10:45 – 11:05	Coffee break
11:05 – 11:50	*Invited 6:* Achim Hartschuh
11:50 – 12:10	*Contributed 6:* Christophe Galland
12:10 – 12:30	*Contributed 7:* Fernando Stavale
12:30 – 12:50	*Contributed 8:* Emanuele Poliani
12:50 – 14:30	Break for lunch
14:30 – 15:00	*Company talk 1:* Emmanuel Leroy Horiba
15:00 – 15:15	*Company talk 2:* Andrey Krayev AIST-NT Inc
15:15 – 15:30	*Company talk 3:* Mickael Febvre Brukernano
15:30 – 15:45	*Company talk 4:* Sergey Zayats NT-MDT Co.
15:45 – 16:15	Coffee break
16:15 – 17:00	*Invited 7:* Marcus Raschke
17:00 – 17:20	*Contributed 9:* Alfred J. Meixner
17:20 – 17:40	*Contributed 10:* Prabhat Verma
17:40 – 18:00	*Contributed 11:* Richard Van Duyne

SECTION CHAIRS

SEPTEMBER 8 . MONDAY

09:15 – 10:15	Carlos Alberto Achete
10:35 – 13:05	Alfred Meixner
14:30 – 16:00	Markus Raschke
16:15 – 18:00	Achim Hartschuh

SEPTEMBER 9 . TUESDAY

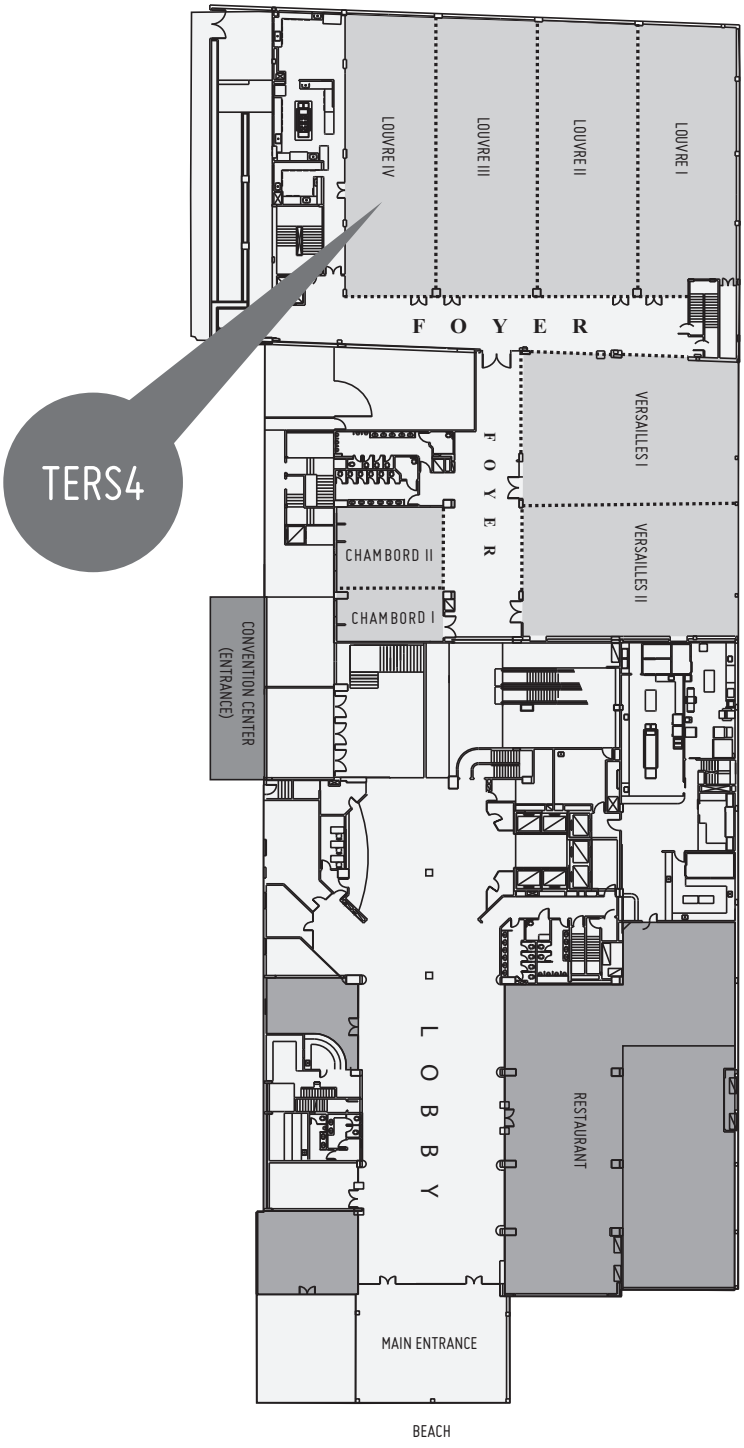
09:00 – 10:00	Ado Jorio
10:05 – 10:45	Prabhat Verma
11:05 – 12:50	Luiz Gustavo Cancado
14:30 – 15:45	Debdulal Roy
16:15 – 18:00	Volker Deckert

LOCATION MAP

The conference will be held at the **Windsor Barra Hotel** in Rio de Janeiro, Brazil.

ADDRESS:
Av. Lucio Costa, 2630
Barra da Tijuca
Phone: +55 21 2195-5000

OPENING SESSION:	Louvre I
PLENARIES:	Louvre I
TERS ROOM:	Louvre IV
POSTER SESSION:	Versailles II


TERS4
LOUVRE IV
LOUVRE III
LOUVRE II
LOUVRE I
FOYER
VERSAILLES I
VERSAILLES II
FOYER
CHAMBORD II
CHAMBORD I
CONVENTION CENTER (ENTRANCE)
LOBBY
RESTAURANT
MAIN ENTRANCE
BEACH

CONTENTS

PLENARIES

INVITED TALKS

CONTRIBUTED TALKS

COMPANY TALKS

POSTERS

PLENARIES

2D ATOMIC CRYSTALS ON TRANSITION METAL SURFACES: GRAPHENE, SILICENE, AND HAFNENE

Hong-Jun Gao[1]

[1] *Institute of Physics, Chinese Academy of Sciences*

The novel properties of graphene-like honeycomb structure have spurred tremendous interest in investigating other two-dimensional (2D) layered structures beyond graphene. In this talk, I will present construction of graphene, silicone, and hafnium honeycomb lattice on transition metal surfaces (TMS) (for example, Ru(0001), Pt(111), and Ir(111)). Molecular beam epitaxial growth technique is used to form the large scale 2D atomic crystals on TMS. Low electron energy diffraction (LEED) and scanning tunneling microscopy/spectroscopy (STM/S) together with density functional theory (DFT) calculations are employed to confirm the formed structure on the TMS. We expect that on the TMS more new 2D crystals could be found and these materials will show very interesting physical property and its promising potential applications in nanoscale devices.

OPTICAL ANTENNAS FOR ENHANCED LIGHT-MATTER INTERACTIONS

Lukas Novotny[1]

[1] *ETH Zurich, Photonics Laboratory*

Optical antennas consisting of plasmonic materials provide extreme light localization and small mode volumes, thereby boosting the sensitivity and signal-to-noise ratio in appli- cations ranging from single photon sources to photodetection. Optical antennas can also be employed to efficiently control and manipulate light on the nanometer scale and to achieve directional emission. I will review the physical properties of optical antennas, present recent results, and discuss applications.

INVITED TALKS

FRONTIERS OF TIP-ENHANCED RAMAN SPECTROSCOPY

Renato Zenobi[1]

[1] *ETH Zürich*

Several important aspects that are important for advancing TERS further will be discussed in this lecture:

» The tip is at the heart of any TERS experiment. There are thus some important practical aspects related to tip longevity. We have recently found chemical and physical protection methods that extend the lifetime of TERS tips from 1…2 days to many weeks.

» Recent claims about the ultimate spatial resolution of TERS, which has been proposed to be in the range of only ≈ 1 nm, will also be discussed, and results from a recent round robin / interlaboratory study on the comparability and reproducibility of TERS will be presented.

» Important applications of TERS will be highlighted, including its capabilities to spectroscopically identify the composition of so-called "2D materials" that are otherwise invisible because they are atomically thin, as well as the possibility to do spectroscopic imaging with a spatial resolution in the ≈ 10 … 60 nm range. Images can now be recorded with full spectral information at every pixel, using large pixel numbers (128x128 .... 512x512) in a reasonable time (on the order of minutes). This will be exemplified with spectroscopic maps obtained on mixed dye layers, segregated lipid domains, biomolecule nanostructures, self-assembled monolayers, and graphene.

SPATIAL COHERENCE IN TERS

L. Gustavo Cançado[1], Ryan Beams[2], Ado Jorio[1], Lukas Novotny[3]

[1] *Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG 30123-970, Brazil*

[2] *Institute of Optics, University of Rochester, Rochester, NY 14627, USA*

[3] *Photonics Laboratory, ETH Zürich, 8093 Zürich, Switzerland*

The Raman effect in crystals is usually treated in the literature as a spatially incoherent process [1, 2]. In other words, the scattered field from different sample points is considered to be spatially uncorrelated. This approach is supported by the early theory of coherence stating that the field emitted by an incoherent source at a given wavelength lambda is spatially uncorrelated on length-scales larger than lambda/2 [3]. As a consequence, correlations on length-scales smaller than lambda/2 are inaccessible in standard light scattering and the signal recorded in the far-field is incoherent. With the advent of near-field optics and nanoscience in general, studies of thermal emitters revealed correlation lengths much shorter than lambda [4–8]. In this talk we show that similar effects underlie near-field Raman scattering and that correlation lengths much smaller than lambda/2 can be extracted from measured data. The dependence of the scattered signal on the tip-sample separation is explored, and the signal enhancement depends on the particular symmetry of a vibrational mode. The model can be applied to extract of the correlation length Lc of optical phonons from experimentally recorded near-field Raman measurements.

[1] Light Scattering in Solids II,Topics in Applied Physics, Volume 50, M. Cardona, and G. Guntherodt (Springer-Verlag, Berlin, 1982).
[2] Scattering of Light by Crystals, W. Hayes, and R. Loudon (John Wiley & Sons, New York, 1978).
[3] W. H. Carter, and E. Wolf, J. Opt. Soc. of Am. 65, 1067 (1975).
[4] R. Carminati, and J. -J. Greffet, Phys. Rev. Lett. 82, 1660 (1999).
[5] A. V. Shchegrov, K. Joulain, R. Carminati, and J. -J. Greffet, Phys. Rev. Lett. 85, 1548 (2000).
[6] H. Roychowdhury, and E. Wolf, Opt. Lett. 28, 170 (2003).
[7] A. Apostol, and A. Dogariu, Phys. Rev. Lett. 91, 093901 (2003).
[8] H. Roychowdhury,and E. Wolf, J. of Mod. Opt. 51, 1603 (2004).

EXPERIMENTAL EVIDENCE FOR HIGH LATERAL RESOLUTION OF TERS UNDER AMBIENT CONDITIONS

Volker Deckert[1], Pushkar Singh[2], Tanja Deckert-Gaudig[2], Prabha Singh[1]

[1] *University of Jena*

[2] *IPHT Jena*

After first hints towards high spatial resolution under ambient conditions with protein structures, thorough experiments under UHV conditions by Dong et al. using an STM TERS setup nicely demonstrated extremely high lateral resolution. At present the theoretical explanation of the is under debate, but it seems clear that a simple electromagnetic model is not sufficient.

We will show further evidence that high not only high lateral resolution can be achieved under ambient conditions, but also the depth resolution is very high. For the latter we examined cytochrome c in the inter membrane space of mitochondria, while the lateral resolution can be better demonstrated on DNA or protein structures.

In order to get a better hold on the lower number of molecules involved in the TERS process we then performed combined TERS and SERS experiments on self assembled monolayers that indicate a different behaviour of the TERS experiments that are in agreement with recent low temperature TERS experiments, indicating a very low number of molecules that contribute to the Raman signal.

RESOLUTION AND ENHANCEMENT IN TERS MICROSCOPY

Satoshi Kawata[1], Atsushi Taguchi[1]

[1] *Osaka University and RIKEN*

Tip-enhanced Raman scattering microscopy has become one of the most promising tools for imaging and analyzing advanced nano-devices and nano-materials. However, the reproducibility of TERS experiments with probes has not been yet satisfactory for TERS users in many applications. In this presentation, I would like to discuss on the resolution and enhancement with TERS systems. We show through simulations that the enhancement varies with the number of grains and the gap distance among grains. The effectiveness of multi-grain probe for TERS imaging is demonstrated with experimental results. In addition, we show our recent results of SERS imaging of a living cell with nano-particle probes.

SINGLE-MOLECULE RAMAN SPECTROMICROSCOPY GOES SUB-NANOMETER

Zhenchao Dong[1]

[1] *University of Science and Technology of China*

Visualizing individual molecules with chemical recognition is a longstanding target in catalysis, bio-science, nanotechnology, and materials science. Molecular vibrations provide a valuable "fingerprint" for this identification. The spectroscopy based on tip-enhanced Raman scattering (TERS) has opened a path to obtain enhanced vibrational signals thanks to the strong localized plasmonic field at the tip apex. In this talk, I shall demonstrate single-molecule Raman spectroscopic imaging with unprecedented spatial resolution down to about 0.5 nm, resolving even the inner structure of a single molecule and its configuration on the surface [1]. This is achieved by a delicate spectral-matching technique that invokes a double-resonance process and resultant nonlinear optical effect, thanks to the exquisite tuning capability provided by low-temperature ultrahigh-vacuum scanning tunneling microscopy. Our nonlinear TERS technique features the use of only a continuous wave laser rather than two pulse lasers. Our findings demonstrate that Raman spectromicroscopy goes intra-molecular and sub-nanometer, which opens up a new avenue to explore chemical identification, photochemistry and bio-imaging at the single-molecule scale.

[1] R. Zhang, Y. Zhang, Z. C. Dong*, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang , and J. G. Hou*, Chemical mapping of a single molecule by plasmon enhanced Raman scattering, Nature 498 (2013) 82-86.

NEW DIRECTIONS IN TIP-ENHANCED NEAR-FIELD OPTICAL MICROSCOPY

Achim Hartschuh[1], Nina Mauser[1], Julia Janik[1]

[1] *Department Chemie & CeNS, LMU Munich, Germany*

We report on our efforts to extend tip-enhanced near-field optical microscopy into further directions. One direction is the application of tip-enhancement to photovoltaic and light-emitting devices as suggested in [1]. We obtained the first high-resolution photocurrent images of carbon nanotube devices using a metal tip to locally enhance optical-to-electrical transduction [2]. We show that the efficiency of the reversed process leading to electroluminescence can be increased as well [3].

[1] P. Bharadwaj, B. Deutsch, L. Novotny, Adv. Opt. Photon. 1, 438 (2009)
[2] N. Rauhut, M. Engel, M. Steiner, R. Krupke, P. Avouris, A. Hartschuh, ACS Nano 6, 6416 (2012)
[3] N. Mauser, N. Hartmann, M. S. Hofmann, J. Janik, A. Högele, A. Hartschuh, Nano Lett. 14, 3773 (2014)

RADIATIVE AND STRUCTURAL DYNAMICS FROM CRYO-TERS AND TIP-ENHANCED PLASMONIC PHOTOLUMINESCENCE AT THE TRANSITION FROM CLASSICAL TO QUANTUM COUPLING

Markus Raschke[1]

[1] *University of Colorado, USA*

We explore new regimes in tip-enhanced Raman and photoluminescence at low-tempeartures and in the quantum tunneling regime. Controlling the emitter-surface distance with sub-nanometer precision by combining atomic force and scanning tunneling distance control, we explore the unique behavior of plasmon dynamics at the transition from long range classical resonant energy transfer to quantum coupling. In contrast to conventional photoluminescence (PL) with nanosecond radiative lifetimes, quenching is completely suppressed because of few-femtosecond radiative lifetimes of a coupled plasmonic emitter. The entire distance behavior from 10's nm to sub-nm can be described using a phenomenological rate equation model and highlights the new degrees of freedom in radiation control enabled by an ultrafast emitter near surfaces. Field-enhanced behavior dominates until the onset of quantum coupling dramatically reduces emission intensity and field enhancement, as verified in concomitant tip-enhanced Raman measurements. In related experiments from high-spectral resolution cryogenic and temperature dependent TERS we gain insight into vibrational dephasing and energy exchange of surface molecules. Spectral diffusion indicates variation in molecular conformation and structural dynamics correlated with theoretical modes.

CONTRIBUTED TALKS

BILLION FOLD INCREASE IN TIP ENHANCED RAMAN SIGNAL

H. Kumar Wickramasinghe[1], M. Chaigneau[2], R. Yasukuni[2], G. Picardi[2], R. Ossikovski[2]

[1] *University of California, Irvine, CA*
[2] *LPICM, Ecole Polytechnique, France*

A billion fold increase in the Raman signal over conventional Tip Enhanced Raman Spectroscopy/Microscopy (TERS) is reported. It is achieved by introducing a stimulating beam confocal with the pump beam into a conventional TERS setup. A stimulated TERS spectrum, closely corresponding to its spontaneous TERS counterpart, is obtained by plotting the signal intensity of the strongest Raman peak of an azobenzene thiol self-assembled monolayer versus the stimulating laser frequency. The stimulated TERS image of azobenzene thiol molecules grafted onto Au<111> clearly shows the surface distribution of the molecules whereas, when compared to the simultaneously recorded surface topography, it presents an image contrast of different nature. The experimentally obtained stimulated gain is estimated at 1.0 × 10^9 which is in reasonable agreement with to the theoretically predicted value. In addition to the signal increase, the signal-to-noise ratio was three orders of magnitude higher than in conventional spontaneous TERS. The proposed stimulated TERS technique offers the possibility for a substantially faster imaging of the surface with respect to normal TERS.

TIP-ENHANCED RAMAN SCATTERING AS A PROBE OF AXIAL ANISOTROPY IN PHOTOREACTIVE POLYMER THIN FILMS

S. S. Kharintsev[1], A. I. Fishman[1], S. G. Kazarian[2], I. R. Gabitov[3], M. Kh. Salakhov[1]

[1] *Kazan Federal University*

[2] *Imperial College London*

[3] *University of Arizona*

In this paper we study a mechanism for inducing and probing axial anisotropy beyond the diffraction limit in side-chain nitroazobenzene (NAB) polymer thin films based on the combined effect of both local dc electrical poling and the longitudinal optical near-field. This is possible due to the orientation and translation diffusion of highly anisotropic NAB chromophores in the glassy environment under electrical and light loads. We discuss the reasons for polymer mass transport photoinduced by highly focused laser beams with 632.8 nm excitation wavelength that is out of the absorption band of chromophore moieties. In particular, a role of trans-cis photoisomerization and angular burning hole effect in making an optical fingerprint on the thin film surface is studied with polarization-dependent far- and near-field Raman spectroscopy. We show that optical-field gradient forces are responsible for both in-plane and out-of-plane translational diffusion of chromophores, even at high laser intensities (~kW/cm2). A longitudinally oriented polymer protrusion with the height of ~3 nm and the full width at half height of ~100 nm is observed at the core of the optical pattern. Optical depletion around the subwavelength protrusion is substantially related to the transverse orientation of chromophores and photobleaching. A highly inhomogeneous high-order laser beam leads to a non-uniform distribution of the optical anisotropy, the chromophores are out-plane aligned at the nanoscale core of the optical pattern and in-plane oriented in the doughnut depletion zone. Finally, we provide evidence for anisotropic and noncentrosymmetric behaviour of the NAB polymer thin film exposed to optical near-field poling with tip-enhanced Raman scattering microscopy and scanning Kelvin probe method.

We acknowledge a financial support from the Russian Foundation for Basic Research (No. 13-02-00758 A).

NANOSCALE IMAGING OF 2D MATERIALS USING TERS

Debdulal Roy[1], Naresh Kumar[1], Weitao Su[1], Andrew Pollard[1], Sandro Mignuzzi[1]

[1] *NPL*

Two-dimensional (2 D) materials have opened up new frontiers in materials science that can potentially lead to more efficient and cost-effective devices for a range of applications. The unique characteristic of all types of 2 D materials is the accessibility of the whole of the surface. This allows the tailoring of electronic properties for advanced applications through suitable engineering processes, but also limits realistic commercialisation prospects since undesired environmental factors, such as surface contamination, can be problematic. In this talk I will describe Raman imaging of 2 D materials such as graphene and MoS2 with a spatial resolution of 20 nm, and demonstrate the possibilities of characterising disorder, contamination, edge-effects and electronic properties of these 'all surface' materials.

TUNING LOCALIZED SURFACE PLASMON RESONANCE ON CONICAL GOLD TIPS

Thiago L. Vasconcelos[1], Braulio S. Archanjo[1], Benjamin Fragneaud[2], Luiz Gustavo Cançado[3], Wagner N. Rodrigues[3], Carlos A. Achete[1]

[1] *Instituto Nacional de Metrologia, Qualidade e Tecnologia (INMETRO), Divisão de Metrologia de Materiais (Dimat), RJ-Brazil*

[2] *Universidade Federal de Juiz de Fora (UFJF), Departamento de Física, MG-Brazil*

[3] *Universidade Federal de Minas Gerais (UFMG), Departamento de Física, MG-Brazil*

Localized Surface Plasmon (LSP) is a resonant collective oscillation of conduction electrons of subwavelength metal nanostructures [1,2]. When LSP is excited, strong optical absorption and scattering take place as local effects. Moreover, LSP exhibits the remarkable property of spectral tunability of its resonance energy by changing the nanostructure size and shape, what makes it suitable for several applications such as Tera-Hertz photodetectors, bio sensing, plasmonic waveguides, Surface Enhanced Raman Scattering (SERS) and probes for Scanning Near-Field Optical Microscopy (SNOM) [1,3]. In the last technique, the wavelength matching of the sample Raman scattering and the metallic probe optical absorption has been shown to play a crucial rule in generating near-field optical images [4,5]. Therefore, the use of LSP resonance in this case would provide a local photon-plasmon coupling on the SNOM probe apex. Here, we will present a reproducible method to tune in the visible range the LSP resonance energy on SNOM conical gold tips. To do so, we have made a superficial cut parallel to its diameter using Focused Ion Beam (FIB) milling. The local optical absorption relative to LSP resonance was measured and mapped using Electron Energy Loss Spectroscopy on a probe-corrected FEI Titan 80-300kV Transmission Electron Microscope. Finally we will show that the FIB cut has limited the resonant area and consequently the cut position relative to the tip apex can be used to tune the LSP resonance energy.

We acknowledge support from CNPQ, FINEP, CAPES and FAPERJ.

[1] E. Petryayeva and U. J. Krull, Analytica Chimica Acta 706, 8-24 (2011),
[2] O. Nicoletti et al., Nature 502, 80-84 (2013),
[3] F. Huth et al., Nano Letters 13, 1065-1072 (2013),
[4] E. Bailoa and V. Deckert, Chem. Soc. Rev., 37, 921-930 (2008),
[5] B. Yeo et al., Chem. Phys. Lett., 472, 1-13 (2009).

SELF-ASSEMBLED NANOCRYSTALS FOR TIP-ENHANCED RAMAN SPECTROSCOPY (TERS)

Tyler J. Dill[1]

[1] *UC San Diego*

There has been much progress recently in developing TERS (Tip-Enhanced Raman Spectroscopy) towards single-molecule spectroscopy, sub-2-nm spatial resolution, and broadband resonant probes. One of the largest remaining challenges is in tip fabrication. These challenges include producing tips with reproducible enhancement factors and resonant wavelengths, ease of fabrication, and tip-lifetime. We are developing TERS active tips that utilize self-assembled plasmonic nanoparticles. Plasmonic nanoparticles can be chemically synthesized in an array of sizes, shapes, and materials. Particles can be tailored to have single-crystalline properties and near-atomically smooth facets, which results in lower losses and allows for stronger near-field localization and enhancement. Control of particle size and shape allows us to control the plasmonic properties, thus tuning the performance of TERS probes. Self-assembly processes such as Langmuir-Blodgett assembly can create highly ordered monolayers of nanoparticles at an air-water interface. These particles can then be controllably transferred to a commercially available AFM tip, making it TERS active. We have observed strong TERS signals for silicon AFM probes coated with silver nanoparticles. These TERS probes are mechanically robust and undergo little morphological change over long periods of scanning in contact mode. We believe that nanoparticle-coated tips provide a promising way to advance TERS by providing repeatable and large signal enhancements.

MOLECULAR CAVITY OPTOMECHANICS: A THEORY OF PLASMON-ENHANCED RAMAN SCATTERING

Christophe Galland[1] ,Philippe Roelli[1], Nicolas Piro[1], Tobias J. Kippenberg[1]

[1] *EPFL*

We present a novel theory of plasmon-enhanced Raman scattering by mapping the problem to cavity optomechanics. Using FEM and DFT simulations we calculate the optomechanical vacuum coupling rate between individual molecules and hot spots of metallic dimers. We find that dynamical backaction of the plasmon on the vibrational mode can lead to amplification of molecular vibrations under blue-detuned laser excitation, thereby revealing an enhancement mechanism not contemplated be- fore. The optomechanical theory provides a quantitative framework for the calculation of enhanced cross-sections, recovers known results, and enables the design of novel systems that leverage dynamical backaction to achieve additional, mode-selective enhancement. It yields a new understanding of plasmon-enhanced Raman scattering and opens a route to molecular quantum optomechanics.

CATHODOLUMINESCENCE SPECTROSCOPY USING A STM: A POWERFUL TOOL FOR NANO-OXIDES CHARACTERIZATION

Israel Fidelis[1], Caio Bosco[1], Fernando Stavale[1]

[1] *Brazilian Center for Physics Research*

Progress in science has been always made through continuous development of innovative techniques either as ground-breaking as the discovery of X-ray diffraction or brainstorming as the invention of the scanning tunneling microscope (STM). This latter has been in recent decades further improved and became the technique of choice for characterization of uncountable materials systems, including biomaterials, nanocomposites and nanoparticles. Scanning probe microscopes (SPMs) are able to measure the variation of the electric or magnetic forces between the probe and the surface, or even move individual atoms and molecules to form artificial arrangements. Their ability to access real space information of surfaces with atomic resolution has changed our perception about materials characterization and opened plenty of room at the bottom. Although SPMs are capable to image surfaces with sub-nanometric resolution, their inherent chemical insensitivity is certainly an important technique drawback. To overcome this disadvantage the photon-STM has been proposed and developed years ago. In a photon-STM, a photon detector is placed near to the tip-sample region and the light emission response of nanometer-sized regions under the tip apex is measured. The photon-STM has been in several investigations used to obtain simultaneously structural, morphological and chemical information of surfaces and nanostructures and opened new possibilities for material characterization. In this contribution, we briefly discuss some of our recent results regarding the light emission properties of metal-oxide systems, such as (a) chromium doped MgO films ; (b) europium-oxides nanoclusters on MgO ; (c) lithium-molybdate nanostructures ; and (d) intrinsic-defects in ZnO films. These oxide systems are of great importance in heterogeneous catalysis, optical-electronic devices and photovoltaics, and the use of local cathodoluminescence spectroscopy offer new insights to investigate them properties in the nanoscale.

NEAR-FIELD LIGHT-MATTER INTERACTION IN TIP-ENHANCED RAMAN SCATTERING AND ITS APPLICATIONS

Emanuele Poliani[1], Christian Nenstiel[1], Stephanie Fritze[2], Armin Dadgar[2], Alois Krost[2], Axel Hoffmann[1], Janina Maultzsch[1]

[1] *Technische Universität Berlin*

[2] *Otto-von-Guericke-Universität Magdeburg*

Many efforts have been made in tip-enhanced Raman spectroscopy (TERS) in order to increase sensitivity and spatial resolution. However, less attention has been paid to the near-field light-matter interaction mechanism, which involves the evanescent field and localized surface plasmons. A deeper understanding of tip-enhanced Raman scattering allows - besides the possibility to define the applicability limit - to obtain information which cannot be obtained with standard Raman spectroscopy [1]. Here we demonstrate the surface sensitivity of TERS and the change of selection rules. The plasmonic interaction strongly modifies the gain for plasmon coupled Raman modes depending on carrier concentration. The effect of electronic charge-density fluctuations is revealed by TERS of GaN layers highly doped with Ge and Si. For highest Si doping, the phonon-plasmon coupling for the non-polar Raman mode is detected for the first time and exploited to extract the sub-wavelength mapping of carrier concentration around an a-Si cluster. The effect of the local strain relaxation on carrier concentration will be also discussed as a function of the morphology.

AMPLIFYING TIP-ENHANCED RAMAN SCATTERING BY TUNNELING THROUGH A SINGLE MOLECULAR JUNCTION

Alfred J. Meixner[1], Kai Braun[1], Xiao Wang[1], Dai Zhang[1], Hilmar Adler[1], Heiko Peisert[1], Thomas Chassé[1]

[1] *University of Tubingen*

Here, we introduce and experimentally demonstrate amplification of the tip enhanced Raman signal from the very low number of molecules enclosed in the optically pumped gap of a scanning tunneling microscope (STM). Amplification occurs via stimulated emission from the recombination of plasmon excited hot electrons with holes in the HOMO of surface bound molecules facing the tip apex. The gap between a sharp gold tip and a flat gold substrate covered with a self-assembled monolayer (SAM) of 5-chloro-2-mercaptobenzothiazole (Cl-MBT) molecules forms an extremely small optical gain medium. When electrons tunnel from the Cl-MBT's highest occupied molecular orbital (HOMO) to the tip, holes are left behind. These can be repopulated by hot electrons induced by the laser-driven plasmon oscillation on the metal surfaces enclosing the cavity. Solving the laser-rate equations for this system shows that the repopulation process can be efficiently stimulated by the gap mode's near field, TERS scattering from neighboring molecules acting as an optical seed and feed-back provided by the cavity plasmon-polariton. Our results demonstrate how electron tunneling confined in a molecular junction inside a plasmonic nano-cavity can amplify near-field enhancement. We anticipate that stimulated emission from an STM junction will advance our fundamental understanding of quantum plasmonics and lead to new analytical applications. Furthermore, this concept represents the basis for novel ultra-small, fast, optically and electronically switchable devices and could find applications in high-speed signal processing and optical telecommunications.

NEAR-FIELD POLARIZATION IN TERS

Toshihiro Mino[1], Yuika Saito[1], Prabhat Verma[1]

[1] *Osaka University, Osaka, Japan*

Polarization analysis in tip-enhanced Raman spectroscopy (TERS) is of tremendous advantage as it allows one to study highly directional intrinsic properties of a sample at nanoscale. However, neither evaluation nor control of the polarization properties of near-field light in TERS is as straightforward as in usual far-field illumination, because of the random metallic nanostructure attached to the tip apex. In this study, we have developed a method to successfully analyze the polarization of near-field light in TERS from the scattering pattern produced by the induced dipole in the metallic tip. Under dipole approximation, we measured the image of the dipole at a plane away from the focal plane, where the information about the direction of the dipole oscillation was intact. The direction of the dipole oscillation was determined from the defocused pattern, and then the polarization of near-field light was evaluated from the oscillation direction by calculating the intensity distribution of near-field light through Green's function. After evaluating the polarization of some fabricated tips, we used those tips to measure TERS images from single-walled carbon nanotubes and confirmed that the contrast of the TERS image depended on the oscillation direction of the dipole, which were also found in excellent agreement with the calculated TERS images, verifying that the polarization of near-field was quantitatively estimated by our technique. Our technique would lead to better quantitative analysis in TERS imaging with consideration for polarization impact, giving a better understanding of the behavior of nanomaterials.

RECENT ADVANCES IN ULTRAHIGH VACUUM AND ULTRAFAST TERS

Richard Van Duyne[1]

[1] *Northwestern University*

Two recent advances in tip-enhanced Raman spectroscopy (TERS) will be presented. First, our current understanding of the adsorbate surface interactions involved in the low temperature (LT), ultrahigh vacuum (UHV) TERS of Ag tip/Rhodamine 6G (R6G) /Ag(111) and other Ag tip/adsorbate/Ag(111) systems will be described. Second, an update on our new results in ultrafast TERS will be presented.

Low temperature (19K) ultrahigh vacuum tip-enhanced Raman spectroscopy (LT-UHV-TERS) has been carried out for the Ag tip/R6G/Ag(111) system. The combination of Raman linewidth narrowing and TD-DFT calculations on the free R6G molecule to describe the potential energy distribution of the normal modes enables the detailed understanding of the adsorbate-substrate interactions that cause substantial shifts between LT-TERS and room temperature (RT) TERS, LT-SERS, and RT-SERS.

In addition to the recent demonstrations that TERS can be used to obtain chemical information with nanometer spatial resolution and low temperature, UHV operation, it should, in principle, also be possible obtain temporal resolution on the ultrafast timescale. Herein, we demonstrate reliable TER signal of Rhodamine 6G (R6G) on Ag(111) in ultrahigh vacuum (UHV) using picosecond (ps)-pulsed excitation. The UHV environment mitigates against irreversible signal loss due to O2 and H2O mediated decay chemistry. Similarly, we find that the rate of SER signal loss under picosecond irradiation is also appreciably attenuated in UHV. Analysis of the decay kinetics suggests that the mechanism responsible for signal loss in ps SERS of R6G is surface diffusion.

COMPANY TALKS

HIGH SPEED TERS IMAGING OF GRAPHENE OXIDE AND OTHER CARBON SPECIES WITH NANORAMAN

Emmanuel Leroy[1], Andrey Krayev[2], Sergey Saunin[2]

[1] *Horiba Scientific*
[2] *AIST-NT Inc*

Graphene is a strong Raman scatterer and this technique has long been used to determine quality and number of layers of such material; however it lacks the spatial resolution that is necessary to study engineered structures in detail.
Scanning Probe Microscopy (SPM), and especially Atomic Force Microscopy (AFM) is a powerful technique to image physical properties of graphene, such as topography, conductivity or other electrical properties.

Combining both techniques is challenging but extremely powerful, as it makes imaging of both chemical and physical properties possible, although conventional Raman only provides limited spatial resolution. The step beyond co-localized AFM and Raman is nanoRaman or nano-spectroscopy in general.

In this talk, we will present the latest development in terms of Tip Enhanced Raman spectroscopy (TERS) that make possible nanoscale imaging of chemical and physical properties of graphene and other carbon species: innovative integration of technologies brings high-throughput optics and high-resolution scanning for high-speed imaging without interferences between the techniques. The latest developments in near-field optical probes now provide reliable solutions for academic and industrial researchers alike to easily get started with nanoscale spectroscopy.

Videos of the measurement in progress:
http://www.youtube.com/watch?v=kDr1njI6CfY
and
http://www.youtube.com/watch?v=HYOI2B7OBaQ

TERS AS A REAL LIFE ANALYTICAL TOOL: HIGH SPEED, HIGH PIXEL DENSITY, CHEMICALLY SPECIFIC NANOSCALE IMAGING OF COMPLEX MULTI-COMPONENT SAMPLES

Sergey A. Saunin[1], Vasily V. Gavrilyuk[1], Dmitry A. Evplov[1], Emmanuel Leroy[2], Andrey V. Krayev[1]

[1] *AIST-NT Inc*

[2] *Horiba Scientific*

Tip Enhanced Raman Scattering (TERS) has been a subject of great scientific interest for 15 years. With recent advances in single-molecule TERS, this interest is expected to grow. Regardless of these recent achievements, the real-life application of TERS as an analytical method has been hampered by extremely long acquisition times, measured in hours, required for collection of reasonably high pixel density TERS maps.

We report successful high pixel density, high speed (less than 10 minutes per map) TERS imaging of complex samples comprised of two species of carbon and self-assembled layers of organic molecules. The spatial resolution routinely obtained in such chemically specific TERS maps is in the 15 - 20 nm range, with the best resolution achieved being 7 nm.

The high speed TERS imaging capability enabled by advanced hardware and software makes TERS a real life analytical method for chemically specific imaging at the nano scale.

TERS ON GRAPHENE

Mickael Febvre[1], Tim Batten[2]

[1] *Bruker nano, Palaiseau, France*
[2] *Renishaw, Wotton Under Edge, UK*

Atomic Force Microscopy as well as Raman Spectroscopy have become indispensable tools in many areas of science and technology. PeakForce Tapping allows the AFM to measure nano-mechanical properties with true atomic resolution but has a gap in that it lacks chemical specificity. Confocal Raman spectroscopy on the other hand fills this gap but has the shortcoming of being a diffraction limited technique.

By seamlessly integrating both techniques, PeakForce Tapping AFM and Raman spectroscopy, and employing TERS at selected locations we will show that there is indeed a path to a Scanning Probe based instrument that allows full material identification on the nanometer scale. Colocalization will be shown on Graphene flake when TERS effect will be observed on Graphene on Copper and Graphene on Gold.

Experimental setup as automatic hotspot searching, tip used and imaging mode will be explained.

RELIABLE CANTILEVER-TYPE TERS PROBES FOR NON-TRANSPARENT SAMPLES

Pavel Dorozhkin[1], Sergey Zayats[1], Artyom Shelaev[1], Sergey Kharintsev[2], Mikhail Yanul[1], Igor Arkov[1], Victor Bykov[1]

[1] *NT-MDT Co., Zelenograd Russia*

[2] *Kazan Federal University, Kazan, Russia*

We present reliable TERS probes based on AFM cantilevers designed to work with opaque samples. The probes are prepared based on so-called "Top Visual" AFM Si cantilevers with application of special metal coating. Protruding "nose-type" shape of the probes allows the Raman laser light to be focused on the probe apex from the top: for use both with transparent and non-transparent samples. AFM probes can have different stiffness and can be optimized for contact and non-contact regimes.

The probes provide guaranteed TERS performance on a test sample (thin layer of BCB organic molecules on Au substrate):

» Enhancement factor >50x (Tip IN vs. Tip. OUT) for ~70% of probes. Typical enhancement factor : > 100x. Some probes reach >500x enhancement.

» TERS (nano-Raman mapping). ~20-70 nm resolution. >50% of probes.

» Remarkable lifetime without considerable enhancement degradation

The TERS AFM probes also feature excellent AFM performance in contact and non-contact regimes since they are prepared based on standard Si AFM cantilevers produced by mass technology. All advanced AFM modes (electrical, magnetic, nanomechanical etc.) are available. High resonance quality factors (for non-contact probes) allow excellent force sensitivity and guarantee long tip lifetime during measurements.

The TERS probes reach their highest performance when used with NT-MDT AFM-Raman instrumentation specifically designed for TERS research.

POSTERS

SIMULATION OF ELECTRIC FIELD OF TAPERED GOLD TIP

Mehdi Zohrabi[1], M Kh Salakhov[1], S S Kharintsev[1]

[1] *Kazan Federal University*

Optical antennas enhance the local light –matter interaction and boost the sensitivity of optical detection and sensing .for example ,antenna –based optical microscopy (TENOM),have been employed to improve the sensitivity and spatial resolution of single molecule fluorescence measurement.a mager challenge in antenna –based micrscopy is that the external lase field use to excite the antenna also irradiateds the sample directly ,this direct irradiation of the sample leads to a ackground signal and limits the signal to noise ratio of measurement.significant background contribution are particularly detrimental in elasticfrequency conserving.thus an optimized light localization to the tip apex and a background suppertion inherent to the near field probe are highly desired in many near field microscopy applications.different approaches to limit this problems have been laid out, such as excitation through confined apertures ,or cantilever –based tip –sample distance modulation.in this article ,we discuse approach towards improved light confinement at ultrasharp metallic tips.this method of converting traveling surface plasmon polaritons into a localized excitation at the tip end is particularly promising.

In this paper, we have designed an gold tapered optical antenna .Maxwell's equations are solved using FDTD metod with lumerical software and by Applying a laser light on the place of grating, we have simulated field intensity at the apex of tip . The diagram clearly shows the excitation of resonant surface plasmon of grating Based on indirect illumination of apex of tip ,we can couple incident radiation to propagating surface plasmon and converting to localized plasmon at the apex of tip and increase confinement of light at the apex of gold tip as a result,in near field optical microscopy increase resolution and decreace background.

FABRICATION OF TERS NANOSTRUCTURED TIPS BY ION MILLING

Bruno N.S. Vivan[1], Alex S. Duarte[1], Julio R. Schoffen[1], Ricardo R.B. Correia[1]

[1] *Instituto de Física - Universidade Federal do Rio Grande do Sul*

Here we report on the fabrication of metallic tips, one the fundamental tools to set up a optical near-field scanning technique based on Tip Enhanced Raman Spectroscopy. The work is based on the development of a tip, which encompasses two different effects observed for the coupling of Surface Plasmon Polaritons (SPP) and their propagation until a modified apex. After shaping the body of a 100 μm gold wire into a conic sharp form by means of electrochemical etching, a focused ion beam milling was used the produce the two characteristic modifications of the tip: I) A periodic structure tens of microns away from the apex set to maximize the SPP coupling and propagation directed to the structure peak. II) A nanometric blade-type apex shape to provide the proper field geometry amplification. We also report on tests performed with the second harmonic scattering of a sub-picosecond pulsed laser source from the nanotip apex to evidence the coupling and enhanced field geometries.

TERS IMAGING OF ORGANIC THIN FILMS ON PLASMONIC NANOSTRUCTURES

Raul D. Rodriguez[1], Evgeniya Sheremet[1], Vladimir Kolchuzhin[2], Ekaterina Rodyakina[3], Jana Kalbacova[1], Jan Mehner[2], Alexander Milekhin[3], Dietrich R.T. Zahn[1]

[1] *Semiconductor Physics, Universität Chemnitz, Chemnitz, Germany*

[2] *Microsystems and Precision Engineering, Universität Chemnitz, Chemnitz, Germany*

[3] *Rzhanov Institute of Semiconductor Physics, Novosibirsk, Russia*

Since the year 2000, when the first experimental demonstrations of tip-enhanced Raman spectroscopy (TERS) were reported, it was clear that the electric field confinement in the cavity formed between a metallic tip and substrate was an important part of the Raman enhancement in TERS. Such configuration gives way to the so-called gap mode. In this work we aim at demonstrating the effect of gap-mode on the TERS contrast and nanoscale imaging using AFM. A 2 nm film of cobalt phthalocyanine (CoPc) evaporated on several plasmonic substrates serves as a Raman scatterer. The TERS experiments were performed in the side illumination/collection configuration using electrochemically etched gold tips specifically designed for AFM-based TERS. First we show the higher Raman signal enhancement of CoPc on a flat gold film as compared to silicon due to near-field coupling between the TERS tip and the film. Additional enhancement of +55% occurred on singularities of the gold film. In order to obtain further enhancement, a periodic array of individual gold particles made by electron beam lithography was fabricated and used in gap-mode TERS. We found that such substrate provided more than 10-fold enhancement on the gold dots as compared to the signal from CoPc on silicon in agreement to numerical simulation results. The role of different imaging modes, contact or dynamic mode, in the Raman enhancement and the spatial anisotropy of the near-field enhancement are also reported. This work contributes to the reproducible chemical imaging of AFM-based TERS with nanoscale resolution in gap-mode.

INTERFERENCE OF ROUGHNESS IN PROPAGATION OF SURFACE PLASMON ON AU FILM

Fabio Lombardi Maximino[1], Antonio Domingues dos Santos[1]

[1] *Universidade de São Paulo*

The number of studies about surface plasmons increases every day because of their potential use in a wide range of applications such as: magneto-optical recording, microscopy, molecular biological detectors, TERS and many others. In our laboratory we use a scanning near-field optical microscope (SNOM) to measure surface plasmons(SP). The SNOM is able to operate in a topographical mode similar to an atomic force microscope. It also operates in an optical mode that allows us to acquire optical images with a red laser (605nm) or violet laser (458nm).

In previous work we note an interference in the propagation of SP. In the literature this interference is caused by surface roughness of the sample due to the grains. Searching to relate this roughness with the interference, we produce four Au films deposited by magnetron-sputtering: one at room temperature, one deposited with liquid nitrogen temperature, one co-deposited with Ag at room temperature and one in high temperature (450°C). The different types of deposition produced films with different grain sizes and roughness. Using SNOM to characterize these samples we noticed that films with higher roughness has a greater interference, while the lower surface roughness presents an interference almost regular. Even with almost flat films the interference still exists, the difference is that if the rough is high the interference causes a huge disturbance on SP and the interference is irregular while for flat films the interference is quite regular and causes a low amplitude disturbance on SP. These results shows this interference is something intrinsic to SP's propagation and not due to roughness.

TIP-ENHANCED RAMAN SPECTROSCOPY ON CARBON NANOTUBES: FROM PROOF-OF-PRINCIPLE EXPERIMENTS TO DEMONSTRATION AT THE DEVICE LEVEL

Jana Kalbacova[1], Raul D. Rodriguez[1], Evgeniya Sheremet[1], Dietrich R.T. Zahn[1]

[1] *Technische Universität Chemnitz*

Since their discovery in 1991 [1] up to now, carbon nanotubes (CNTs) have attracted attention of scientists and engineers. One of the striking application is their integration into field effect transistors (FETs) as channel material [2].

We present a study of CNT bundles deposited on gold substrate and a wafer-scaled CNT-FET device. The experiments were performed using a TERS instrument in the side illumination/collection configuration with all-metal probes for AFM [3]. In gap mode, we achieved a spatial resolution on a single CNT below 20 nm and were able to follow the defect concentration along the CNT. We also studied the channel area of a FET device, however, the gap-mode is not possible here, due to the wafer-scale technology (on silicon oxide/silicon substrate). The TERS results show that the different CNT bundles in the same transistor chanel can differ from one another in defect concentration.

Our contribution makes a step towards nanoscale characterization at the device level and opens the door for further understanding the advanced device properties at the nanoscale.

We thank Dr. Sascha Hermann and Prof. Stefan E. Schulz for providing the CNT-FET structures.

This work was supported by: Cluster of Excellence "Center for Advancing Electronics Dresden", DFG Research Unit FOR1713, and DFG project ZA146/22-1, RFBR 13-02-00063_a". The authors thank AIST-NT Inc. and HORIBA Scientific, especially Dr. Andrey Krayev, for the essential experimental support. This work was performed in the context of the European COST Action MP1302 Nanospectroscopy.

[1] S. Iijima: "Helical microtubules of graphitic carbon", Nature 1991, 56-58.
[2] S. J. Tans et al.: Room-temperature transistor based on a single carbon nanotube Nature 393.6680 1998, 49-52.
[3] R. D. Rodriguez, et al.: Compact metal probes: A solution for atomic force microscopy based tip-enhanced Raman spectroscopy. Review of Scientific Instruments 83.12 2012, 123708.

OPTICAL IMAGING OF DIELECTRIC NANO-STRUCTURES WITH TIP ENHANCED RAMAN SPECTROSCOPY

Mischa Nicklaus[1], Julien Plathier[1], Andreas Buescher[1], Andreas Ruediger[1]

[1] *Institut National de Recherche Scientifique*

Semiconductor industry requires analytical methods with nanometer precision for the analysis of nanostructures deposited on various substrates. Chemically-sensitive methods like confocal Raman or IR-spectroscopy are diffraction limited and do not provide access to the nano-scale. To make chemical characterization available at the nanoscale, we work on tip enhanced Raman spectroscopy (TERS) for optical imaging beyond the diffraction limit. This aperture-less near-field scanning microscopy technique generates localized surface plasmons at the apex of a scanning probe microscope tip to image the sample's surface. The backscattered light is spectrally resolved to reveal structural and chemical information based on Raman scattering and fluorescence. To investigate electrically insulating nanostructures such as dielectrics grown on non-transparent substrates, we scan by AFM with tuning fork probes and on-site produced tips under optical side-access. In this work, we present side-access TERS and scans on epitaxially grown PbTiO3 nano crystals with an optical resolution of 6 nm.

SYNCHROTRON BROADBAND NANO-FTIR ENDSTATION AT LNLS

Raul Freitas[1], Francisco Maia[1], Christoph Deneke[2], Thierry Moreno[3], Paul Dumas[3]

[1] *Brazilian Synchrotron Light Laboratory*

[2] *Brazilian Nanotechnology National Laboratory*

[3] *SOLEIL Synchrotron*

Scattering-type Scanning Near-Field Optical Microscopy (s-SNOM) is an established technique for optical analysis of materials in the nanometer range. In the s-SNOM, the resolution of the optical measurement is only limited by the size of the antenna, which is in the most of the cases a metallic AFM tip with radius smaller than 50 nm. Recent works have demonstrated s-SNOM carrying out IR imaging and FTIR with resolution better than 100 nm using lasers and black body sources [1]. Concerning the use of thermal sources, the application field will greatly benefit from the use of alternative broadband light sources with higher brilliance, which is a key requirement for easier operation and faster data recording in, among others, the investigation of new materials e.g. 2D structures based on few atomic layers and internal structures of biological samples.

Synchrotron radiation (SR) can meet basic requirements of an ideal light source for s-SNOM such as: i) large spectral range (from terahertz to hard X-rays), ii) high brilliance in the mid-IR range (up to 1000 times more brilliant than thermal sources), iii) polarized and iv) short time structure (hundreds of MHz pulsed light). Some synchrotron facilities have recently demonstrated the feasibility of using SR as the infrared source for s-SNOM [2-4].

In this work we show preliminary results of the new IR beamline of the LNLS, which will be dedicated to nano-FTIR experiments. First results confirm the ability of the endstation on performing nano-FTIR with spatial resolution better than 50 nm. Construction details, beamline specification for external users and potential applications will be presented in this presentation.

[1] F. Huth et al., Nature Materials 10, 352-356 (2011).
[2] Peter Hermann et al., Optics Express 21, 2913-2919 (2013).
[3] Jeffrey D' Archangel et al., Optics Express 21, 17150-17160 (2013).
[4] H. Bechtel et al., PNAS, 201400502 (2014).

ENABLING COMPARABILITY IN BACK-SCATTERED TERS INSTRUMENTATION VIA LITHOGRAPHIC TEST STRUCTURES

Erin Wood[1], Angela R. Hight Walker[1]

[1] *NIST, USA*

Tip-enhanced Raman spectroscopy promises unprecedented spatial resolution and selectivity; however this burgeoning technique is not yet truly robust. Tip size, shape and composition as well as variations in instrumental setup may cause deviation in the resultant spectra, even with the same sample. In order to account for these problems and enable comparability between different instruments, we propose to use a 3-D lithographically-printed, strained silicon standard which will act as both a calibration as well as a benchmark test for instrument robustness. This proposed test structure also will allow for further development and enhancement quantification of TERS instrumentation. Current progress on TERS mapping of the 3-D sample allows us to resolve individual SiGe@Si lines with widths of 32 nm. We also present methodology to allow for robust TERS-active probes using gold as the plasmonic enhancing materials.

TERS IMAGING OF CARBON NANOSTRUCTURES AND ORGANIC MOLECULES WITH VARIOUS TYPES OF TERS PROBES: STM, TUNING FORK, AFM CANTILEVER

Artem Shelaev[1], Mikhail Yanul[1], Sergey Zayats[2], Victor Bykov[1], Pavel Dorozhkin[1]

[1] *NT-MDT Co., Moscow Russia*

[2] *NT-MDT America, USA*

We present TERS mapping results on various carbon materials (carbon nanotubes, graphene, graphene oxide) and on organic molecules on Au substrate. Different types of TERS probes are used and their performance is compared: etched metal probes in STM feedback regime, metal probes on tuning fork in normal force feedback regime, AFM cantilevers in contact and non-contact regimes. TERS spatial resolution reached is close to 10 nm.

Mass produced cantilever-type AFM TERS probes are presented. Probes can be used in top illumination regime: for non-transparent samples. Net enhancement factors (tip IN / tip OUT signal ratio) >2000x are observed for some probes.

Experimental results of tip-assisted optical nanolithography are presented. Photobleaching of photosensitive organic molecular layer is produced by light localized at the end of the TERS probe. Resulting pattern is scanned by TERS using the same probe. Estimated resolution of optical lithography patterning is ~50 nm.

NOTES

INDEX

INDEX

W

Y

Z

SPONSORED BY

ZEISS

FEI™

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

CAPES

Ministry of
Science, Technology and Innovation

BRAZILIAN GOVERNMENT
BRASIL

ORGANIZED BY

REDE BRASILEIRA
DE PESQUISA E INSTRUMENTAÇÃO
EM NANOESPECTROSCOPIA ÓTICA

UFMG
UNIVERSIDADE FEDERAL
DE MINAS GERAIS

INMETRO

ACADEMIA
BRASILEIRA
DE CIÊNCIAS
MCMXVI