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25-29 June 2012
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Program and Book of Abstracts
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NANOSEA 2012
International Conference
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NAUTILUS ROOM
12:30 - 13:00 NANOMATERIALS AND NANOTECHNOLOGY: CONCLUDING REMARKS
NANOSEA 2012 International Conference

NANOSEA 2012 International Conference is the fourth edition of NanoSEA, six years after the successful start in July 2006 at Aix-en-Provence (France), four years after NANOSEA 2008 held in the magnificent Villa Mondragone Conference Centre, and two year after NANOSEA 2010 held at the unforgettable Cassis, French Riviera.

NANOSEA 2012 will be held, from 25 to 29 June, in Santa Margherita di Pula (Cagliari, Italy), situated in the middle of the Mediterranean Sea, at the four star Hotel Flamingo Resort (www.hotelflamingo.it). The Congress Centre of the Flamingo Hotel Resort has a wonderful view on the beach with its blue-green colour together with inviting bays, granitic rocks, nuraghi and roman ruins.

General Information

Research on nanostructures self-assembled encompasses fundamental issues in crystal growth and the scaling of materials properties to molecular dimensions, and work on possible applications of nanoscale assemblies in advanced devices. The goal of this conference is to bring together the broad, multidisciplinary community of researchers who are interested in the field of nanostructures and the opportunities for future high-impact science and technology related to such field.

The Conference will provide a common forum for scientists operating in all the fields of nanostructures from their formation and modelling to their properties and applications. The conference will cover the physics of nanostructures at the nanoscale, new fabrication procedures of nanostructures with well defined size, shape and composition, and also:

- large-scale patterning obtained by spontaneous structuring as well as local probe nano-patterning for size and position control of nanostructures;
- theoretical and experimental efforts dedicated to a better understanding of the formation, evolution and organisation of nanoscale systems;
- fundamental and new issues in nucleation, crystal growth, surface and interface atomistic mechanisms and electronic structure;
- optical, electrical, magnetic and mechanical properties representative of the self-assembled systems; Novel properties induced by low scale nanostructures.

Finally, new insights on short-term and future/futuristic device applications will be of prime interest in the framework of this Conference.
Scope

NANOSEA 2012 will primarily focus on the following topics that are of strong current interest in fields of nanostructures self-assembling and nanopatterned substrate:

**Nanostructured Materials:**
- Semiconductor - Metallic - Organic - Biological - New materials and structures

**Nanostructures classes:**
- Quantum dots, quantum wires and quantum wells - Nanotubes and nanorods - Graphene layers - Nanoparticles and Nanoprecipitates - Nanoporous material - Very thin multilayers and superlattices

**Local structure of nanostructures:**
- Effects of local structure on properties in nanostructured materials - Quantitative characterization of atomic arrangements - Characterization of nanoparticle surfaces - Characterization of internal interfaces

**Self-assembling techniques:**
- Nanopatterning by lithographic techniques - Ion-beam lithography and patterning - Nanopore fabrication and Pore filling - Substrate nanostructuring - Co-polymer template - Surface passivation - Functionalisation and catalysts - Nanofabrication

**Modelling:**
- Self-organisation and pattern formation - Thermodynamics and kinetics of nucleation and growth - Ab initio theory for spintronic materials and spin transport - Defects and impurities - Non-radiative and relaxation processes - Transport

**Properties:**
- Electronic and optical - Magnetic - Size dependent properties and transport - Mechanical - Structure, microstructure, and morphology

**Applications:**
- Novel microelectronic device - Nanoelectronic devices - Molecular devices - Nanodevice fabrication technology, characterization, properties and modelling - Photonic and photovoltaic devices - Chemical and biological sensors - Multifunctional spin devices - Magnetic random access memories (MRAM) - Other applications in medicine, biology, energy and environment…
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JUNE 25 MONDAY

NAUTILUS ROOM

10:00 - 10:30 Welcome Address
De Crescenzi, Dipartimento di Fisica, Università di Roma Tor Vergata, Roma, Italy
Puppin, CNISM, Dipartimento di Fisica, Politecnico di Milano, Milano, Italy
Condensed matter physics in Italy

10:30 - 12:30 PLENARY SESSION

10:30 - 11:10 Tersoff, IBM Watson Research Center, Yorktown Heights, New York, USA
PLENARY Complex dynamics in nanowire growth

11:10 - 11:50 Wiesendanger, Institute of Applied Physics and Interdisciplinary Nanoscience Center Hamburg, University of Hamburg, Germany
PLENARY From Model-Type Nanomagnets to Atomic Spin Logic Devices

11:50 - 12:30 Tosatti, SISSA, CNR-IOM Democritos, and ICTP, Trieste, Italy
PLENARY Nanofriction Theory and Simulation

12:30 - 13:00 Exhibitors

13:00 - 16:30 Lunch and Break

16:30 - 19:30 III-IV NANOWIRES

16:30 - 17:00 Jagadish, Department of Electronic Materials Engineering,
The Australian National University, Canberra, Australia
KEYNOTE III-V compound Semiconductor Nanowires
for Optoelectronic Device Applications

17:00 - 17:30 Polimeni, Dipartimento di Fisica, Sapienza Università di Roma, Roma, Italy
INVITED Band structure of high-quality wurtzite GaAs
in InGaAs-GaAs core-shell nanowires

17:30 - 18:00 Glas, CNRS-Laboratoire de Photonique et de Nanostructures,
Route de Nozay, Marcoussis, France
KEYNOTE III-V nanowire growth: kinetics, statistics and quantum dot formation

18:00 - 18:15 Galicka, Institute of Physics PAS, al. Lotnikow 32/46, Warsaw, Poland
INVITED First-Principles Study of Doped III-V nanowires
18:15 - 18:30 Ishii, Tottori University, Koyama, Tottori, Japan
Self-assembled formation of GaP/GaAs/InP nanowires on graphite

18:30 - 18:45 Kriegner, Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz, Linz, Austria
Structural investigation of GaInP nanowires using X-ray diffraction

18:45 - 19:00 Lehmann, Chemnitz University of Technology, Semiconductor Physics, Chemnitz, Germany
Raman Mapping on GaAs/In28Ga82As Smart Tubes - Stress Made Visible

19:00 - 19:15 Millinchick, Department of Materials Science and Engineering, University of Michigan, USA
Formation and Characterization of Focused Ion Beam Produced InAs Semiconductor Nanospikes

19:15 - 19:30 Quintero, Dpto. Física Aplicada, Universidad de Vigo, Vigo, Spain
Ultralong refractory glass nanofibers produced by Laser Spinning

ASTREA ROOM

16:30 - 19:30 MAGNETIC NANOSTRUCTURES

16:30 - 17:00 Kamieniarz, Faculty of Physics, A. Mickiewicz University, Poznań, Poland
INVITED
Anisotropy, geometric structure and frustration effects in molecule-based nanomagnets

17:15 - 17:30 Bussetti, Department of Physics, Politecnico of Milan, Milano, Italy
The metastable bcc phase of ultra-thin Ni layer on Fe(001) studied by scanning tunneling microscopy

17:30 - 17:45 Carbucicchio, Physics Department, University of Parma, Parma, Italy
Effects of the elemental layer thickness on the properties of Fe/Co grown at 200°C

17:45 - 18:15 Cini, Dipartimento di Fisica, Universita di Roma Tor Vergata and INFN, Roma, Italy
INVITED
Magnetic moments, pumping and memory storage in connected nanoscopic rings

18:15 - 18:30 Ciprian, Physics Department, University of Parma, Parma, Italy
Magnetic and structural properties of FePd thin films induced by the annealing temperature
18:30 - 18:45  Granitzer, Institute of Physics, Karl Franzens University Graz, Graz, Austria
Magnetic behaviour of Ni deposits within magnetic field assisted etched porous silicon

18:45 - 19:00  Tiberto, INRIM, Electromagnetics, Torino, Italy
Magnetic properties of Fe-(Pt,Pd) thin films patterned by self-assembling of polystyrene nanospheres

19:00 - 19:15  Lee, Bio-IT Convergence Center, Korea Institute of Ceramic Engineering & Technology, Korea
Preparation of Ni-modified Heterogeneous Magnetic Mesoporous Silica For Biomolecular Immobilization

CYPREA ROOM

16:30 - 19:30  Si-Ge NANOSTRUCTURES

16:30 - 17:00  Aqua, Institut des Nanosciences de Paris, Université Pierre et Marie Curie and CNRS, Paris, France
Organizing effect of a patterned substrate on strained quantum dots

17:00 - 17:15  Persichetti, Dipartimento di Fisica, Università di Roma “Tor Vergata”, Roma, Italy
Effects of elastic field anisotropy on the heteroepitaxial growth of Ge quantum dots on vicinal Si surfaces

17:15 - 17:30  Richard, Aix-Marseille University – IM2NP, Marseille and ESRF, Grenoble, France
Tracking defects in Si(001) and in Ge nanostructures grown on Si(001): an X-ray study

17:30 - 17:45  Aouassa, IM2NP, CNRS, AMU, Marseille, France
Ordered arrays of Si and Ge nanocrystals via dewetting of pre-patterned thin films

17:45 - 18:00  Bischoff, Institut de Science des Matériaux de Mulhouse, Université de Haute Alsace, Mulhouse, France
Growth of Ge and Si crystalline nanostructures on an insulating LaAlO$_3$(001) substrate

18:00 - 18:15  Carrada, CEMES/CNRS, Toulouse, France
Low energy ion beam synthesis of Ge nanocrystals in HfO2/SiN dielectric stacks for non-volatile memory applications

18:15 - 18:30  Bergamaschini, L-NESS and Materials Science Department, University of Milano-Bicocca, Milano, Italy
Fast pit filling and 3D island formation during Ge deposition on pit-patterned Si(001) substrates
Italy is a country well known all over the world for different reasons. Many of them are banalities, other represent true strength points of the country. Two of them are science and education. The Italian contribution to the overall scientific production is proportionate to the gross domestic product in spite of the fact that the R&D expenditure amounts to less than one percent. This lack of funding is mostly due to the absence of private investments and one of its more serious consequences is the so called "brain drain" phenomenon. Every year thousand of young scientists leave the country but, due to the excellent quality of our education system, they can easily find a position wherever they like. Optimistically we can consider this an investment for the future instead of a loss of national richness.
Complex dynamics in nanowire growth

*J. Tersoff* and K. W. Schwarz

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In growth of semiconductor nanowires by the Vapor-Liquid-Solid (VLS) process, it is common for nanowires to grow in different orientations, or kink from one direction into another, or grow along the surface. In addition, *in situ* observations reveal a multiplicity of intriguing oscillatory growth modes. Simulations using a new theoretical approach [1-2] makes it possible to model the growth and understand many of these puzzling behaviors.

The prototypical case of Au-catalyzed Si nanowires shows some particularly interesting features. Wires growing in the $\langle 111 \rangle$ direction have sawtooth-textured sidewalls. Wires growing in the $\langle 110 \rangle$ direction are smooth-sized, but have angled tips. Experimental observations reveal qualitative differences in growth dynamics between these two cases. Detailed comparison with theoretical simulations explains this behavior as originating in geometrical frustration [3], due to the absence of facets parallel to the $\langle 111 \rangle$ direction. Such detailed comparisons between theoretical simulations and *in situ* experimental observations provide a powerful new approach to understanding the complex dynamics of nanowire growth.

From Model-Type Nanomagnets to Atomic Spin Logic Devices

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The developments of novel magnetic materials as well as spin-based electronics are hot topics of current research in materials science and solid state physics. Both research fields could profit tremendously from atomic-scale insight into magnetic properties and spin-dependent interactions at the atomic level. Based on the development of spin-polarized scanning tunneling microscopy (SP-STM) [1] we have recently established the novel method of single-atom magnetometry [2,3] which allows the measurement of magnetization curves and the determination of magnetic moments on an atom-by-atom basis. While the sensitivity level of single-atom magnetometry is below one Bohr magneton, it can easily be combined with the atomic-resolution imaging and manipulation capabilities of conventional STM, thereby offering a novel approach towards a rational material design based on the knowledge of the atomic-level properties and interactions within the solid state [4]. Moreover, an atom-by-atom design and realization of all-spin logic devices [5] has recently been demonstrated by our group based on the combined knowledge derived from surface physics, nanoscience, and magnetism. Alternatively, self-assembly of atomic magnetic chains on nanostructured substrates has been employed in order to create model-type systems for atomic-scale information transfer based on the concept of vector-spin chirality [6].

Nanofriction Theory and Simulation (*)

E. Tosatti

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Thirty years after the invention of the STM the physics uncovered by nanosize probes is still a flourishing subject. Nanofriction represents the main active front of development in the physics of tribology, the wide field which encompasses first of all mechanical friction, adhesion and wear, but also less conventional dissipation phenomena, including electronic and magnetic ones.
In this lecture I will use recent theory and mostly simulation work in our group to illustrate some ideas in this rich field.

(*) Dedicated to the memory of Rodolfo Del Sole
III-V compound Semiconductor Nanowires for Optoelectronic Device Applications

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Semiconductor nanowires are intensively being investigated due to their unique growth mechanisms and novel physical properties. In this study, various III-V semiconductor nanowires and related nanowire heterostructures were grown epitaxially on GaAs, InAs, InP (111)B or Si (111) substrates by metalorganic chemical vapor deposition (MOCVD) using Au nanoparticles as catalyst.

We demonstrated that the AlGaAs shell layer can efficiently suppress the surface related non-radiative combination and improved the carrier lifetime significantly in GaAs nanowires. Nearly intrinsic exciton lifetimes (~1 ns) were obtained in these core-shell nanowires [1], which are comparable to high quality two-dimensional double heterostructures. In GaAs/GaP core-shell nanowires, the strain between the core and shell can be utilized to engineer the electronic structure of the GaAs nanowire core [2].

Pure ZB InAs nanowires, free of twin defects, and pure WZ nanowires free of stacking faults were achieved by carefully tuning the growth parameters [3]. This ability to tune crystal structure between twin-free ZB and stacking-fault-free WZ not only will enhance the performance of nanowire devices but also opens new possibilities for engineering nanowire devices, without restrictions on nanowire diameters.

We were also able to achieve mixed phases of ZB/WZ structures in a single InP nanowire. Time resolved photoluminescence measurements have shown a type II band alignment in these ZB/WZ mixed phase nanowires. Extremely long carrier lifetime (up to 8400 ps) was observed in WZ dominant nanowires [4].

Acknowledgments: This research is supported by the Australian Research Council and Australian National Fabrication Facility established under Australian Government NCRIS Program.

References
Band structure of high-quality wurtzite GaAs in InGaAs-GaAs core-shell nanowires


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(4) IMM-CNR, via del Fosso del Cavaliere 100, 00133 Roma, Italy
(5) High Field Magnet Laboratory, Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 7, 6525 ED Nijmegen, The Netherlands
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At ambient pressure, wurtzite, WZ, lattice structure cannot form in bulk III-(As,P) semiconductors [1], whilst it grows in nanowire, NW, form [2], thus providing an additional degree of freedom for the realization of nano-heterostructures. Despite the high interest of these WZ structures, several of their fundamental electronic properties are still not well assessed.

We investigate the electronic properties of WZ GaAs in InGaAs-GaAs core-shell NWs by photoluminescence, PL, and PL excitation spectroscopy as a function of light polarization, temperature (up to RT), and magnetic field (up to 30 T). We observe unprecedented narrow (<1 meV) excitonic lines reflecting the high structural and optical quality of the material. We find that WZ GaAs has a band gap 10 meV greater than zincblende, ZB, GaAs. This energy difference is one order of magnitude smaller than expected [3]. Transitions of WZ GaAs involving different critical points of conduction and valence bands are observed up to RT and their symmetry addressed by exploiting selection rules for light polarization. The diamagnetic shift of the exciton ground state provides precious information concerning carrier reduced mass and symmetry of the lowest conduction band, till now unsolved issues. Finally, hot carrier luminescence is observed, with carrier temperatures in excess of 600 K at lattice temperature of 310 K that has interesting prospects for photoconversion applications.

III-V nanowire growth: kinetics, statistics and quantum dot formation

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Despite important progress in the recent years, the understanding of the intricate processes that operate during nanowire growth is still far from being stabilized. However, these growth mechanisms strongly impact the morphology, the structure and the local composition of the nanowires, and hence their physical properties.

I shall discuss recent studies that combine experimental investigations and modeling of the formation of III-V semiconducting nanowires and of their heterostructures, and offer choice examples of crystal growth in a confined medium of nanometric dimensions.

Nanowires often grow in the vapour-liquid-solid mode from an apical liquid droplet, whose volume is of the order of a zeptolitre. The many paths via which this droplet (which is continuously consumed) may be replenished produce original growth kinetics, the quantification of which yields values of several key parameters [1,2].

Over and above these "average" kinetics, the depletion of the droplet induced by the formation of each new nanowire monolayer reduces the fluctuations in the time-distribution of the nucleation events. This reduction manifests itself in sub-Poissonian nucleation statistics and self-regulated growth [3].

The formation of highly mismatched heterostructures is much easier in nanowires than in the planar geometry, thanks to an efficient stress relaxation at the nanowire sidewalls [4]. It is then somewhat surprising that the coherent deposition of a mismatched material on the top facet of a nanowire may result in the formation of islands occupying only a fraction of this facet, reminiscent of Volmer-Weber or Stranski-Krastanow growth. Our modeling of this effect seems confirmed by experiments recently carried out by others in the case of the catalyst-free growth of nanowires of group III nitrides.

First-Principles Study of Doped III-V nanowires

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The potential application of GaAs and InAs nanowires in novel electronic devices requires controllable p-type and n-type conductivity. The problem of doping of nanowires has become now a major challenge to the growers of one-dimensional III-V semiconductor structures. It occurs that specific growth conditions for nanowires, their crystal structure and orientation of their side facets may lead to different incorporation behavior than known for planar layers [1].

To explain the observed phenomena we study theoretically the properties of GaAs and InAs nanowires, in which one cation/anion is substituted by a dopant. Since the III-V semiconductor nanowires can grow in both, zinc-blende (ZB) and wurtzite (WZ) structures, we check whether the crystal structure of the wire has an impact on the doping level and the distribution of impurities in III-V nanowires and, most important, on the electronic properties of the doped nanowires. We consider ZB nanowires oriented along (111) axis and WZ nanowires along (0001) axis. Using ab initio methods we have calculated the formation and segregation energies of III-V nanowires, in which Be atom substitutes cation and Si substitutes either anion or cation atom. To study the electronic properties we have calculated the density of states of the doped nanowires.

The calculations have shown that the distribution of impurities in GaAs and InAs wires as well as their conductivity depend crucially on the crystal structure. Similar results have been recently obtained for GaAs nanowires doped with Mn, where a structure-dependent ferromagnetism was predicted [2].

The support of EC network SemiSpinNet (PITN-GA-2008-215368) is gratefully acknowledged.

Self-assembled formation of GaP/GaAs/InP nanowires on graphite

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The nanowires of III-V compound semiconductors are interesting in view of application to nano devices. Recently, we found the self-assembled formation of nanowires of III-V compound semiconductors on a graphite substrate. The results are confirmed in first-principles calculation. Our typical SEM image of GaP nanowires formed on graphite is shown in figure 1.

![GaP: side view](image)

Figure 1
GaP nanowire on graphite

For the confirmation of the nanowire formation, we perform the DFT calculation using the program code VASP. As shown in the previous works[1,2], GaN and AlN can be epitaxially grown on graphite and the calculated binding energy between graphite and nitrides is large. However, for GaP, GaAs and InP, the binding energy between graphite and epitaxial grown layer is negative. Therefore, for GaP, GaAs and InP, the epitaxial growth does not occur. Instead of the epitaxial growth, the nanowire formation is most stable for GaP, GaAs and InP. Moreover, the crystal orientation and the polarity of grown GaP/GaAs/InP are confirmed by using the DFT calculation.

References
Structural investigation of GaInP nanowires using X-ray diffraction


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Semiconductor nanowires open the possibility to combine materials in epitaxial growth, which are usually incompatible due to lattice mismatch [1].

In this work the structure of ternary Ga$_x$In$_{1-x}$P nanowires is investigated with respect to chemical composition and homogeneity. The wires were grown by metal-organic vapor-phase epitaxy [2]. For the investigation X-ray energy dispersive spectroscopy (XEDS) as well as X-ray diffraction (XRD) is used. Whereas the composition of single wires can be investigated in the XEDS, in XRD large ensembles of wires are investigated. Using laboratory XRD tools average chemical composition as well as compositional ranges in the ensemble of nanowires can be detected. Furthermore the identification of stacking defects and the distinction between the cubic zincblende and the hexagonal wurtzite phase are possible. Compositional variations within single wires were found along the nanowire axis. XRD reveals a variation of the materials composition on the order of about 19%. The use of modern synchrotron sources, were beam-sizes of the order of several 10 µm are available, enables us to investigate how the composition changes locally on the sample by recording diffraction patterns at different positions.

Raman Mapping on GaAs/In$_{20}$Ga$_{80}$As Smart Tubes – Stress Made Visible


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Smart tubes are rolled-ups of two or more strained thin films of semiconductors or metals: After the epitaxial growth of thin films having different lattice constants, the sacrificial adherence layer to the substrate is removed. Due to stress relaxation the films roll up forming tube structures.

To describe this role-up process using mechanical FEM simulations, precise knowledge of the present micro-scale stress values is mandatory. Raman spectroscopy is an optical, hence non-destructive technique, very sensitive to lattice distortions. Therefore, it offers a sophisticated possibility to locate and map stress without any mechanical interaction with the sampled object.

Here we present a study on GaAs/In$_{20}$Ga$_{80}$As smart tubes with a diameter of 7 µm on a GaAs (100) substrate. The smart tubes are rolled up to a dedicated distance, leaving bare substrate behind on one side of the smart tubes and an unrelaxed thin film stack on the opposing side. This allows a characterisation of all three important regions. The measurements are performed using a Horiba LabRam spectrometer with excitation wavelengths of 514 nm and 325 nm. Comparing the GaAs and InGaAs LO phonons of strained and relaxed films, in-plane and out-of-plane stress tensor components can be determined. It can be seen for irregular shaped smart tubes (cones) that taper regions show a larger shift of the InGaAs LO phonon, indicating larger stress, but only small shift of the GaAs LO phonon.

Raman mapping pictures of the characterised smart tubes will be presented and the results of the stress determination will be discussed.
Formation and Characterization of Focused Ion Beam Produced InAs Semiconductor Nanospikes

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We report on a Ga⁺ focused ion beam (FIB) erosion method for creating indium droplet capped InAs semiconductor spike nanostructures and examine their resulting microstructural and electronic properties. Under specific conditions, normal incidence FIB irradiation can erode InAs films to create high aspect ratio spikes, or “nanospikes,” with average heights of several hundred nanometers and maximum heights greater than 800 nm. Nanospike formation has been found to proceed via an ion-induced droplet masking process [1]. Metallic In droplets form on the InAs surface due to preferential sputtering of arsenic and nanospikes form under the In droplets as the surrounding material recedes. Nanospike creation using an InAs film grown on an InP substrate has revealed that nanospikes will not form on regions of exposed InP. This difference in the FIB response of InAs and InP may be exploited to create nanospikes in regular arrays by pre-patterning an InAs/InP heterostructure to locally control InAs film thickness and In droplet location. The structures of nanospikes created using both InAs and InAs/InP heterostructures have been examined by transmission electron microscopy (TEM), by scanning transmission electron microscopy (STEM), and by STEM energy dispersive spectrometry (EDS). The nanospikes possess a metallic indium cap, an ion damaged outer layer, and a range of internal structures. Some nanospikes have a single crystalline core that matches the orientation of the original InAs film, while others are heavily ion damaged and polycrystalline. Producing nanospikes by templating as described above has been found to produce a higher proportion of nanospikes with continuous single crystalline cores. Nanospike electrical properties have been characterized using a combined in-situ TEM/nanoprobe technique, which allows for simultaneous TEM imaging and current-voltage measurements. Furthermore, microstructural changes arising from the applied current can be correlated with matching changes in the IV characteristics. The nanospikes have been found to be conductive and show non-Ohmic IV behavior. However, the conductivity of the individual nanospikes varies and is determined by the microstructure of each spike. With this in mind, the nanospike electrical data has been analyzed to determine how nanospike structure controls carrier transport, and nanospikes with crystalline or partially crystalline cores have been found to be the most conductive. The ion-disrupted yet still conductive structure of the nanospikes may make them useful for nanoscale thermoelectric applications.

Ultralong refractory glass nanofibers produced by Laser Spinning

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Laser Spinning is a new technique for the production of ultralong amorphous ceramic nanofibers with lengths up to several centimeters [1, 2]. It employs a laser to melt a small volume of a solid precursor material while a high pressure gas jet drags it. Thus, the molten material forms glass fibers as result of its viscous elongation by the drag force and rapid cooling by the convective heat transfer promoted by the gas jet. This technique allows large quantities of nanofibers to be made with specific, controllable chemical compositions.

The analysis of the process revealed that the dimensions and temperature of the molten volume together with its viscosity to surface tension ratio are the main factors governing the formation of the nanofibers. Therefore, control of these parameters allows for the production of amorphous nanofibers of non-ready glass former materials with very fragile melts. Specifically, the viscosity of the melt can be controlled independently of its surface tension by adjusting the relative humidity of the assist gas. And consequently, the unprecedented synthesis of very long glass nanofibers from refractory fragile melts is reported. This outcome demonstrates its capability for the synthesis of glass nanofibers with different compositions with applications in the field of fire retardant fabrics, catalysis or high refractory materials.

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References
Anisotropy, geometric structure and frustration effects in molecule-based nanomagnets

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In this talk we review our results of comprehensive study of molecular nanomagnets recently synthesized in the form of the complex chromium-based molecules with bond defects and some 3d metal impurities as well as some homo- and bimetallic chains with non-collinear anisotropy axes. We focus on effects of anisotropy, geometry and frustration appearing in various thermodynamic properties of the nanoscale magnets which are described by Heisenberg-like spin models and simulated by accurate numerical methods [1,2]. We show that bond-dependent exchange anisotropy is needed to model magnetic torque in the Cd-dopped chromium ring [1]. We argue that only in the limit of infinite rings (n→∞) frustration can be considered as the opposite to bipartitness in the odd numbered (3 ≤ n ≤ 9) S=3/2 quantum spin rings both homo- and hetero-metallic. We analyse the influence of exchange interactions and anisotropy with collinear and non-collinear anisotropy axes on magnetic susceptibility of S=3/2 and s=1/2 chains composed of Cu ions linked to different 3d and 5d ions as well as of the Mn(III)-based single-chain magnet [3,4]. We reach the remarkable consistency of the DFT estimates of the magnetic couplings in pure and doped Cr₈ molecules [5] and provide strong support to the spin models exploited in the literature.

References:
The metastable bcc phase of ultra-thin Ni layer on Fe(001) studied by scanning tunneling microscopy

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The interest in magnetic materials has been spurred by the ability to realize metastable phases experimentally through epitaxial growth on single-crystal substrates acting as templates. Examples include face-centered-cubic (fcc) iron and body-centered-cubic (bcc) nickel. Phase diagrams derived from total-energy calculations for these bulk metastable structures predict a stable magnetic state at some lattice constant. In the ultrathin-film region [one to two monolayers (ML)], interesting properties, such as enhanced moments, have also been predicted.

In the past, the structure of the bcc phase of nickel grown epitaxially on Fe(001) substrates has been studied using low-energy electron-diffraction (LEED) and reflection high-energy electron-diffraction (RHEED) techniques [1,2]. The bcc-fcc Ni transition is interpreted, at the present state-of-art, in terms of a not-continuous Bain’s path [3] or equivalent more detailed transformations. It means that, up to about six layers, the nickel is found to grow in a bcc manner, and above this thickness a slight distortion occurs, eventually leading to c(2x2)-like LEED and RHEED patterns. The latter is consistent with a distortion and rotation of the Ni super-structure, respect to the Fe(001) substrate.

In this talk we show, for the first time, the morphology evolution of Ni ultrathin and thin films (up to 40ML) on clean Fe(001) at RT. We used an in-situ scanning tunneling microscopy (STM) to check the surface evolution during each step of Ni growth in our molecular beam epitaxy (MBE) chamber. We observe an intermediate new phase transition between the Ni bcc (1x1) and the fcc c-(2x2). The latter has been interpreted in terms of a Ni surface cell distortion not followed by the rotation.

Our findings can help the current debate about the microscopic changes that occur in the formation of the Ni/Fe interface [4].

References
Effects of the elemental layer thickness on the properties of Fe/Co grown at 200°C

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Fe/Co multilayers show a large saturation magnetization and very soft magnetic properties. Depending on the growing conditions, Fe/Co can show a large in-plane uniaxial anisotropy, which can be exploited for the development of magnetic recording devices.

Many works have been devoted to the study of Fe/Co multilayers, however little attention has been paid to the changes of the Fe/Co microstructure and magnetic properties induced by the growing temperature.

In the present work Fe/Co multilayers were grown at 200°C onto monocrystalline MgO-(100), naturally oxidized Si-(100) and glass substrates by means of a molecular beam epitaxy system.

Structural, microanalytical and magnetic characterization was performed by X-ray Diffraction (XRD), Conversion Electron Mössbauer Spectroscopy (CEMS), Magneto-Optical Kerr Effect magnetometry (MOKE), Atomic and Magnetic Force Microscopy (AFM/MFM).

The growing temperature affects the atom mobility and the degree of Fe/Co intermixing, giving rise to materials showing peculiar magnetic properties. Depending on the substrate nature and crystallinity, an appreciable out-of-plane magnetization component establishes whose strength is highly influenced by grain sizes and interface roughness. On the other hand the establishing in the system of an in-plane uniaxial anisotropy largely depends on the anisotropy of the Co layer in the multilayer stack.
Magnetic moments, pumping and memory storage in connected nanoscopic rings

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In future quantum computers, the information will be encoded and processed in molecular-sized objects. We consider a quantum ring connected to leads and the current which is excited by biasing the circuit in the absence of external magnetic field. The magnetic moment that arises in this way depends on the current distribution inside the ring. By solving theoretical models in different geometries, we show that a memory unit can be operated by threading suitable magnetic fields into a ring-shaped molecule properly connected to the external circuit. Currents can be excited in rings by time-dependent magnetic field even in classical Physics, but in nanoscopic rings they behave differently. The usual laws of linear circuits fail. It is by exploiting the quantum properties that one can build a memory device, in which the operations of writing and erasing can be efficiently performed. Moreover we show that, unlike classical rings, nanoscopic ones can also work as electron pumps, capable of driving currents out of a ring into the external circuit. An arbitrary amount of charge can be transferred from one side to the other by the field within the ring.

Our theory [1,2] should stimulate experimental realizations of such devices. The motivation is strong, since quantum computers will vastly overperform present-day ones for important special tasks while saving energy.


Magnetic and structural properties of FePd thin films induced by the annealing temperature

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The controlled and reproducible growth of thin films constituted by anisotropic phases showing large coercivity and remanence is of great importance in many technological fields. Recently an increasing interest is addressed to the study of systems that, grown at high temperature, undergo a disorder-order phase transformation with the establishing of a tetragonal structure, the L10 phase, characterized by a large uniaxial magnetocrystalline anisotropy.

The magnetic properties are strongly dependent on the film morphology and microstructure, and can be finely tailored by means of the growing parameters and suitable bufferlayers. This feature is a key issue in the information storage field where the main challenge is to obtain materials constituted by very small magnetically-decoupled grains, each one representing a bit of information.

In this work FePd thin films 9 nm thick were e-beam evaporated at different temperatures onto MgO-(100) monocrystals with or without a thin Pd underlayer. The characterization has been carried out by means of x-rays diffraction, atomic and magnetic force microscopy and magneto-optical Kerr effect magnetometry.

The results show that (001)-oriented and well order L10-FePd films can be grown in a very narrow temperature range. The magnetic properties are strongly correlated to the film morphology. The highest perpendicular anisotropy was found for films grown at 600°C onto a Pd underlayer 1 nm thick, because of the formation of well disconnected islands.
Magnetic behaviour of Ni deposits within magnetic field assisted etched porous silicon

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In the frame of this work the magnetic behaviour of a ferromagnetic nanocomposite has been investigated. The system consists of magnetic field assisted etched mesoporous silicon utilized as matrix and of electrodeposited ferromagnetic Ni-structures. First, within the pores of standard porous silicon matrices – anodized without magnetic field - Ni nanostructures have been deposited, whereas their shape and arrangement determine the coercivity and remanence of the samples. Second, porous silicon anodized in the presence of a magnetic field has been employed as matrix for metal deposition. In using a pulsed current comparable metal wires longer than one micrometer have been reached in both cases. Magnetic field assisted etching results in smaller pore-diameters, larger distances between the pores and less dendritic growth. These changes lead to greater coercivities, higher remanence and enhanced magnetic anisotropy due to the higher aspect ratio of the deposits and because of less magnetic interactions between the metal structures of adjacent pores.
Magnetic properties of Fe-(Pt,Pd) thin films patterned by self-assembling of polystyrene nanospheres

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Arrays of monodisperse magnetic nanoparticles with high magnetic anisotropy are currently studied for magnetorecording. Nanolithography techniques are extensively employed to prepare submicrometer arrays of magnetic dots/holes. In this frame, polystyrene nanosphere (PN) lithography has been recently exploited for magnetic thin films nanostructuring on large scale [1,2]. Such a technique is presently considered a valid alternative to conventional e-beam lithography due to its low-cost and large covering area for a variety of applications (i.e. spintronics, magnetic sensing, ultrahigh-density magnetic recording).

In this work, Fe$_5$Pt$_{57}$ thin films were epitaxially deposited by RF sputtering on a MgO(100) substrate heated at T = 400 °C to promote the formation of the L1$_0$ tetragonal phase. Patterned L1$_0$ FePt films were obtained by assembling commercially available PN nanospheres monolayer (starting mean diameter ranging in the interval 100 ± 500 nm, reduced by reactive ion etching) on a continuous thin films (thickness 10 nm). Subsequently, dot arrays were obtained by submitting the film to sputter etching with Ar$^+$ ions (final dots diameter 80 ± 400 nm) [1]. Conversely, arrays of antidot in Fe$_{50}$Pd$_{50}$ sputtered thin films (thickness 50 nm) on a Si substrate have been created by exploiting an alternative lithographical method using polystyrene nanospheres as diffraction masks in combination with a mercury lamp [2]. A monolayer of polystyrene nanoparticles (NP, starting mean size ≈ 800 nm) is deposited on a layer of resist properly patterned by exposures to an UV lamp aimed to invert the polymer. In this way, the individual spherules in the self-assembled planar array behave as optical lenses to generate regular diffraction patterns on the photoresist. At the end of the process, holes (diameter ≈ 300 nm) with circular shapes are generated in the magnetic film [2]. Such a lithographical procedure has the advantage of avoiding the use of reactive ion etching process to further reduce dot diameter possibly detrimental to the magnetic properties. In this case, the order-disorder transformation towards the L1$_0$-ordered tetragonal phase has been induced by post deposition annealing in vacuum ($T_a=823$ K for 10 minutes).

Sample microstructure was studied by means of SEM and AFM microscopy in all studied films. Room-temperature hysteresis loops were measured by an Alternating Gradient Magnetometer in the parallel and perpendicular configuration confirming the presence of the tetragonal phase in all patterned samples. MFM microscopy was exploited to study the magnetic domain pattern (in the remanent and demagnetised state) revealing a complex multidomains structure in both compositions. The effect of patterning (i.e. dot/hole diameter and mutual distance) on the magnetic properties of the Fe$_4$Pt$_{53}$ and Fe$_{50}$Pd$_{50}$ thin film will be studied in details.

Preparation of Ni-modified Heterogeneous Magnetic Mesoporous Silica
For Biomolecular Immobilization

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In this study, we present a novel method for mesoporous silicas which are functionalized with Fe and Ni particles to support His-tagged proteins. Mesoporous silicas were combined with iron (II) chloride tetrahydrate for initiating magnetizing process, followed by reduction in H₂ media. The nickel (II) chloride hexahydrate was introduced into pore and surface of heterogeneous magnetic mesoporous silicas (HMMS) by wet impregnation process. The resulting materials were reduced in a flowing of H₂ at 500 °C for 2h, thereby producing Ni particles on the surface of the HMMS. The Ni-HMMS was characterized by various state-of-the-art techniques, such as WAXS, FE-SEM, TEM, SQUID and nitrogen sorption. Ni-HMMS showed high adsorption level of His-tagged protein from Escherichia coli lysate. In addition, the purified His₆-CatA was observed high enzyme activity. It suggests that Ni-HMMS system provides contribution for maintain stable protein structure as well as simplified protein purification process.

References
Organizing effect of a patterned substrate on strained quantum dots

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A strained film coherently deposited on a substrate with a small lattice mismatch undergoes a morphological instability driven by surface diffusion. It eventually evolves into self-organized quantum dots with a typical length scale given by the ratio of the film surface energy and elastic energy density. We study the evolution of this instability on a patterned substrate with an egg-carton like shape. We investigate the competition between the organizations resulting both from the substrate and the instability, which is ruled by the ratio between the instability and pattern length scales. We use a continuum description accounting for elasticity, surface energy and wetting interactions [1]. We characterize the kinetic phase diagram as a function of time, film thickness and the length scales ratio. We show that in the instability first stage, the film surface can skip from a configuration in phase with the substrate to either an out-of-phase or a non-ordered configuration depending on the pattern wavelength and annealing time [2]. We discuss different initial conditions given by different deposition flux, and their influence on the surface evolution. We will then discuss the self-organization of quantum dots in the long time dynamics of the instability resulting from the non-linear dynamics. Of special interest is the correlation between the pattern corrugation and the islands location which is still controversial from the experimental point of view [3,4].

References :
Effects of elastic field anisotropy on the heteroepitaxial growth of Ge quantum dots on vicinal Si surfaces

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Engineering the growth of strained epitaxial films is a fascinating perspective in modern nanoscale science. To this purpose, the challenge is to control the strain-relief mechanisms which play a key role in the growth of nanostructures. This can be done "artificially," e.g., exploiting patterning surface features or multilayered structures. A conceptually different approach is the manipulation of heteroepitaxy through intrinsic properties of the substrate. To make this prospect feasible, one has to identify (1) distinct properties, which have impact on the growth process, and (2) a simple and reliable way of tuning them. In strained-layer epitaxy, the nature of the elastic field is a crucial parameter by definition. Since the elastic forces in solid materials act at the nanometer range, these interactions are particularly suited for bottom-up fabrication of semiconductor quantum dots. This talk will discuss the possibility to control the elastic environment of interacting Ge/Si islands by modulating the substrate orientation with miscut angle [1].

First, we will show that a fine shaping of Ge islands is possible by changing the miscut angle. This offers a direct way to easily alter the elastic-interaction potential among islands, which strongly depends on the detailed island's shape [2-3].

Then, the breaking the isotropy of elastic interactions with miscut will be discussed as a potential way to force the growth of Ge on vicinal Si surfaces towards completely different pathways than on the flat substrate, as well as to determine the local spatial ordering of nanostructures [4-6].

Finally, we will discuss the application of continuum elasticity theory implemented within a finite-element model as a powerful tool for simulating strain-related effects. Elastic energy values can be plugged into a total-energy scheme together with the surface energies of island facets. The resulting model can predict the morphological transitions of three-dimensional islands observed by experiments.

Tracking defects in Si(001) and in Ge nanostructures grown on Si(001): an X-ray study


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Plastic relaxation and formation of defects is a crucial issue in the epitaxial growth of nanoparticles and thin films. Indeed, defects generate a local strain in the crystalline lattice which affects its surroundings and may lead to undesired optoelectronic effects such as reduced charge carrier lifetime or nonradiative recombinations.

Here we present a direct non-destructive method based on x-ray diffuse scattering close to forbidden reflections to detect defects and investigate their structure inside Si crystals [1] and Ge islands grown on Si(001) [2]. This technique allows identifying the defect type and measuring the strain field generated by defects with a high sensitivity to the defect type. Besides, while defects have been well-characterized on as-grown samples, little is known concerning their initial formation and their evolution during growth because of the lack of an adequate technique. We will demonstrate that x-ray diffraction can be used in situ to study the formation of defects during the growth of Ge islands on Si(001) [3]. The dependence of in-plane spacing between interfacial dislocations, defect size and density are analyzed as a function of Ge-deposit. It is found that the introduction of additional defects is preferred to relieve strain during growth.

Ordered arrays of Si and Ge nanocrystals via dewetting of pre-patterned thin films

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New processes of Si and Ge island formation have recently been developed for fabricating quantum dot based microelectronic devices. The processes make use of the dewetting mechanism which involves a transformation of a 2D thin film into an array of isolated 3D islands due to a morphological instability. It is the balance between the surface and interfacial energies of the thin film and the substrate that defines this equilibrium morphology. The energetic informs about the global energy of the system, but the evolution of each component will depend on the local energetic changes in its immediate vicinity.

We show that self-organization of monodisperse ultra-small nanocrystals (NCs) into large scale patterns with ad hoc features can be created via templated dewetting. The process makes use of solid state dewetting of a thin film (amorphous or crystalline) templated through lithographic pre-patterning. The solid state dewetting initiated at the edges of the patterns controllably creates self-assembly of NCs with ad hoc placement and length scales different from the original patterns. The NC size is tuned by varying the nominal thickness of the top film while their position results from the association of film retraction from the edges of the patterns and Rayleigh-like instability.

Patterns consisting of lattices of lines and holes were prepared either by electron beam lithography (EBL) or by Alloy-Liquid-Metal Ion Source Focused Ion Beam (ALMIS-FIB) nanowriting. Focused Ion Beam was also carried out in a Tescan LYRA1 XMH dual-beam FIB workstation operating at 30 keV. This FIB is equipped with a mass-filtered ultra-high resolution focused ion beam COBRA-FIB from Orsay Physics, which has an ultimate resolution of 5 nm (using Ga⁺ ions). Patterning was performed using either single element (Ga⁺ ions) or AuGe alloy sources (Au⁺⁺ or Ge⁺ ions).

The use of a combination of nanopatterning and dewetting of the templated films produces precise alignments of ultra-small NCs with size and position tunable at will. In the examples presented on Fig. 1, amorphous Ge thin films have been prepatterned by FIB to create lines and concentric squares and circles extending over 100 µm (pitch ~ 100 nm). In these images the NCs have a mean diameter of about 25 nm. The process developed provides new routes for the fabrication of self-organized nanostructures for generic applications.

Fig.1: Self-organization of ultra-small nearly monodisperse Ge NCs (25 nm large) into 2D periodic patterns of lines, squares and circles.
Growth of Ge and Si crystalline nanostructures on an insulating LaAlO$_3$(001) substrate

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Non-volatile flash memories embedding nanocrystals (NC) are promising devices useful in computers, mobile phones or USB keys. The insertion of semiconducting (SC) NC in an insulating matrix requires the elaboration of complex "oxide/SC/oxide/Si(001)" heterostructures. We have studied the initial growth mechanisms of Si and Ge by molecular beam epitaxy on a LaAlO$_3$(001)-c(2x2) reconstructed substrate. Chemical and structural properties were investigated in-situ, by X-ray photoelectron spectroscopy, X-ray photoelectron diffraction and electron diffraction (LEED and RHEED), and ex-situ by atomic force microscopy and high-resolution transmission electron microscopy.

Above 500°C a Volmer Weber growth mode is observed, characterized by the immediate formation of crystalline nano-islands. These islands are relaxed and present an abrupt interface with the substrate. A unique epitaxial relationship is pointed out for Si islands where the Si(001) planes are parallel to the LaAlO$_3$(001) ones, but rotated by 45° in the [001] direction [1, 2]. Some of the Ge islands present a preferential relationship epitaxy, similar to that of Si, but with an additional rotation of 5° with respect to the growth axis, allowing to compensate the strain due to a higher lattice parameter mismatch (5%) [3, 4].

References
Low energy ion beam synthesis of Ge nanocrystals in HfO$_2$/SiN dielectric stacks for non-volatile memory applications

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Nanocrystal (NC) based memories are attractive candidates for replacing standard flash memories. The use of discrete storage points at the place of a continuous floating gate allows using thinner oxides for charge transfer, and hence, higher endurance, lower operation voltage and consumption, and faster writing/erasing times. Recently, the replacement of the gate oxide (SiO$_2$) by a dielectric with higher permittivity (high-k) has been proposed in order to obtain very thin equivalent oxide thickness and to improve data retention and programming speed. Finally, using germanium nanocrystals (Ge-NC) instead of silicon is expected to increase the retention times because of Ge smaller band gap which should provide a deeper potential well for the stored charges.

We propose an original memory device structure consisting of Ge-NC as storage elements, HfO$_2$ as high-k tunnel oxide and SiN$_x$ as control dielectric. For this, Ge$^{74}$ ions are implanted at low energy through a 5 nm HfO$_2$/12 nm SiN$_x$ high-k dielectric stack. After thermal annealing, a 2D layer of Ge nanocrystals is obtained close to the HfO$_2$/SiN$_x$ interface. Varying the ion implantation conditions (energy, dose) we are able to control the structural and electrical properties of these devices. In this work we present the effect of these variations on the structural characteristics of the Ge-NCs (size, density and position) as observed by Transmission Electron Microscopy (HREM, EFTEM) and Raman spectroscopy. The electrical properties indicate that charge storage predominantly takes place in the Ge-NCs. Significant memory windows with good retention properties have been observed indicating the feasibility of these stack structures for low operating voltage, non-volatile memory devices.
Fast pit filling and 3D island formation during Ge deposition on pit-patterned Si(001) substrates

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Ge deposition on pit-patterned Si(001) substrates is a viable procedure for obtaining spatially ordered arrays of uniform 3D islands [1]. Despite the impressive literature, some aspects of the process remain unclear. In particular, recent experiments suggest that deposition of a few (2-3) ML of Ge on pit-patterned Si(001) triggers a massive flow of Si atoms inside the pit [2,3], causing strong pit reshaping. Here we show that a continuum model including surface diffusion, elastic relaxation, and surface Si/Ge intermixing, is able to capture such surprising behaviour. The model is a direct extension of the one presented in [4], with the important addition of a term accounting for the dependence of the diffusivity on the local Ge content. Under conditions representative of the typical experimental ones, our simulations predict fast pit filling during the first stages of growth, followed by nucleation of 3D SiGe islands inside the pit, prior to complete pit filling.

Nanocrystal Memories fabricated by Ultra Low Energy Ion Beam Synthesis

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Nanocrystal-based memories could potentially become an evolutionary replacement for the polycrystalline silicon used in conventional programmable flash memory for today’s electronic equipment. In nanocrystal (NC) based metal-oxide-semiconductor (MOS) memory structures a fine tuning of the NCs characteristics (NC location in the gate oxide, size and surface density) is required for the pinpointing of optimal device architectures.

Ultra-low energy (typically 1 keV) ion beam synthesis (ULE-IBS) is a powerful technique for the controlled synthesis of two-dimensional (2D) arrays of Si NCs embedded in thin (<10 nm) SiO₂ layers. Both EEPROM-like and NVRAM-like transistors have been fabricated by coupling ULE-II and annealing under oxidizing ambient. Our NC-based memory devices show comparable data retention and endurance characteristics than the actual SONOS-like structures [1]. The trade-off between programming and data retention in NC memories can be further improved by several strategies. The first one consists in gate oxide engineering through the replacement the SiO₂ matrix by high-κ dielectrics. We present an innovative architecture where HfO₂ acts as tunnel oxide between the Si substrate and the 2D array of Si-NCs embedded in a thin SiN top layer [2]. The second solution lies in energy band engineering by using a two-layer structure (with Si and Ge NCs) with adequate band-offset between upper and lower NCs [3]. At last, the replacement of semiconducting particles by metal based dots (In₂O₃) is proposed as a way of obtaining a higher conduction-band offset.

Minority diffusion length and carrier storage dynamics by using nano-EBIC technique

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High resolution electron beam induced current (HR-EBIC) technique [1] is used on Ge nanocrystals (NCs) deposited on SiO2/Si(001) structures [2] to analyse the induced current spectral dependence as a function of the NCs geometrical features. The technique enables to determine the effective diffusion length L_{eff} as a function of electron beam irradiation energy (E). The carrier storage dynamics in NCs is also studied. The mechanisms of the electrical behavior of the AFM probe in contact with the sample are explained with the help of band diagrams of the AFM-tip/sample contact, which show that holes dominate the electric transport and storage. The effective diffusion length increases with the electron beam at weak energy, reaches a maximum and then decreases at high energy (Fig. 1). The decrease of L_{eff} was never noticed previously. The energy position of the L_{eff} maximum depends on the NC size [3]. The study of the carrier storage dynamics at E = 5 keV and I = 1.5 nA (the electron probe current), reveals that the charge of the NC takes a long time (t > 6 sec) even if the carrier generation under the e-beam irradiation is immediate (Fig. 2). A simple model based on capacitances in series with a resistance is introduced to explain the carrier storage in the NC, and the immediate discharge through the AFM-tip. The main capacitances are the NC capacitance C_{NC} ~ 26.3 aF, and the Ge oxide capacitance C_{ox} ~ 6.5 \times 10^{-16} F attributed to the Ge oxide layer which is naturally formed at ambient atmosphere on the Ge NCs. The resistance is found to be ~ 2 \times 10^{17} \Omega.

![Fig. 1](image1)

*L_{eff} variation as a function of e-beam energy*

![Fig. 2](image2)

*Carrier charge and discharge in NCs*

SiGe dots on Si(001) – Still able to surprise?

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The spontaneous formation of defect-free three-dimensional islands during deposition of Ge on clean Si(001) surfaces was first reported more than 2 decades ago [1]. In spite of its apparent simplicity and extensive research [2], the Ge/Si heteroepitaxial system is still able to reveal surprising phenomena and properties.

In this talk we will provide an overview of our recent work on the field. In particular we will report on island shape and compositional oscillations which occur during Ge deposition on hole-patterned Si-substrates [3] and on a new method to “stretch” conventional hut-clusters [1] into micron-long nanowires [4]. The latter are very appealing for quantum transport experiments with single nanostructures [5]. Finally we will show that, by stacking Ge/Si layers, we obtain a material with room-temperature thermal conductivity which can be fine-tuned between a ultralow value of 1 W/mK [6, 7] and that of Silicon (~150 W/mK) by simply varying the thicknesses of the constituent Ge and Si layers. This feature makes Si-Ge multilayers interesting for research in the field of nanostructured thermoelectric materials.

References
**JUNE 26 TUESDAY**

**NAUTILUS ROOM**

8:30 - 10:00  **NANOELECTRONICS AND NANOFABRICATION**

8:30 - 9:00  **KEYNOTE**  
*Simmons, Centre of Excellence for Quantum Computation, University of New South Wales, Sydney, Australia*  
*Single Atom Devices for Quantum Computing*

9:00 - 9:30  **KEYNOTE**  
*Schneider, Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*  
*Dynamical Coulomb blockade, quantum oscillations, and superconductivity in nano-sized electrical contacts*

9:30 - 10:00  **INVITED**  
*Simbrunner, Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz, Austria*  
*The Epitaxial Growth of Rod-Like Molecules and Implications for the Fabrication of Lasing Nano-Fibers*

10:00 - 10:30  Coffee break

**NAUTILUS ROOM 10:30 - 13:00  POSTER PRESENTATION**

13:00 - 16:30  Lunch and break

16:30 - 19:30  **ORGANICS**

16:30 - 17:00  **KEYNOTE**  
*Di Fabrizio, Italian Institute of Technology and Università degli studi Magna Grecia di Catanzaro, Italy*  
*Few/single molecule detection based on plasmons and superhydrophobicity down to attomolar concentration*

17:00 - 17:15  
*Borghetti, Donostia International Physics Center, San Sebastian, Spain*  
*Evidence for charge transfer at the stable organic/organic interface of the F16CuPc/PEN:F16CuPc/Au(111) heterolayer architecture*

17:15 - 17:30  
*Cappellini, Department of Physics, University of Cagliari and Istituto Officina dei Materiali (CNR), Cagliari, Italy*  
*Electronic and optical properties of TIPS-substituted pentacene: a (time dependent) density functional theory study*

17:30 - 17:45  
*Yeryukov, A.V. Rzhanov Institute of Semiconductor Physics, Novosibirsk, Russia*  
*Surface enhanced Raman scattering by organic and inorganic analytes on laterally ordered arrays of Au nanoclusters*

17:45 - 18:00  
*Muelleger, Department of Solid State Physics, Johannes Kepler University, Linz, Austria*  
*All-Organic Radical Nanochains on a Surface*
18:00 - 18:15 **Polat**, Department of NanoScience & NanoEngineering, Istanbul Technical University, Istanbul, Turkey
Fabrication and Characterization of Poly(anthranilic acid)/ Poly(vinyl pyrrolidone) Electrospun Nanofibers

18:15 - 18:30 **Pusceddu**, Institut Laue Langevin, Grenoble, France
Morphological and structural study of calcium hydroxide nanoparticles in aqueous suspension

18:30 - 18:45 **Requist**, SISSA, Trieste, Italy
Kondo phenomena in small metal-contacted organic radical molecules

18:45 - 19:00 **Stoffelen**, Molecular Nanofabrication group, MESA & Institute for Nanotechnology, University of Twente, Twente, The Netherlands
Size-tunable supramolecular nanoparticles locked by cucurbit[8]uril

19:00 - 19:30 **Hietschold**, Solid Surfaces Analysis Group, Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany
Scanning Tunneling Microscopy and Spectroscopy of Ultrathin Metal Phthalocyanine Films on Ag and HOPG

**ASTREA ROOM**

8:30 - 10:00 **NANO BIOLOGY**

8:30 - 9:00 **Zahn**, Computer Chemistry Center, University of Erlangen, Germany
The interplay of collagen and ions in biominetic nanocomposites: mechanisms of nucleation, growth control and the design of materials properties

9:00 - 9:15 **Chang**, Korea Institute of Ceramic Engineering and Technology (KICET), Korea
Amino acid side chain-like surface modification on magnetic nanoparticles for highly efficient separation of mixed proteins

9:15 - 9:30 **Casalis**, SISSA-Elettra Nano-Innovation Laboratory, Sincrotrone Trieste, Trieste, Italy
Self assembly of nanostructures of DNA and protein on gold (111)

9:30 - 9:45 **Nkoua**, Università degli studi di Trieste, ELETTRA, Sincrotrone Trieste, Trieste, Italy
Effect of the ionic strength on the surface-tethered ssDNA molecules

9:45 - 10:00 **De Angelis**, Istituto Italiano di Tecnologia (IIT), NanoBioScience Department, Genova, Italy
Water soluble nanosponges for drug delivery applications

10:00 - 10:30 Coffee break

**NAUTILUS ROOM** 10:30 - 13:00 POSTER PRESENTATION

13:00 - 16:30 Lunch and break
16:30 - 19:00  Si-Ge NANOWIRES

16:30 - 17:00  Sutter Eli, Center for Functional Nanomaterials, Brookhaven National Laboratory, New York, USA
   In-situ microscopy of nanoscale phase behavior – Understanding growth, doping, and metastable phase formation in semiconductor nanowires

17:00 - 17:30  Voorhees, Department of Materials Science and Engineering, Northwestern University Evanston, USA
   Vapor-Liquid-Solid Nanowire Growth: Liquid Dynamics and Wire Composition

17:30 - 18:00  Heinig, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany
   Si nanowire networks for 3rd generation solar cells

18:00 - 18:15  Ruiz-Gomes, Aix-Marseille Université, CNRS, IM2NP, France
   Si Nanowires Organized Growth for Band Gap Engineering

18:15 - 18:30  Meija, Institute of Chemical Physics University of Latvia, Riga, Latvia
   Ge nanowires based multipositional bi-stable nanoelectromechanical switches and improvement of their operational conditions

18:30 - 19:00  Miao, Key Laboratory of Renewable Energy and Gas Hydrate, Chinese Academy of Sciences, P.R.China
   Spectroscopic ellipsometry analysis of Er doped ZnO thin films

CYPRE A ROOM

8:30 - 10:00  SEMICONDUCTOR NANOWIRES

8:30 - 9:00  Giri, Department of Physics and Centre of Nanotechnology, Indian Institute of Technology Guwahati, Guwahati, India
   Inorganic/Organic and Inorganic/Metal Based ZnO Nanowire Heterostructures for Highly Efficient UV Photodetection

9:00 - 9:15  Neykova, Institute of Physics, Academy of Sciences of the Czech Republic and Czech Technical University, Prague, Czech Republic
   ZnO nanorod arrays for highly efficient thin film a-Si and micromorph solar cells

9:15 - 9:30  Lozzi, Department of Physics, University of L’Aquila, L’Aquila, Italy
   Metal-doped TiO2 nanofibers deposited by electrospinning

9:30 - 9:45  Krahne, Istituto Italiano di Tecnologia, Genova, Italy
   Charge Transport in nanoscale “all-inorganic” networks of CdSe nanorods linked by Au domains

9:45 - 10:00  Charaborty, Istituto Italiano di Tecnologia, Genova, Italy
   Optical and Photoelectrical Properties of Au-decorated CdSe Nanowires

10:00 - 10:30  Coffee break
NAUTILUS ROOM  10:30 - 13:00  POSTER PRESENTATION

13:00 - 16:30  Lunch and break

16:30 - 19:30  NANO OXIDES

16:30 - 17:00  Tanemura, Guangzhou Institute of Energy Conversion, Guangzhou, China
& Nanostructures Research Laboratory, Nagoya, Japan
A Low Cost Preparation of VO2 Thin Films with Excellent Thermochromic Properties
from a Solution-Based Process

17:00 - 17:15  Toccafondi, CNISM and Dipartimento di Fisica, Università di Genova, Genova, Italy
Spectroscopic ellipsometry measurements on nano-granular TiO2 thin films

17:15 - 17:30  Shafiei, School of Chemistry Physics and Mechanical Engineering, Queensland University
of Technology, Brisbane, Australia
WO3 nanoplatelet based Schottky diodes for hydrogen gas sensing applications

17:30 - 17:45  Umek, Solid State Physics Department, Jožef Stefan Institute, Ljubljana, Slovenia
Determination of the Local Coordination and Valence States of Cobalt in Sodium Titanate
Nanoribbons

17:45 - 18:00  Boninelli, MATIS IMM-CNR, Catania, Italy
Optical and structural properties of Eu and C co-doped silicon oxides films

18:00 - 18:15  Farahdyar, Department of Chemistry, Faculty of Science and Department of Chemistry,
Faculty of Basic Sciences, Islamic Azad University, Iran
Preparation and characterization of nanophotocatalyst based nano-sized Nickel oxide loaded
on porous Titanium dioxide and study of photocatalytic activity

18:15 - 18:30  Rakhimova, Siberian Federal University, Krasnoyarsk, Russia
The electron-microscope investigation of quantum dots in Ni-NiO thin films

18:30 - 18:45  Rodriguez, Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany
Nanoscale Physico-Chemical Imaging of Oxide and Semiconductor Nanoparticles: Stepping
Beyond the Diffraction Limit with Enhanced Raman Spectroscopy

18:45 - 19:00  Grosso, Laboratoire Chimie de la Matière Condensée de Paris, CNRS, Université Pierre
et Marie Curie, Paris, France
Novel strategies to construct nanostructured coatings from sol-gel solutions

19:00 - 19:15  Farahmand, Department of Physics, Varamin Pishva Branch, Islamic Azad University,
Varamin, Iran
Size and Structural Study of ITO Nanoparticles Prepared by Co-precipitation
and Hydrothermal Liquid Phase Method

19:15 - 19:30  Ebrahimi, Faculty of IRAN Ministry of Education, Teheran, Iran
Synthesis of Vanadium Oxide Nanotubes from V2O5 Gel via an Ultrasonic
and Hydrothermal Method
Abakeviciene, Department of Physics, Kaunas University of Technology, Lithuania
Co-precipitation synthesis and characterization of NiO-YSZ nanocomposite powders

Abakeviciene, Department of Physics, Kaunas University of Technology, Lithuania
Synthesis of GDC thin films by the novel aqueous sol-gel citrate-precursor method

Ambrosone, SPIN-CNR, Dipartimento di Scienze Fisiche, Università di Napoli “Federico II”, Napoli, Italy
Nanostructured silicon carbon thin films grown in PECVD

Ammar M, PMLNMH, Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia
Hydration-dehydration performance of (Na+, Cs+) exchanged smectite: effect of the charge location and the cation nature

Barberio, Dipartimento di Fisica Università della Calabria, Rende (Cs), Italy
Growth and characterization of carbon nanotubes based heterostructures

Barth C, CNR-SPIN, Aix-Marseille University, Marseille, France
Growth and work function studies of NaCl thin films on silver

Bongiovanni, Dipartimento di Fisica, Università di Cagliari, Italy
Charged exciton dynamics in colloidal quantum dots investigated by transient nonlinear photoluminescence spectroscopy: from the single pulse to the megahertz excitation regime

Boytsova, Academy of Sciences of the Czech Republic, Prague Czech Republic
A process of nanomachining a nanoporous anodized aluminum oxide by chemical photolithography for sensor applications

Cannas, Dipartimento di Scienze Chimiche, Università di Cagliari, Italy
Engineering of colloidal magnetite and cobalt ferrite nanoparticles for biomedical applications

Cappellini, Department of Physics, University of Cagliari and IOM-CNRS Cagliari, Italy
Many-body effects in the electronic and optical properties of materials for UV applications: the case of barium fluoride

Carjova, M.sc.ing. Riga Technical University, Latvia
Research on physical-mechanical properties of nanostructured ion-plasma wear-resistant coatings

Cilmo, INFN and Dipartimento di Scienze Fisiche, Università degli Studi di Napoli “Federico II”, Napoli, Italy
Modelling and simulation of a silicon-CNT photodetector

Colin, Université de Poitiers, France
Patterning of thin film surfaces: effect of misfit stress on the morphology of ring-shaped and bilayer islands

De Angelis, IIT, NanoBioScience Department, Genova, Italy
Breaking the diffusion limit of nanosensors through super hydrophobic and nano plasmonic structures

De Carvalho, Departamento de Ciência dos Materiais, FCT-UNL, Caparica and ICEMS Lisboa, Portugal
CuXs thin films: main properties and device application

Enculescu, National Institute of Materials Physics, Magurele, Romania
Emissive properties of dye-doped polymer thin films containing metallic nanostructures

Farhadyar, Department of Chemistry, Islamic Azad University, Tehran, Iran
Preparation and Characterization of Nanosized Zinc Oxide on Zinc Sulfide and study of photocatalytic activity

Favre, AMU, CNRS, IM2NP (UMR 7334), Marseille, France
Self-organization of Au nanodots by ALMIS-FIB induced dewetting

Filippov, Department of Physics, Chemistry and Biology, Linköping University, Sweden
Raman scattering studies of Ni-coated ZnO nanorods

Goncharenko, Department of Physics, National Cheng-Kung University, Taiwan Institute of Semiconductor Physics & National Academy of Sciences of Ukraine, Kyiv, Ukraine
Three-dimensional broadband epsilon-near-zero nanostructured metamaterials

Huner, Department of Chemistry, Istanbul Technical University, Turkey
The effect of dielectric constant on electrochemical properties of copolymer 3,4-Ethlenedioxythiophene and p-TSP
Iacomi, Faculty of Physics, “A.I.Cuza” University, Iasi, Romania
Structural Studies on Layered Silicone - Silver Composites

Iacomi, Faculty of Physics, “A.I.Cuza” University, Iasi, Romania
In2-(x+y) SnxZnyO3 thin films for transparent electronics

Kamieniarz, Faculty of Physics, A. Mickiewicz University, Poznań, Poland
The quantum heteronmetallic zigzag chains and isolated centers with bridged Re(IV) and Cu(II) or Ni(II) magnetic complexes

Kim, Department of physics and Research Institute for Natural Sciences, Hanyang University, Seoul, Korea
Thermal stability and charge loss mechanism of V3Si nano-particles memory device

Kołpaczynska, Faculty of Chemistry, University of Warsaw, Pasteura 1, Warsaw, Poland
Self-assembly of gold nanoparticles covered with rod-like, H- and II-shaped liquid crystal ligands

Kral, Institute of Physics, Academy of Sciences of Czech Republic, Prague, Czech Republic
Power-law decay of quantum dot photoluminescence

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Metalomesogens modified by electronoaccepting and electronondonering groups, used for functionalize metal nanoparticles

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Hydrogel contact lenses as the nanodetector of free radicals

Lavareda, Dep. de Ciência de Materiais, Faculdade de Ciências e Tecnologia (UNL), Caparica, Portugal
Determination of Majority Carriers Type in Semiconductors Via TFT Structure

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Nanoscale p/n Junction Depth Control by Emitter Pre-deposition at Room Temperature

Loiseau, Laboratoire d’Etudes des Microstructures - ONERA-CNRS - Chatillon France
Studying the growth of single wall carbon nanotubes by Transmission Electron Microscopy and computer simulation

Marcus, ICMAB-CSIC, Spain
“Ultra-High density of ordered Ge Quantum Dots on FIB patterned Si(001) substrate

Mardare, Alexandru Ioan Cuza” University, Faculty of Physics, Iasi, Romania
The Influence of the Nb Content on Some Physical Properties of the Titania Thin Films

Matei, National Institute of Materials Physics, Magurele, Romania
Tailoring the properties of zinc oxide nanowire arrays by pulsed electrodeposition

Millunchick, Department of Materials Science and Engineering, University of Michigan, USA
A Unified Formulation of Homoepitaxial Growth, Droplet Formation and Crystallization for Compound Semiconductors

Muniz Miranda, Dipartimento di Chimica “U. Schiff”, Università di Firenze, Sesto Fiorentino, Italy
Nanostructured films of metal particles obtained by laser ablation

Mura, King’s College, London, UK
Self-Assembly of Flat Organic Molecules on Metal Surfaces Subtitle: A Theoretical Characterisation of STM Images

Nitti, Department of Physics, University of Bari, Bari, Italy
Co-sputtering and analytical characterization of ZnO nanoparticles-fluoropolymer thin films for antimicrobial applications

Noskov, Siberian Federal University, Krasnoyarsk, Russia
The features of morphology and surface fracture in 100G13L steel with high impact strength

Pak, Quantum-Function Research Laboratory and Department of Physics, Hanyang University, Korea
Structural and optical properties of ZnO films deposited on graphene by sputtering method

Peddis, ISM-CNR, Area della Ricerca, Monterotondo Scalo, Roma and Dipartimento di Scienze Chimiche, Università di Cagliari, Italy
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Novel piezoelectric ceramic-polymer nanocomposites for optical components

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CuO/TiO2 heterojunction for photocatalytic H2 evolution under simulated sunlight irradiation

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N-ALKylation of poor nucleophilic anilin and derivatives with alcohols by a hydrogen autotransfer process catalyzed by copper oxide nanoparticles

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Synthesis of Nano-copper chromite catalysts (CuCr2O4) for employ in several organic reaction

Rigoni, Dip. di Mat. e Fis. and Interdisciplinary Laboratory for Advanced Materials Physics, Università Cattolica, Brescia, Italy
Enhancing the sensitivity of carbon nanotube arrays for the detection of sub-ppm concentrations of ammonia in urban environments

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Heat and erosion resistant nanostructured coatings for the gas turbine engines

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Synthesis and applications of hierarchical ZnO – CNT hybrid architectures

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Nanostructured Pb1-3x/2LaxZr0.2Ti0.8O3, ferroelectric thin films for electro-optical applications

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Morphological studies on the noble metal nanoparticles-multiwalled carbon nanotube composites

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Optimization of conditions to fabricate high sensitive non-enzymatic Hydrogen peroxide sensor

Sleczkowski, Institut des NanoSciences de Paris, Université Pierre et Marie Curie, Paris, France and MESA & Institute for Nanotechnology, University of Twente, Enschede, The Netherlands
Control of Discotic Liquid Crystalsmonolayer self-assemblies by molecular engineering

Soban, Faculty of Electrical Eng., Czech Technical University and Inst. of Phys, Acad. of Sciences of the Czech Republic, Praha, Czech Republic
CVD graphene on silicon dioxide influence of hydrophobic interlayer

Toccafondi, CNISM and Dipartimento di Fisica, Università di Genova, Genova, Italy
Yeast Cytochrome C monolayers on gold substrates: an UV-Vis investigation by spectroscopic ellipsometry

Todea, Faculty of Physics & Institute of Interdisciplinary Research in Bio-Nano-Sciences, Babes Bolyai University, Cluj-Napoca, Romania
Nanostructured surface changes of aluminosilicate microspheres immersed in simulated body fluid

Optical and structural properties of organic-inorganic hybrid perovskite (C12H25NH3)2PbI4 quantum wells embedded in porous anodic alumina

Zhukov, Dpto. de Fís. Mater., UPV/EHU San Sebastián and IKERBASQUE, Basque Foundation for Science, Bilbao, Spain
Tailoring of domain wall dynamics in amorphous microwires

Zhukova, Dpto. de Fisica de Materiales, Fac. Químicas, UPV/EHU, San Sebastián, Spain
Magnetic and transport properties of Co-Cu microwires with granular structure
Single Atom Devices for Quantum Computing

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Over the past decade we have developed a radical new strategy for the fabrication of atomic-scale devices in silicon [1]. Using this process we have demonstrated few electron, single crystal quantum dots [2], conducting nanoscale wires with widths down to ~1.5nm [3] and most recently a single atom transistor [4]. We will present atomic-scale images and electronic characteristics of these atomically precise devices and demonstrate the impact of strong vertical and lateral confinement on electron transport. We will also discuss the opportunities ahead for atomic-scale quantum computing architectures and some of the challenges to achieving truly atomically precise devices in all three spatial dimensions.

References
Dynamical Coulomb blockade, quantum oscillations, and superconductivity in nano-sized electrical contacts

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Electrical contacts between nano-engineered systems are expected to constitute the basic building blocks of future nano-scale electronics. However, the accurate characterization and understanding of electrical contacts at the nano-scale is an experimentally challenging task. Here we employ low-temperature scanning tunneling spectroscopy to investigate the conductance of individual nano-contacts formed between flat Pb islands and their supporting substrates. We observe a suppression of the differential tunnel conductance at small bias voltages due to dynamical Coulomb blockade effects. The differential conductance spectra allow us to determine the capacitances and resistances of the electrical contacts which depend systematically on the island-substrate contact area. Calculations based on the theory of environmentally assisted tunneling agree well with the measurements [1]. Moreover, we study the linewidth of unoccupied quantum-well states in these ultrathin Pb islands, grown on Si(111) on two different Pb/Si interfaces. A quantitative analysis of the differential conductance spectra allow us to determine the electron-electron (e-e), electron-phonon (e-ph), and the interface contributions to the lifetime [2]. The energy gap of these superconducting Pb islands, in a thickness range between 60 and 5 monolayers, is found to decrease from its bulk value as a function of inverse island thickness [3]. Corresponding values of the critical temperature $T_c$, estimated using the bulk gap-to-$T_c$ ratio, are in quantitative agreement with ex-situ magnetic susceptibility measurements. The present findings facilitate quantitative investigations of electrical nano-contacts and are important for future studies of the physical and chemical properties of supported nano-structures in relation to superconductivity, magnetism, and catalysis.

The Epitaxial Growth of Rod-Like Molecules and Implications for the Fabrication of Lasing Nano-Fibers

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Motivated by the affinity to form highly crystalline organic nano-needles the epitaxial growth of rod-like molecules e.g. para-hexaphenyl (p-6P) or sexi-thiophene (6T) on various substrates e.g. muscovite-, phlogopite-mica and KCl has been investigated intensively [1, 2, 3]. It turned out that p-6P in combination with muscovite mica represents an outstanding material combination [1]. In particular, the low substrate surface symmetry in combination with the resulting molecular alignment is the key to well ordered, parallel aligned nano-fibers providing highly polarized blue fluorescence and laser action [4].

In a first step we will highlight the growth mechanisms of p-6P and 6T self-assembled nano-fibers by comprehensive morphological and structural investigations. Based on this analysis the potential of other material systems e.g. 6T to obtain optical resonators and in further consequence lasing will be discussed. We will demonstrate that more complex approaches have to be found in order to fabricate highly parallel self-assembled nano-structures being the key to shift the lasing wavelength from the blue to the green or red spectral range.

In the second part we will focus and introduce an alternative approach to obtain highly parallel nano-fibers. In recent years, heteroepitaxy of organic-organic nanostructures has been demonstrated as a valuable technique to explore the full potential of organic semiconductors for optoelectronic applications. It has been shown that crystalline and highly ordered heterostructures with different morphology and molecular orientations can be realized by heteroepitaxy starting from conjugated oligomers, aimed at tailoring their optical properties and transport characteristics [1-4]. We demonstrate that organic-organic heteroepitaxy can also be applied to produce multilayered organic nanofibers with high crystallinity, well-defined epitaxial relationship among different materials’ phases, sharp molecular azimuthal order, and long-range morphological homogeneity [9]. In consequence, we are convinced that the presented advance could lead to a general approach in order to tune the polarized fluorescence and lasing action of nano-fibers in a broad spectral range.

References
Few/ single molecule detection based on plasmonics and superhydrofobicity
down to attomolar concentration

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We report novel micro and nanofabrication techniques for single molecule detection by generating surface plasmons, thus giving a giant electric field. Self-similar Ag-nanosphere based plasmonic devices are fabricated using e-beam and electroless techniques for characterization of biomolecules. Si micropillars would constitute a superhydrophobic surface which deliver the ability of confining dilute biomolecules into a bounded region of the plane. Major novelty resides in combined use of micro and nano-structures. The fabrication of advanced biophotonic nanostructures such as tapered nanoantenna or regular patterns of micro lenses, positioned upon the pillars, would permitting the identification of proteins in the single molecule regime.
Evidence for charge transfer at the stable organic/organic interface of the F_{16}CuPc/PEN: F_{16}CuPc/Au(111) heterolayer architecture.

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Interface phenomena at the nanoscale level are of crucial importance in the emerging fields of nanoscience. However, achieving sharp interfaces and layer-by-layer growth for a combination of two different materials has always been a major challenge. In the last decade, different groups have accurately characterized bi-component molecular networks in intimate contact with metal crystal surfaces [1]. However, organic heterolayers with high crystal quality and sharp interfaces have never been achieved, since segregation and phase separation phenomena at interfaces typically arise. Recently, the epitaxy of donor/acceptor (namely, F_{16}CuPc/PEN) heterolayers beyond the monolayer/metal contact has been studied [2]. While STM measurements have shown that the direct sequential donor/acceptor stacking is not possible due to interface alloying and segregation, the 3:1 PEN:F_{16}CuPc monolayer blend is a stable platform that permits crystal growth of F_{16}CuPc on top. In this study, we investigate the electronic properties of a second layer of pure F_{16}CuPc on the stable 3:1 PEN:F_{16}CuPc/Au(111) interface through a combination of surface-sensitive techniques (XPS, NEXAFS) and first principles theory (DFT). Relevant core level shifts in the XPS spectra and new electronic states in NEXAFS spectra of the F_{16}CuPc overlayer are observed and related, on the base of an effective potential approach, to the flow of charge occurring at the organic/organic interface.

References
Electronic and optical properties of TIPS-substituted pentacene: a (time dependent) density functional theory study

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Molecular organic semiconductors in general and functionalized oligoacenes in particular are currently the object of large interest because of their applications in optoelectronics devices such as FET, LED or solar cells [1]. Pentacene and its derivatives, for example, are considered to be benchmark for thin-film devices with high hole mobility [2]. Substitution of acenes with different functional groups can determine precise control of electronic properties and molecular ordering for fabrication of organic electronic devices. Triisopropylsilylethynyl (TIPS) derivatives of oligoacenes are of specific interest [3]. The present study is devoted the computational analysis of TIPS-substitute pentacene. Electronic, optical, and transport properties of TIPS-substituted pentacene have been here determined using density functional theory (DFT) and time-dependent DFT. We computed: (i) electron affinities and first ionisation energies; (ii) quasiparticle correction to the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap; (iii) molecular reorganization energies; (iv) absorption spectra of neutral and ±1 charged systems. The excitonic effects are estimated by comparing the optical gap and the quasiparticle corrected HOMO-LUMO energy gap. We discuss in detail the comparison between pure pentacene molecule and its TIPS-substitue counterpart, as well as the comparison with the available experimental data.

References
Surface enhanced Raman scattering by organic and inorganic analytes on laterally ordered arrays of Au nanoclusters

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The surface enhanced Raman scattering (SERS) is one of the most powerful optical methods for studying tiny amount of both organic [1] and inorganic [2] substances put in the vicinity of metal nanoclusters (NCs). The SERS intensity to the great extent depends on localized surface plasmon resonance meaning coincidence of the laser light energy to the surface plasmon energy in the metal NCs. Varying the NC size and spacing between metal NCs one can achieve the optimal resonance conditions and gain the maximal SERS signal.

We report on the results of micro-Raman study of both organic and inorganic analytes posing ultrathin cobalt phthalocyanine (CoPc) films and CuS nanocrystals, respectively. These analytes were deposited on laterally ordered arrays of Au NCs formed by electron beam lithography on Si and GaAs substrates. It was shown that the fabricated samples serve as effective SERS substrates for both types of analytes.

A few monolayer thick CoPc films were formed on the arrays by organic molecular beam vapour deposition. CuS nanocrystals with average size of about 6 nm were prepared using the Langmuir-Blodgett technology [3].

The SERS study of CoPc films demonstrates the strong dependence of Raman intensity of vibrational modes in CoPc on the laser excitation wavelength as well as on the NC size and spacing between metal NCs. Tuning the optimal resonance conditions the maximal enhancement factor of 2x10^7 was achieved (Fig.1).

Raman mapping for CuS nanocrystals deposited on the optimized arrays (Fig.2) shows the Raman scattering by optical phonon mode of CuS only for the areas where the nanocrystals brought into the immediate contact with metal NCs while nanocrystals on bare substrates reveal no signal that confirms SERS effect by CuS nanocrystals.

Fig.1. 1- SERS and 2- Raman spectra of CoPc film. Fig.2. Scheme of Au NC array with CuS nanocrystals.

All-Organic Radical Nanochains on a Surface

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Recently growing interest in sp-magnetic systems with reduced dimensions has been driven not only by the prospects for spintronic applications due to expected large spin coherence times. Sp-magnetism continues to challenge the common understanding of magnetism at the atomic scale, as well. We report low-temperature scanning tunneling microscopy (LT-STM) and –spectroscopy (STS) studies on all-organic magnetic nanochains formed by the self-alignment of stable hydrocarbon radicals on a single crystal Au surface. The stable radicals preserve their singly occupied sp-derived molecular orbitals and related magnetic properties. This is evidenced via point spectroscopy by the observation of three typical Kondo characteristics used in the literature to confirm the surface Kondo effect. Spectroscopic imaging of radical chains reveals extended two-dimensional Kondo patterns. They span several nm² across the substrate area even into regions of the pristine Au substrate, indicating the involvement of surface-state electrons from the substrate. The single adsorbed radicals exhibit a handedness as revealed by topographic STM imaging at the single-molecule level, which leads to an enantio-selective chain growth and the formation of structurally different domains of neighboring radical chains. We observe structural effects of different packing motifs on the radical’s empty states resonances. The energy of the lowest unoccupied molecular orbital resonance may be reduced by up to 0.5 eV.
Fabrication and Characterization of Poly(anthranilic acid)/ Poly(vinyl pyrrolidone) Electrospun Nanofibers

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Special properties of electrospun nanofibers make them suitable for a wide range of applications from medical to consumer products and industrial to high-tech applications for capacitors, aerospace, drug delivery systems, battery separators, energy storage, and fuel cells. Conducting polymers have conjugated bonds and can differ from the other polymers with their properties. Poly(anthranilic acid) (PANA) is the conducting polymer that is a carboxylic acid containing of polyaniline. Due to its limited molecular weight, electrospinning of PANA was not successfully realized, so the blend of PANA with poly(vinyl pyrrolidone) (PVP) in dimethylformamide (DMF) and in mixture of ethanol (EtOH) and DMF was used. Moreover, polymer blends of PVP and PANA are used to form nanofiber with electrospinning method, molecular weight of PVP was 1300000. Finally, the electrospun nanofibers were characterized via spectroscopic techniques i.e., UV visible and FT-IR, and also by scanning electron microscopy (SEM). According to the SEM results, diameter of the nanofibers decreases in DMF than the mixture of EtOH/DMF. Also, nanofiber diameter decreases with the increase of the conducting polymer ratio in the blend which might be explained by the dielectric properties of PANA.

![Fig.1: Scanning Electron Micrograph of PVP/PANA Nanofibers a) PANA/PVP (1/15) in EtOH/DMF (50/50) b) PANA/PVP (1/10) in DMF](image)

References:
Morphological and structural study of calcium hydroxide nanoparticles in aqueous suspension

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Nanometric calcium hydroxide (nanolime) is used in Cultural Heritage conservation in order to reduce the limitation of the traditional lime treatments. Nanolime is successfully employed on mural paintings, stuccoes and frescoes: refurbishments of architectonical surfaces are considered too [1-4].
Nanolime is typically produced by a chemical precipitation process starting from a sodium hydroxide solution added drop wise to a calcium chloride one [5 and ref. in]. In this work, we have considered an original variant of the synthesis method by adding a surfactant agent in the initial solutions, in order to drastically reduce the time needful for preparation [6]. After pouring the solutions, we have performed several deionised water washings to remove the produced sodium chloride and the surfactant too. In particular, three nanolime aqueous suspensions have been produced considering different surfactant content.
Morphology analysis of the obtained Ca(OH)₂ particles was carried out by transmission electron microscopy (TEM). We have found that the nanoparticles are regularly shaped, hexagonally plated and with side dimensions generally ranging from 200 nm and 40 nm; in particular, increasing the surfactant content, the particle dimension tends to decrease, reaching diameter of 20 nm or less.
Data have been analyzed by means of the Rietveld method and we have investigated the structure of Ca(OH)₂ particles directly in suspension in terms of cell parameters, atomic coordinates, bond lengths and angles; we have determined morphology and preferred crystallographic orientation too.

References
Kondo phenomena in small metal-contacted organic radical molecules

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Few instances of the Kondo effect in adsorbed organic molecules are known. Kondo resonances have recently been observed in dI/dV measurements of an O₂ monolayer on the reconstructed Au(110)-1x2 surface [1]. The NO molecule is similar to O₂, but it has S=1/2 instead of S=1 in the gas phase. We have investigated the possibility of observing zero-bias Kondo anomalies in the conductance of the NO molecule on Ag(111) and Au(111) surfaces using a combined DFT/many-body approach [2]. The case of NO on Au represents a lacuna in the experimental literature. Spin-polarized DFT calculations predict that on both Ag and Au surfaces and over a range of coverage, the molecule adsorbs in a bent configuration at the top site. The molecule retains one unpaired electron in an antibonding pi orbital, and we calculate its hybridization with the surface. The resulting Kondo resonance is characterized by many-body calculations based on the DFT results. The same approach is also applied to other interesting organic radical molecules, such as thiazyl radicals.

Size-tunable supramolecular nanoparticles locked by cucurbit[8]uril

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Nanoparticles (NP) are materials in three dimensions and of huge interest in research due to their size-specific properties. Supramolecular chemistry is a powerful tool in chemistry and offers the opportunity to assemble molecular units into ordered structures via specific but non-covalent interactions. The combination of both fields is promising, since stable, but reversible 3D-assemblies can be used for a variety of applications.

The present study shows the fabrication of size-tunable supramolecular nanoparticles utilizing molecular recognition of small building-blocks. Naphthol-PAMAM, naphthol-PEG and methyl-viologen-functionalized poly(ethylene imine) were synthesized and used to form a ternary non-covalent complex in presence of cucurbit[8]uril. DLS and SEM analysis show that size tuning of the spherical particles is accomplished by tuning the concentrations and ratio of the two naphthol-derivatives in aqueous solution.
Scanning Tunneling Microscopy and Spectroscopy of Ultrathin Metal Phthalocyanine Films on Ag and HOPG

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We have studied ordered adsorbate films of CoPc, SnPc and Lu(Pc)₂ in-situ evaporated on Ag(111) and HOPG(0001) substrates by UHV STM/STS. Whereas CoPc is a planar molecule with a fourfold symmetry axis, SnPc is non-planar (shuttle-ock shape) and Lu(Pc)₂ is a sandwich-type really 3-dimensional double-decker molecule.

We show how the interplay between molecule-substrate and molecule-molecule interactions determines the two-dimensionally periodic adsorbate structure [1]. SnPc shows two different single-molecular adsorbate configurations – the central Sn atom directed “up” or “down”, respectively, with respect to the substrate plane [2 - 5]. The ground state is suggested having a chess-board pattern due to alternating “up” and “down” molecules whereas for higher temperature additional “down” defects appear [3, 5]. There is an irreversible switching possible for single “up” molecules into the “down” state on Ag(111) by the STM tip [4, 5]. Lu(Pc)₂ on Ag(111) shows also a chess-board pattern due to different molecular twisting angles with respect to the unit cell edges [6].

STS in combination with photoelectron spectroscopy helps substantially to understand the electronic structure of the adsorbate-substrate interface and to explain the regular adsorbate structures [4 - 6].

Some first information about the structure of adsorbate layers following the monolayer coverage will be elucidated [6].

References:
The interplay of collagen and ions in biomimetic nanocomposites: mechanisms of nucleation, growth control and the design of materials properties

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We report on a recently developed molecular simulation approach to the investigation of ion association to collagen, apatite nano-particle nucleation and nano-composite formation. Collagen takes a lead role throughout the different stages of biomineral precipitation by selectively coordinating ions, inducing the formation of specific crystalline motifs and by imposing hierarchical growth mechanisms from the nano- up to the meso-scale. Based on such detailed nucleation studies we designed a scale-up model of a biomimetic hydroxyapatite-collagen nanocomposite model with similar protein content to enamel. This allowed the molecular dynamics simulation of mechanical load (akin to biting), and unraveled a molecular mechanism for the absorption of shock energy and hence the avoiding of brittle fracture. Here, collagen locally acts as a ‘plasticizer’ by providing a peculiar route to sacrificing local ordering at the sake of global structural integrity, and establishing a self-healing mechanism for this nano-composite.

Amino acid side chain-like surface modification on magnetic nanoparticles for highly efficient separation of mixed proteins

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The work reports on the realization of specific functionalized Si-MNPs for effective protein separation through surface modification with various amino acid side chain-like functional groups such as thiol (-SH), disulfide (-S-S-), carbon chain (-Cn), carboxyl (-COOH), amine (-NH2), and aldehyde (-CHO). This study also suggests an improved and convenient method for the synthesis of functionalized Si-MNPs by hydrolysis condensation with silan-coupling agents. The protein adsorption effects in a coexistent mixed state are explored using various proteins, which have different isoelectric point (pI) values and molecular weights, in order to elucidate the binding performance of different proteins one solution. The adsorption efficiency of bovine serum albumin (BSA; 66 kDa; pI = 4.65) and lysozyme (LYZ; 14.3 kDa; pI = 11) is 70-100% with various amino acid side chain-like functional groups. However, the adsorption efficiency of a mixed protein solution of BSA and LYZ was different. Although the relatively bulky BSA molecule displayed 50% and 20% adsorption corresponding to pH 4.65, and pH 11, respectively, the smaller LYZ provided almost 100% adsorption at both pH 4.65 and pH 11. Furthermore, we show that protein adsorption effects in a coexistent mixed state using various proteins, which have different pI values and molecular weights, in order to elucidate the binding performance of different proteins one solution. We believe that our study described in this manuscript will be very helpful for the development of protein separation system by magnetic nanoparticles.
SELF ASSEMBLY OF NANOSTRUCTURES OF DNA AND PROTEIN ON GOLD (111)

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After having solved the structure Self Assembled Monolayers (SAMs) of thiols on gold in 2008 [1] we have moved on to study the application of self assembly of organic complex molecules (DNA, RNA and protein) on the same surface.

To do this we use multiple techniques.

The first is AFM-based and is called NANOGRAFTING, a technique invented by G.Y.Liu in 1997 [ . It consists of stimulating with the tip of an AFM the self-assembly of the organic polymers, properly terminated with a thiol link in a monolayer of a protein-repellent molecule the choice of which is restricted at present to a thiol functionalized poly-ethylene-glycol. It turns out that the AFM-stimulated assembly produces monolayers (which we call NAMs to contrasts them with the well known SAMs) are much more compact and structurally sound than their cousins.

We have applied these nanostructures to the following problems: 1) the first realization of an Elisa-type test on the nanoscale [2] 2) the orientation of prion proteins on surfaces using site-specific antibodies [3] and 3) the first measurement of the kinetics of helicase-type enzymes of human cells [4] .

The second technique is based on MEMS and constists of making vertical oscillating micro pillars that have several advantages over their older cousins i.e. the oscillating cantilevers. These advantages are: 1) the factor of 100 reduced mass which is responsible for a factor of 100 gain in sensitivity 2) a factor of 1000 higher oscillating frequency which is again responsible for at least a factor 100 in sensitivity and last but not least 3) the possibility of growing hundreds if not thousands parallel pillars that allow for the multiplexing of the sensor’s signals [5].

This work was done in close collaboration with my colleagues L.Casalis of SENILab@ELETTRA Trieste M.Lazzarino of IOM-CNR Trieste and L. Floreano and A. Morgante of ELETTRA Trieste.

Effect of the ionic strength on the surface-tethered ssDNA molecules

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Abstract: The understanding of the effect of counter-ions on assembling of ssDNA at surfaces is a crucial intermediate step for biomolecular detection including DNA microarray and nanoarrays. Counter-ions in fact, play a key role in the behaviour of the DNA strands both in solution and on surfaces. In this study, we produced ssDNA nanostructures via Atomic Force Microscopy (AFM) nanolithography, and we investigated salt screening effect on the conformation of ssDNA on gold surface. A systematic experimental measurement of the relative height of the ssDNA nanografted monolayer in salted buffer solution with ionic strength between 0.001-3M was investigated.
Water soluble nanosponges for drug delivery applications

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Modern nano-systems are gaining the potential of revolutionize cancer treatment, but in order to manage the most advanced approaches high costs and specializations are required. Here we present water soluble nanosponges which can be easily fabricated and handled without employing expensive techniques, while still providing essential features such as high payload, biodegradability, no toxicity, long term storage, release triggering, and multiple loading. The nanosponges were fabricated by ultra-sonication of thin films of nano-porous silicon. Particle sizes can be adjusted in the range of 30-500 nm, whereas the internal porous structure is in the range of 2-5 nm. Through a spontaneous physi-sorption, a wide range of drugs can be loaded in water at room temperature, without covalent bonding, and additional chemical reactants [1] (direct incubation of nanosponges and drugs in water). Under physiological conditions, nanosponges dissolve releasing the payload in about 120 hours. Being dependent on the pore size and environmental conditions, the dissolution rate can be accurately adjusted, and can take from a few hours to a few weeks. For pH value below 5, the nanosponges don’t dissolve allowing long term storage.

To demonstrate that the proposed nanocarrier is really suitable for practical applications, we introduced a tumor specific peptide, able to play the double role of targeting molecule and therapeutic agent [2]. Through a set of experiments performed both in vitro and in vivo we demonstrated that the proposed nanocarrier increases the bioavailability of the peptide and then enhances both targeting and therapeutic effects, without evidence of toxicity [3].

In-situ microscopy of nanoscale phase behavior – Understanding growth, doping, and metastable phase formation in semiconductor nanowires

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Semiconductor nanowires (NWs), self-assembled nanostructures that can be prepared in high-yield processes based on vapor-liquid-solid (VLS) growth, could become the basis for electronic device architectures that avoid complex top-down processing. Central to the VLS process is a liquid metal-semiconductor alloy seed drop whose equilibrium with the adjacent NW governs all aspects of the growth. Given the small size of the alloy drop, typically few tens of nanometers, the known binary bulk phase diagrams cannot provide a reliable basis for predicting growth phenomena. Hence, we have developed in-situ microscopy techniques to establish the nanoscale phase diagrams of alloy seed drops used in VLS NW growth. Variable-temperature transmission electron microscopy on individual Au-Ge alloy seeds at the tips of Ge NWs was used to measure the size-dependent phase diagram of the nanoscale alloy [1, 2].

We demonstrate the predictive power resulting from knowledge of the true phase diagram of the nanoscale VLS seed drop in several examples: (i) Control over the local, position-dependent diameter of the growing NW; (ii) homogeneous doping of the growing NW by dopant incorporation via the VLS drop [3]; and (iii) formation and stabilization of metastable phases in NWs in a near-equilibrium process that operates only at the nanoscale and involves VLS drops trapped in a metastable liquid state, which then causes the crystallization of a metastable solid segment at the NW tip [4]. Our findings demonstrate general avenues for synthesizing nanowire heterostructures involving controlled morphologies, doping, and access to metastable solid phases, applicable to the wide range of materials of which nanowires are grown by the VLS method.

Vapor-Liquid-Solid Nanowire Growth: Liquid Dynamics and Wire Composition

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Abstract
During vapor-liquid-solid (VLS) growth of nanowires, molecules from the vapor contact a liquid catalyst, decompose, and feed the growth of the solid wire. Since the liquid droplet is located at the tip of the wire and is pinned, a wire can then grow that is of nanometer diameter and micron length. A stable liquid droplet on top of the wire is thus an essential requirement for VLS nanowire growth. By changing the gas it is possible to dope semiconductor wires. A uniform and controlled dopant concentration is essential for device applications. The conditions for steady nanowire growth are examined with a particular emphasis on the dynamics and stability of the liquid droplet, the dopant concentration and its spatial distribution within the wire. The means by which droplets detach from the wire or form on top of a wire growing from a substrate are examined using a phase field method that incorporates fluid flow in the droplet, physically realistic dynamics of the vapor-liquid-solid contact line, and diffusion in the liquid. We find that the liquid-droplet depinning process is on a timescale that is many orders of magnitude faster than the growth rate of the wire. We have developed a model for dopant incorporation at the faceted solid-liquid interfaces that are present during nanowire growth and compare these predictions to P-doped Ge nanowires grown using a liquid Au catalyst.
Si nanowire networks for 3rd generation solar cells


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Large-scale self-structuring by spinodal decomposition of metastable SiO is a very promising synthesis process of novel nanostructured Si absorbers for 3rd generation solar cells [1]. The SiO layers have been produced by different techniques, sputtering, CVD and e-beam evaporation. Spinodal decomposition has been activated by Rapid Thermal Processing (RTP) and laser annealing. When the volume fraction of Si exceeds ~30% after the phase separation SiO → 0.5SiO₂ + (1-0.5x)Si, then Si forms a nanowire network. Energy-Filtered Transmission Electron Microscopy (EFTEM) studies show that nanowires have diameters of a few nanometers with a narrow distribution. This is in excellent agreement with large-scale simulations based on bit-coded kinetic Monte-Carlo accelerated by Massive Parallel Programming on NVIDIA graphic cards using a CUDA code. There is a considerable Si band gap widening due to quantum confinement in the nanowire network. As the wire diameter coarsens with time of heat treatment like d~t₀.₃₃, the band gap of the Si nanosponge can be optimized for solar cell application. Using an atomistic pseudopotential method, the band gaps of sponge have been studied. Finally it will be shown that up-scaling of the nanotechnology described above to large-scale PV cell production is under way by industrial partners.

Self-organization of Au nanodots by ALMIS-FIB induced dewetting

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The self-organization of Au catalysts has become a challenging field of research to enable the ordering of semiconductor nanowires. Several ways have been followed including lithographic tools. We present in this work an original dewetting process based on Focused Ion Beam (FIB) direct writing to create ad hoc patterns of Au nanodots. Alloy Liquid Metal Ion Sources (Au, Ge and Ga ions) were used in FIB lithography to control the self-organization of spatially ordered gold (Au) nanodots which serve as catalysts for the formation of epitaxial Si and Ge nanowires. The process involves the solid-state dewetting of ultra-thin bi-dimensional Au layer, patterned along one-dimensional or two-dimensional arrays. The behaviour of a 8 nm Au film on Si in a process of reactive solid-state dewetting is presented. The films were annealed at a range of temperatures (500-600°C) in ultra-high vacuum (UHV) atmosphere. The resulting alloy and silicide nanodots formed by film dewetting and film reaction with the substrate are examined by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The formation of Au nanodots, their size and density and their structural, chemical and morphological evolution are measured as a function of annealing conditions, of the Au layer nominal thickness and of the patterning conditions (ion beam dose, distance between patterns…). Striking changes in the morphology and self-organisation are observed following the FIB dose and the distance between the patterns (Fig. 1). We show that the deposition of a Au film on Si(111) gives rise to a thin nanocrystalline Au wetting layer which transforms during dewetting into Au-Si nanodots. Thanks to transmission electron microscopy measurements, we characterize both the Au wetting layer and the binary Au-Si catalysts.

Figure 1: SEM images of the homogeneous Au nanodots self-organised by FIB induced pre-patterning for two different exposure conditions: (a) D=500 nm and (b) D=250 nm. The mean size of the dots is 150 nm and 50 nm in (a) and (b) respectively. The comparison with unpatterned areas at the bottom of the images is clearly visible.
Ge nanowires based multipositional bi-stable nanoelectromechanical switches and improvement of their operational conditions.

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Nanoelectromechanical systems (NEMS) have attracted great attention due to their small size, low mass and high on-off ratio. Due to their small sizes and nanometer scale, they can achieve operational frequency in THz range, and integration density up to $2 \cdot 10^{12}$ cm$^{-2}$ [1]. There has already been showed promising results for Ge nanowires as active elements for gate-less two terminal NEM switches [2], that work because of fine balancing of electrostatic, elastic, adhesion and Van der Waals forces, but, due to the unique and different contact properties of each nanowire/electrode contact, fabrication of such switches becomes very difficult.

In this paper we present in-situ SEM investigation of other possible operating mechanisms of single clamped nanowire based NEMS switch. We also propose a multi-positional switch without gate electrode, that was realized in situ SEM.

Spectroscopic ellipsometry analysis of Er doped ZnO thin films

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We have reported a low-cost and fast formation of highly efficient Er centers in ZnO thin films for strong luminescence at near-infrared region. The thin films have been prepared on quartz substrate by a sol-gel spin coating method. As a high sensitivity tool for the detect of trace of Er dopant in ZnO film, spectroscopic ellipsometry is employed to evaluate the dielectric function and band structure. Pure ZnO thin film shows very sharp band structure. The films with 0.05 at% Er dopant, annealed at 600 °C and 800°C show similar sharp band structure but with dopant level in the band tail. The films with 0.05 at% Er dopant, annealed at 400 °C are very close to those of pure ZnO. While the samples annealed at 1000 °C are on the verge of amorphous, and the flat curve of photon energy dependent $\varepsilon_i(E)$ is observed. Excellent agreement was achieved between the SE analysis results and those of XRD and PL emission.
Inorganic/Organic and Inorganic/Metal Based ZnO Nanowire Heterostructures for Highly Efficient UV Photodetection

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The extremely sensitive conductivity of the ZnO nanowires (NWs) to UV light exposure makes it a very important candidate for use as optoelectronic switch or UV photodetector. However, ZnO NWs fail to show very high sensitivity and ultra fast response, which is an essential requirement for a useful photodetector. As the photodetection of the ZnO NWs is a surface controlled property, therefore it is expected that modification of the surface of the NWs by making heterostructure with suitable material could improve the photodetection property. In this context, we fabricated two new types of heterostructures; one with decorating Au nanoparticles (NPs) and other with coating of organic semiconductor, anthracene for a highly UV sensitive photodetector. In addition, we also studied the combined effect of Al doping and Au NP decoration on the ultrafast photoresponse of ZnO NW heterostructures.

Well aligned ZnO NWs array was grown on the Si(100) substrate by vapor–liquid–solid (VLS) technique using combined ZnO seed and Au catalyst layers [1]. Au/ZnO heterostructure was fabricated by directly depositing small Au NPs on the surface of the NWs by sputter deposition technique. While, ZnO/anthracene heterostructure was fabricated by dip coating technique. Compared to the as–grown NWs, Au/ZnO system shows large enhancement of one order of magnitude in UV photosensitivity and faster photoresponse and reset times [2]. ZnO/anthracene system exhibits six–fold enhancement in the photosensitivity and much faster photoresponse with response and reset times below one second [3]. The wavelength dependence of photodetection shows complete visible blindness, which is highly beneficial for UV photodetection. To understand the origin of this improvement from the heterostructures, we also studied the absorption and photoluminescence (PL) properties. Al doped ZnO NWs/Au NP heterostructure shows a major improvement in photoresponse time and improved photosensitivity [4]. The mechanism of improved photosensitivity and ultrafast photoresponse will be discussed in details.

References:
ZnO nanorod arrays for highly efficient thin film a-Si and micromorph solar cells

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Hydrothermal growth is highly appealing because it offers the possibility to grow directly high optical and electronic quality ZnO nanostructures at low temperature and over large areas.

In this work, we report on hydrothermal growth of large area, high quality, single crystalline ZnO nanorods, perpendicularly oriented towards the TCO substrate. In order to get well defined spacing and arrangement of ZnO nanorods over the area, we used electron beam lithography (EBL). Vertically aligned ZnO nanorods were grown in an aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine at 75-95 °C, with the growth rate 0.5-1µm/h.

The morphology of the nanostructures was visualized by scanning electron microscopy (SEM, Raith e-LiNE). The electrical, optical and surface properties of nanostructured ZnO films, which are decisive for high thin film silicon (amorphous, microcrystalline) solar cell efficiency [1], were investigated in details. First results on self-organized nanorods arrays for solar cells will be presented too.

References
Metal-doped TiO₂ nanofibers deposited by electrospinning

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Titanium dioxide (TiO₂), thanks to its interesting properties as nontoxicity, low cost and high chemical stability, has been extensively investigated for several applications in which, following light absorption, the generated charges can be usefully applied, as for photovoltaic systems [1] and photocatalytic devices [2]. However, due to the wide intrinsic energy gap of TiO₂ (between 3.0 and 3.2 eV, depending on the crystalline structure), only a small fraction of the solar spectrum can be used to promote the electron-hole pair formation. In order to reduce the energy gap and, therefore, increase the fraction of the solar spectrum that can be absorbed, different approaches have been used, mainly by doping TiO₂ with metals or anions [3]. In this work we will present our results on the deposition, by means of the electrospinning technique, of TiO₂ nanofibers doped with metals (iron, copper, tungsten). These nanofibers have been characterized by SEM, XPS and XRD for morphological, chemical and structural analyses, respectively. The effect of the metal concentration on the photocatalytic properties of these nanofibers have been investigated through the study of the degradation of a pollutant-model (Rhodamine 6G) by using a visible lamp as light source.

References
Charge Transport in nanoscale “all-inorganic” networks of CdSe nanorods linked by Au domains

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Charge transport across metal-semiconductor interfaces at the nanoscale is a crucial issue in nanoelectronics, and semiconductor nanorod chains linked by Au particles are an ideal model system in this respect. We investigated the electrical properties of networks in which CdSe nanorods were connected (“nanowelded”) by Au nanoparticles with well-defined metal-semiconductor interfaces[1, 2]. As deposited networks frequently manifested small Au domains at the lateral facets of the nanorods. Thermal annealing removed these lateral Au domains and resulted in larger Au particles within the nanorod junctions, which also increased the cross section of the Au-CdSe interface. The networks were positioned on interdigitated electrodes by dielectrophoresis, and the conduction of the devices was investigated at room and cryogenic temperatures. We will report on the impact of the annealing on the current-voltage curves and discuss our room temperature data in terms of the Schottky-Richardson model that describes thermionic emission over a metal-semiconductor interface. The network devices showed an increased conductivity at low temperature after annealing, and the current voltage curves could be described by charge tunneling.

*References*

Optical and Photoelectrical Properties of Au-decorated CdSe Nanowires

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We decorated CdSe nanowires (NW) fabricated by solution phase synthesis [1] with Au domains following the procedure introduced by Mokari et al. [2] for growing metal domains onto the tips semiconductor nanorods. The size and density of the Au clusters could be tuned by the Au precursor concentration that was added to the CdSe NW solution. Typical diameters of the NWs and Au particles were of the order of some tens of nanometers. Following the synthesis we observed ripening of the Au domains on the lateral NW facets in solution that resulted in a more pronounced plasmon resonance peak (centered at 560 nm) in the optical absorption spectra, as compared to the fresh solution. We fabricated electrical devices by drop casting the aged NW solution onto interdigitated Au electrodes followed by solvent evaporation. The photoconduction of the Au-decorated NWs was several orders larger than that of the bare CdSe NWs, making them an interesting material for photovoltaic applications. We will discuss the photocurrent-voltage curves recorded at different temperatures, photocurrent spectra, as well as scanning photocurrent microscopy experiments that revealed the spatial generation of charge carriers.

References
A Low Cost Preparation of VO₂ Thin Films with Excellent Thermochromic Properties from a Solution-Based Process

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This paper describes a solution-based route to synthesize vanadium dioxide thermochromic thin films by using vanadium pent oxide (V₂O₅) and oxalic acid (H₂C₂O₄) as source material, which is fairly cheap and practical. The VO₂ films were fabricated on glass substrates by spin-coating technology followed by thermal annealing in N₂ flow. The effect of annealing temperature on the morphology, crystal structure, and optical properties of the fabricated films were investigated by means of scanning electron microscope (SEM), X-ray diffraction (XRD) and ultraviolet-visible-near infrared spectrophotometer (UV-VIS-NIR), respectively. SEM images indicated that the films obtained by this method are quite homogeneous and dense, and the particle size increased with the annealing temperature. VO₂ films annealed at relatively low temperatures are nearly pure monoclinic phase (M phase) with a preferred orientation of (011)M confirmed by XRD. The VO₂ films obtained also exhibit excellent visible transparency and switching property at near-infrared (NIR) wavelengths across the metal-insulator phase transition (MIPT) at 450 ℃, the optical contrast (ΔT) of VO₂ films at the mid-infrared region around 2000 nm attains as high as 50 %.
Spectroscopic ellipsometry measurements on nano-granular TiO₂ thin films

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We have investigated the optical, morphologic and electronic properties of nanogranular TiO₂ films deposited onto silicon substrates by means of supersonic cluster beam deposition (SCBD)[1], using spectroscopic ellipsometry (SE), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). Nanogranular (and nanoporous) TiO₂ films are promising for biological and gas-sensing applications[2,3] and may even be exploited for applications in hybrid photovoltaic devices. Detailed knowledge of nanogranular TiO₂ is a pre-requisite for the investigation of its response to the deposition of selected molecules. AFM images revealed a characteristic surface roughness arising from the random stacking of the spheroidal nanoparticles during the low-energy deposition from the supersonic beam. High-resolution XPS measurements showed the presence of a good oxide stoichiometry with only a small fraction (< 3% typ.) of non-stoichiometric oxide species. Previous Raman and TEM measurements indicated an amorphous cluster structure with embedded rutile, anatase and brookite nano-crystals [1]. SE investigations in the wavelength range 245-1700 nm were performed on various films in the 20-150 nm thickness range. The mixed amorphous/crystalline structure and the complex morphology of these nanogranular films introduce some drastic changes in the optical properties of these films with respect to crystalline TiO₂ thereby making the modeling of these systems a particularly challenging task. Initial efforts were focused on simple models based on the rutile and anatase optical properties found in literature. Bruggeman Effective Medium Approximation (B-EMA) was used in order to model the complex film morphology (e.g. presence of nano-voids in the porous structure), in analogy with our recent works on gold nanoclusters films [4-6]. Improved agreement, with a fair qualitative description of the SE data, was obtained modeling the optical properties of the TiO₂ fraction by means of the so-called P-Semi approach. The relatively high mean squared error of these fits calls for further refinements of the model, especially in the absorption-edge region and towards the infrared, where a relevant absorption is observed. To this end, transmission measurements on transparent samples are planned. In situ SE spectra of nanoporous TiO₂ films immersed in ethanol will be also shown.
WO₃ nanoplatelet based Schottky diodes for hydrogen gas sensing applications

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In this paper we present results obtained on a Schottky diode based on nanostructured WO₃ thin films for hydrogen (H₂) gas sensing applications. Schottky diode based sensors with a nanostructured metal-oxide layer have exhibited high sensitivity towards reducing gases such as hydrogen [1-2]. The nanostructured WO₃ thin films were synthesized via an acid boiling method, which is a fast and inexpensive aqueous nanostructuring technique [3]. Tungsten thin films with ~1µm thickness were deposited onto the SiC substrates by RF sputtering. Samples were then placed into a reflux apparatus containing 200 mL of 1.5M HNO₃ at 50°C for 2hrs. The as-deposited sample was subsequently annealed at 500°C in 90% O₂ in Ar atmosphere for 4 hrs to obtain the WO₃ films.

The morphological characterisation of the sputtered tungsten layer using SEM revealed uniformly dispersed tungsten nano-grains on SiC with diameters of ~20-70 nm. Fig. 1 shows the SEM micrograph of nanostructured WO₃ layer which consists of randomly oriented nanoplatelets with lengths of 100-700 nm and thicknesses in the order of 20-60 nm. A SEM image taken at 45° rotation (Fig.1 inset) shows the thickness of the annealed acid-etched films as ~3.3 µm, which consist of two layers: (a) nanoplatelets layer on top and (b) non-porous layer below. The current-voltage (I-V) characteristic and dynamic response of the diodes were measured in the presence of air and 1% H₂ gas balanced in air from 25 to 300°C. Upon exposure to 1% H₂, voltage shifts of 0.64, 0.93 and 1.14 V were recorded at temperatures of 120, 200 and 300°C, respectively at a constant forward bias current of 500 µA. Fig. 2 shows dynamic response of the sensors towards H₂ with different concentrations at 300°C. The experimental results indicated the Pt/nanostructured WO₃ Schottky diodes are suitable for H₂ gas sensing applications.

![Fig. 1 SEM micrograph of WO₃ nanostructures](image)

![Fig. 2 Dynamic response of the sensor towards H₂ with different concentrations at 300°C](image)

**Reference**

Determination of the Local Coordination and Valance States of Cobalt in Sodium Titanate Nanoribbons

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Sodium titanate nanostructures are typically synthesized hydrothermally from TiO₂ and NaOH(aq) between 100–200 °C [1]. It is expected that inclusion of transition metal into these nanostructures will modify their physical properties. Up to now it was found out that the presence of Cu²⁺ ions [2] in the reaction mixture induces the formation of partly rolled titanate slabs, whereas the presence of Cr³⁺ [3] has no influence on the formed morphology. On the other hand cathodoluminiscence properties are being significantly improved in the sodium titanate nanoribbons and nanotubes doped with Cr³⁺ [3].

In order to shed light on the basic mechanisms behind the transition metal doping of titanates, this work aims at determining the position of cobalt ions in the formed product when the doping ions are part of the reaction mixture (in situ doping). More specifically we address the following questions:

- do the dopant ions (Co²⁺) accumulate between the titanate layers, do they exchange with the Ti atoms in the TiO₆ octahedra or do they form CoTi₂O₇ phases low in titanium content?
- can we distinguish Co²⁺ local coordination at different sites using electron paramagnetic resonance (EPR)?
- do Co²⁺ ions change oxidation state under applied reaction condition and what is distribution of cobalt ions in different oxidations states in the sample?

For in situ doping the starting material used was TiO₂ doped with Co²⁺ and hydrothermal conditions were chosen to promote the growth of nanoribbon structures. The prepared material was characterized by SEM, TEM, XPS, XRD, and local probe techniques HAADF-STEM in combination with EELS and EPR. Cobalt distribution regarding the oxidation states was determined with transmission X-ray microscopy (TXM).

References
Optical and structural properties of Eu and C co-doped silicon oxides films

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Europium-based materials are known for their intense and stable emission in the visible region. Eu is stable in both its divalent and trivalent oxidation states. In particular, emission of Eu$^{2+}$ is much stronger, being allowed for electric dipole transition rules and is characterized by a broad peak, centered in the wavelength range 400-600 nm, while that of Eu$^{3+}$ presents several sharp lines at around 600 nm.

In this work we compare the optical and structural properties of silicon oxide films, grown by RF magnetron sputtering on Si substrates and doped with Eu or co-doped with Eu and SiC. The study has been performed as a function of the Eu content of the films and of the annealing temperature. SiC addition produces a strong enhancement of the room temperature photoluminescence signal due to Eu$^{2+}$ with respect to the film only doped with Eu. The chemical and structural characterization of these materials, performed by Energy Filtered Transmission Electron Microscopy and Scanning Transmission Electron Microscopy, reveals an extensive Eu clustering in films containing only Eu. Crystalline structure, size and composition of the clusters, as well as their thermal evolution, have been studied in detail. On the other hand, the codoping induces a significant reduction of Eu clustering, enhancing the fraction of optically active Eu ions. The relevance of the present data for the development of Eu-based light sources of interest for Si photonics will also be discussed.
Preparation and characterization of nanophotocatalyst based nano-sized Nickel oxide loaded on porous Titanium dioxide and study of photocatalytic activity

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Abstract

Nanotechnology can provide the way to purify the air and water resources by utilizing semiconductor nanoparticles as catalysts and/or sensing systems. Semiconductor nanostructures can also play an important role in developing smart materials that can simultaneously sense and destroy harmful chemical contaminants from the environment. Such an application seems to be important as the concern over chemical contamination of drinking water and air needs to be addressed. Application of semiconductor nanoparticles as photocatalysts is still limited by the fact that they respond only to UV-excitation. Continued efforts to extend the response to the visible range have met with limited success. Semiconductor–metal nanocomposites that improve the selectivity and efficiency of the photocatalytic process are expected to draw the attention of future research. In this work, nano-sized nickel oxide was synthesized from precursors containing nitrate nickel as nickel source and loaded on the porous TiO₂ that synthesized by tetra butoxy titanium (TBT) at present starch. As prepared material, nanosize nickel oxide loaded by TiO₂ was investigated by using X-ray diffraction (XRD), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR). Photocatalytic activity of the samples, Nickel oxide loaded on the titanium dioxide were finally evaluated by degrading of the methyl orange under irradiation of UV light. The results showed that the nanosized nickel oxide enhances the photocatalytic activity of pure titanium dioxide.

Key words: Nanosized nickel oxide; Photocatalytic activity; titanium dioxide; Semiconductor
THE ELECTRON-MICROSCOPE INVESTIGATION OF QUANTUM DOTS IN N-INIO THIN FILMS

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The aim of this investigation is finding out the possibility of quantum dots producing at Ni-NiO thin films surface by creation NiO islets with nanometer size. To reach these purposes we need to solve the following tasks: to reveal special optical properties of Ni-NiO thin films, to find out the dependences of nickel films structural and magnetic properties after oxidation; to analyze thin magnetic structure revealed by high-resolution electron microscopy.

To create the nickel oxide islets with nanometer proportion is very difficult, because NiO covers the film with solid layer. It is revealed that there is no oxide film at the initial state because the film is covered by thin carbon layer during the evaporation in the simple vacuum camera VUP-2K type and then becomes protected from oxidation. During the process of annealing at the surface heated below 500°C the carbon burns and local oxidation of Ni in the form of islets with nanometer size takes place. To reveal the sizes and shapes of NiO quantum dots the annealed samples were under high-resolution transmission electron microscope JEOL-2010 (Picture 1).

References
Nanoscale Physico-Chemical Imaging of Oxide and Semiconductor Nanoparticles: Stepping Beyond the Diffraction Limit with Enhanced Raman Spectroscopy


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During last two decades atomic force microscopy (AFM) has become a key tool in nanoparticle (NP) research complementing classical techniques like electron microscopy [1]. Nonetheless one of the greatest limitations in AFM is the lack of chemical sensitivity. In this contribution we explore the possibility to obtain physico-chemical properties of nanostructures with details as good as the spatial resolution obtained in AFM. To this end a customized tip-enhanced Raman spectroscopy (TERS) [2] setup with side illumination/collection optics is developed by combining a Horiba LabRam spectrometer with an Agilent AFM 5420 (Fig. 1). Following a method for electrochemical AFM [3], custom-made gold and silver all-metal cantilevers are fabricated and used for the first time in an AFM TERS experiment. Determination of the spatial resolution and enhancement intensity for AFM tips with different size and shape under different excitation wavelengths (488, 514, 633 nm) is performed for a set of different oxide (α-Fe₂O₃, TiO₂, ZnO; size 15 – 80 nm) and semiconductor (CdSe, CdS; size 2 – 20 nm) NPs. Beyond chemical imaging, from the 3D morphological mapping of the nanostructures by AFM and the chemical identification in TERS, a direct correlation of phonon confinement with particle size and shape is discussed.

Fig. 1. Towards chemical imaging with nanoscale resolution: 3D morphological characterization of iron oxide NPs by AFM and their chemical fingerprint using Raman spectroscopy.

References

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Novel strategies to construct nanostructured coatings from sol-gel solutions.

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The development of supported novel integrated nano-materials is driven by the economical, ecological, and social pressures to handle miniaturised high technology devices, especially in domains requiring ultra-fast technological evolution, such as microelectronics, medical therapy and diagnosis, and energy conversion. As a consequence, material chemists have the challenge to synthesize and integrate smaller and smaller pieces of matter into more and more complex architectures and at the lowest possible cost. To achieve this goal, “top-down” and “bottom-up” approaches exist with advantages and drawbacks making them often complementary. In this communication, we will demonstrate that complex hierarchical structures can be achieved when combining chemical advanced bottom-up strategies, such as self-assembly of block copolymer and sol-gel chemistry, together with liquid solution processing such as dip-coating.[1] We will show that did-coating is an extremely versatile process to prepare thin nanostructured metal oxide (e.g. SiO₂, TiO₂, SrTiO₂, Al₂O₃, etc.) films from liquid solution and that it has been used for many decades without taking advantage of its whole potentiality.[2] Indeed, it is a simple and very versatile method to obtain large surfaces of ordered 2D or 3D functionalised nanomotifs such as nanopores, nanopillars, nanodots, nanopillars, or even nanocathedrals that have demonstrated great potential interests for application in optics [2], catalysis [3], microelectronic [4], photovoltaic [5], or nanofluidics [6]. We will then show that these approaches can be combined with others conventional top-down technologies such as reactive ions etching, optical and nano imprint lithography to construct even more complex multiscale morphologies.

References
Size and Structural Study of ITO Nanoparticles Prepared by Co-precipitation and Hydrothermal Liquid Phase Method

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Indium tin oxide (ITO) nanoparticles were prepared by two hydrothermal and liquid-phase co-precipitation method under given conditions with solution of indium chloride (InCl₃·4H₂O), tin chloride (SnCl₄·5H₂O) in ethylenediamide solution. The sample powder was characterized by X-ray Diffraction (XRD) and scanning electron microscopy (SEM) analysis after heat treatments. The effect of two different ammonia and ethylenediamide participants were studied on the ITO size distribution through liquid-phase co-precipitation route by SEM images. Also, the influence of the size and structure of ITO nanoparticles by two hydrothermal and co-precipitation method were compared. The SEM results showed that, the size of the ITO particles prepared by ethylenediamide co-precipitation were increased to 120 nm. The XRD and SEM results showed that, the size and crystallinity of the ITO particles prepared by hydrothermal method were increased compared to co-precipitation liquid phase route. The XRD results also indicated that I₄₀₀/I₂₂₂ was decreased to 21.67 by hydrothermal method.

Synthesis of Vanadium Oxide Nanotubes From V_2O_5 Gel Via An Ultrasonic And Hydrothermal Method

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Vanadium oxide nanotubes have been prepared by using two types of amine, hexadecylamine and hexylamine. The amines and V_2O_5.nH_2O gel were combined via ultrasonic method for better mixing and distribution. This was followed by one- step hydrothermal treatment between 1to7days. The main objective of the study is to produce good quality VO_X-NTS at the fastest synthesis time. Well-developed vanadium oxide nanotubes using hexadecylamine template were obtained with just two days of hydrothermal treatment. More recently there has been much interest in synthesizing and characterizing new vanadium oxide host/ guest compounds. These compounds have open structures and the ability to intercalate atoms or molecules. They have the potential to be used as catalysts, molecular sieves, absorbents and energy storage devices[1,2]. The important catalytic and electrochemical properties of vanadium oxide as well as the unique shape of the nanotubes has been the impetus for studying this novel type of nanostructured material. However, it is not yet clear how organic molecules act as structure-directing templates and cause such a deep structural evolution of bulk crystalline V_2O_5 into nanoscrolls[3]. Vanadium oxide nanotubes can be organized into a high yield and a unique multilayer’s structure. The interlayer distance can be controlled by a proper choice of structure- directing templates involved in the hydrothermal process. In hydrothermal synthesis, the reaction path is sensitive to the experimental conditions such as temperature, pH and hydrothermal treatment time [4].

References

Co-precipitation synthesis and characterization of NiO-YSZ nanocomposite powders

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Nickel-yttria stabilized zirconia (Ni-YZS) cermets are still the promising material for the one anode material of solid oxide fuel cells (SOFCs). According to variety of prefabrication of NiO-YSZ composite particle methods, the co-precipitation method can provide high quality products with lower cost than other build-up processes [1]. The synthesis of nano-sized NiO-YSZ composite particles is a promising route for achieving superior hydrogen oxidation characteristic of the Ni-YSZ electrode. The nanostructure and electrical properties of NiO-YSZ nanocomposite powders prepared by co-precipitation method were investigated. The electrochemical properties of the Ag/NiO-YSZ/Ag components were studied using impedance spectroscopy at frequencies ranging from 0.1 Hz to $10^6$ Hz in the temperature range from 200 to 600 °C with 20 degrees increment, in humidified hydrogen (∼ 3% H2O/H2) atmosphere. The structure of composite powders was characterized by scanning electron microscopy (SEM) and X-ray diffraction measurements (XRD). The nanostructure and electrical properties of NiO-YSZ composite powder were studied for the entire 50, 60, 70 wt% of NiO contents of composites. The crystallite size of such powder varies between 8.6 and 7.7 nm for NiO cubic phase and between 6.6 and 7.9 for YSZ cubic phase.

References
Synthesis of GDC thin films by the novel aqueous sol-gel citrate-precursor method

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Gadolinia doped ceria (GDC) shown much higher ionic conductivity at relatively low temperatures (400-800 °C) and have been extensively studied as most promising electrolyte materials for intermediate temperature solid oxide fuel cells (SOFCs). The sol-gel method has the advantages of a good control of the starting material and of the processing parameters, a high purity of the raw materials, the low temperature of the process and the homogeneity of the product due to the possibility to control the starting solution [1].

The synthesis of thin films of 10 mol% Gd2O3 doped CeO2 was carried out on silicon (Si) substrate from the aqueous Gd-Ce-O nitrate-citrate sols dissolved in ethanol or isopropanol, respectively, using spin-coating technique. All obtained samples were repeatedly annealed at 400 °C temperature after spin-coating procedure and fully characterized by X-ray diffraction (XRD) analysis. XRD data exhibited that at 400 °C temperature nano-sized Gd0.1Ce0.9O1.95 thin films with cubic (Fm-3m) crystal structure have been formed. TG/DTA analysis was performed in order to estimate the decomposition mechanism of the synthesized gels as well as the crystal phase purity of the final product annealed at 400 °C, 600 °C and 800 °C temperatures. The morphological features of obtained coatings were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The quality of obtained coatings was controlled by UV-vis reflectance spectroscopy.

References
Nanostructured silicon carbon thin films grown in PECVD

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Nanostructured silicon carbon thin films composed of Si nanocrystallites embedded in silicon carbon matrix are promising materials for photovoltaic applications, UV photodetectors and visible light emitting devices. The deposition on large scale, necessary for industrial applications, is usually done by PECVD. In this work the optical, electrical and structural properties of nanostructured silicon-carbon thin films deposited in rf-PECVD system have been investigated. The studied samples were grown from silane (SiH₄) + methane (CH₄) gas mixtures highly diluted in hydrogen H₂ with different rf power in the 10-80 W range. The other deposition conditions were: substrate temperature of 250°C, CH₄/(CH₄+SiH₄) ratio of 0.5, pressure of 249 Pa, H₂/(SiH₄+CH₄) dilution of 159 and total gas flow rate of 223.4 sccm. The optical absorption data, obtained by UV-Vis-NIR spectroscopy, have revealed the presence of a mixture of amorphous and crystalline phases while the Raman measurements have pointed out that Si crystallites have two size distributions and the increase in rf power leads to a decrease in crystalline fraction of films from 70 to 15%. RBS and ERDA analyses have been used to determine the evolution of H and C contents as well as the variation of mass density with rf power. FTIR spectra have shown that in the amorphous matrix carbon is preferentially bonded to Silicon. Finally, the photosensitivity of nanostructured films, measured under white light illumination of 100 W/cm² in AM1 condition, is found to increase by two orders of magnitude with the decrease in crystallite size from 10 to 3 nm.

Hydration-dehydration performance of \((\text{Na}^+, \text{Cs}^+)\) exchanged smectite: effect of the charge location and the cation nature

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This works aims at investigating the bonds between dehydration–hydration behaviors, charge location and the ionic radius in the case of dioctahedral smectites. For that, a natural montmorillonite and beidellite with different charge location (respectively di and tri-octahedral) was selected. The starting samples were exchanged in first time with \(\text{Na}^+\) cation followed by a cesium (i.e.\(\text{Cs}^+\)) cationic exchange process. The evolution of hydration behaviors was investigated by varying %RH condition. All exchanged samples were studied “\textit{in situ}” using XRD analysis with her both qualitative and quantitative analyses. This method allowed us to characterize the evolution of structural’s parameters deduced from the proposed theoretical Mixed Layers Structure (MLS) used to fit experimental XRD patterns.

Obtained results, in the case of \(\text{Na}^+\) and/or \(\text{Cs}^+\) exchangeable cations, shows an increase of hydration heterogeneity degree in the case of dioctahedral smectite (beidellite) characterized by a relatively low number of Mixed Layers Structure. For the same sample, the \(\text{Cs}^+\) exchange process induces a hydration homogeneity trends. This result was interpreted by a new interlamellar space organization along \(c^*\) axis which are confirmed by studying the evolution of relatives abundances related respectively to dehydrated 0W, monohydrated 1W, bihydrated 2W layers along the hydration-dehydration process.
Growth and characterization of carbon nanotubes based heterostructures

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In this work we present a study of growth and characterization of carbon nanotube (CNT) based heterostructures. The composites was prepared with chemical mix techniques which is a sequence of mixing, evaporation and drying processes that lead to the formation of composites whit a uniform network of microparticles overlapped by CNT. In particular we growth heterostructures constituted by CNT and by a metal (silver), a semiconductor (zinc sulphide) or an insulator (Lithium fluoride, TiO$_2$ anatase, Alumina Al$_2$O$_3$, Zinc Oxide ZnO) indicated by X.

The prepared samples were characterized with SEM analysis, energy dispersed X-ray measurements (EDX), X-ray photoelectron spectroscopy (XPS) and Auger Electron Spectroscopy. The analysis showed that the samples are formed by a direct contact between CNT and X component, in fact SEM images show CNTs wrapped around anatase micrometer particles. Nevertheless only in the case of Lithium Fluoride and Silver XPS measurements show the presence of chemical bonds between CNT and X component.
Growth and work function studies of NaCl thin films on silver

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Sodium chloride thin films on metal surfaces are important thin film systems, which are used to decouple the intrinsic electronic properties of atoms, molecules and clusters from metal surfaces [1-3] as well as reducing the work function of a metal surface [4]. Hence it is crucial to understand the growth at the interface to characterize the physical properties of such systems.

In this work, the morphology of NaCl thin films deposited on Ag(001) surfaces has been characterized in ultrahigh vacuum by noncontact atomic force microscopy (NC-AFM) and Kelvin probe force microscopy (KPFM) as a function of substrate temperature. As previously observed for MgO/Ag(001) [5], NaCl deposition on the Ag sample at 373K leads to a higher density of islands one mono-layer (ML) thick. As the temperature is increased, the density decreases and the islands grow predominantly as multi-layered islands with their average size increasing. Islands of up to 500 nm in size can be grown which stands in strong contrast to the MgO thin film system (max size: 20 nm for 1ML nominal film thickness) [5]. Local work function variations monitored by Kelvin probe force microscopy (KPFM) show that the NaCl islands exhibit a strong dark Kelvin contrast with respect to the Ag substrate as soon as the first ML is formed. This corresponds to the expected reduction of the work function of the silver surface by the NaCl film [4]. A clear tip-sample distance dependency in the Kelvin contrast is observed.

The NaCl film morphology, the surface work function of silver in dependency on the thickness of the NaCl islands but also the distance dependency of the Kelvin voltage will be discussed in the contribution.


Figure 1. Topography image (left) and corresponding KPFM image (right) of a NaCl thin film deposited on Ag(001). (500 x 500 nm²).
Charged exciton dynamics in colloidal quantum dots investigated by transient nonlinear photoluminescence spectroscopy: from the single pulse to the megahertz excitation regime.

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Colloidal semiconductor nanocrystals can be the material of choice for a wide variety of optical applications owing to their tuneable optical gaps and their easy processability. Nanocrystals can be used as light absorbers and emitters in optoelectronic devices such as light-emitting diodes, photodetectors and solar cells. Furthermore, colloidal quantum dots represent a remarkable alternative to organic fluorophores in a wide range of life science applications as they exhibit good photostability, large absorption cross-sections and narrow emission lines.

Charge carrier trapping is a key phenomenon in nanocrystal because it reduces the quantum efficiency of light emission. Inorganic surface passivation through the growth of shells of various thicknesses can remove most of trap states yielding increased photoluminescence quantum yields. Nevertheless, trapping of one carrier at the outer surface can still occur upon light illumination, albeit at much lower rate. These charge-split states decay non-radiatively and are long living. A nanocrystal with a charge carrier confined in the core is often referred to be in a low emissive state: photon absorption generates in fact charged excitons, which are weakly emitting because of fast Auger nonradiative recombination.

In colloidal nanocrystals, recombination rates of trapped carriers span from several megahertz to a few hertz. The control of the optical excitation rate can thus be used to tune the degree of charge accumulation in the quantum dot. Here we report time-resolved photoluminescence studies of CdS/CdSe core/shell nanocrystals in solution and in films under pulsed laser excitation. Excitation rates were varied from the single pulse to the megahertz regime, with the aim of investigating the charging dynamics and the ensuing effect on the photoluminescence quenching. For laser fluences much below one exciton per pulse, the photoluminescence of nanocrystals in solution showed characteristic features of the emission of negatively charged excitons. The overall trion contribution to light emission increased at high frequency following a power law, without, however, identifying a distinct lifetime timescale. In solution, the population of charged states was found to be very low, resulting in a weak photoluminescence quenching. On the contrary, films of colloidal nanocrystals showed a strong reduction of the light emission quantum yield in the megahertz excitation regime, with contributions from both negatively and positively charged nanocrystals.
A process of nanomachining a nanoporous anodized aluminum oxide by chemical photolithography for sensor applications

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The objective of this work is to study the approach to influence and modification of form surface using advanced lithographic methods. In particular we concentrated on the self-organization processes due to the synthesis and modification of film nanoporous anodic alumina surface, which is promising as well as substrate for film gas-sensor.

The microstructured surface was obtained by combining anodization of Al-foil and photolithography on thin film of nanoporous Al₂O₃. All films were prepared by the two-step anodization of aluminum (pore diameter of cylindrical channels from 15 nm to 200 nm; interpore distance from 50 to 500 nm, film thicknesses 30 µm). We used photoresist mask with basic parallel stripes (the width of tracks 35 µm), with meander (“the snake”), where width of the strips and spaced 110 µm, in model experiments and with composite shape as well as gas-sensor substrate. Modified layer of the material after chemical lithography were determined using atomic force microscopy and scanning electron microscopy. The structure of the porous matrix is not destroyed; also photolithography process resolution is about 2 µm.

Thus, this technique can be used as an alternative to plasma-based etching of Al for applications, in which economical benefits overcome technological limitations.

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Engineering of colloidal magnetite and cobalt ferrite nanoparticles for biomedical applications

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During the last decade, there have been extensive interests focused on magnetic nanoparticles (MNP) mainly due to the large potential in biological, diagnostic and medical applications. Because magnetic properties are size-dependent, obtaining narrow nanoparticle size distribution is an important requirement in magnetic NP syntheses[1]. It has been widely shown that the non-aqueous routes are more efficient in producing stable colloidal nanoparticles with narrow size distribution, high crystallinity and tunable size and shape, however, this approach typically produces hydrophobic nanoparticles limiting their applications in biological and medical fields. Thus, their transferring into water seems to be an essential step before any application. In this work hydrophobic magnetic nanoparticles have been converted into hydrophilic biocompatible systems through different approaches.

Hydrophobic magnetite and cobalt ferrite nanoparticles have been prepared by surfactant – assisted high-temperature thermal decomposition of metallorganic compounds. Transferring of the oleic acid stabilized nanoparticles into water has been performed through suitable surface coating with functionalizing molecules, low porous or high porous mesostructured silica [2] and phospholipids [3]. TEM, XRD, FTIR, SQUID techniques have been used in order to characterize the obtained systems.

Many-body effects in the electronic and optical properties of materials for UV applications: the case of barium fluoride

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Alkaline earth fluorides such as CaF$_2$ and BaF$_2$ whose fundamental band gaps are larger than 10eV are very important materials for many optical applications. Recent strong demand for lens materials operating in nanolithography is occurring. BaF$_2$ is the fastest luminiscent material that has been found to date [1] and exhibits superionic conductivity [2]. Despite his potential in technological applications BaF$_2$ has not attracted much theoretical studies until now. In the present paper we present for the first time the electronic excitations and optical spectra of BaF$_2$ employing state-of-the-art techniques based on density functional theory and many-body perturbation theory. We use the perturbative GW scheme for the electronic self-energy to calculate single-particle excitation properties as the energy bands and the density of states (DOS). The role of many-body effects turns out to be of fundamental importance for these single-particle properties. We show moreover that also for optical properties many-body effects, treated within the Bethe-Salpeter equation framework, are crucial to allow reasonable comparison with existing experimental spectra. For both, single-particle and two-particle effects, we explore the possibility of using simplified schemes which could reduce the computational effort, maintaining the physical results reliable foreseeing possible future applications in nanoscopic structures.

References
Research on physical-mechanical properties of nanostructured ion-plasma wear-resistant coatings

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The research considers different testing methods and facilities used by the author for the evaluation of physical-mechanical properties of materials and parts with wear-resistant coatings. The paper includes technological characteristics of creating coatings using the methods of ion-plasma sputtering and ion implantation. It analyses the results received during experimental research of microstructure and chemical composition of the obtained coatings by using a scanning electron microscope with micro analyzer.

It substantiates the modes of testing and proposes criteria for the evaluation of coating wear resistance. It is suggested to carry out abrasiveness tests by using cylindrical rotating specimens made of the material being tested and sample plated specimens. The abrasiveness of a coated plunger is defined from average linear wear of specimens during a certain friction path. It is suggested to carry out the evaluation of wear resistance of restored parts from the results of comparative fast test which defines relations between the wear rates of the restored surface and the sample surface tested in the same conditions.

Tribological tests have been conducted using an automated tribometer according to “ball and disc” scheme (rotational motion module) and “ball and plate” scheme (reciprocal movement module). The method and microhardness measurement instrumentation considered in this paper made it possible to evaluate the quality of basic material and coatings. On the basis of the obtained diagrams of coating plastic-elastic deformation, it is suggested to evaluate the strength of different types of coatings (see Fig.1).

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**Fig. 1.** The results of nano-indentation of the coating:
1 – time curve of indentation depth \( h \); 2 – time curve of normal force \( P \)
Modelling and simulation of a silicon-CNT photodetector

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We present a modeling and simulation study for a new photodetector obtained by growing multiwall carbon nanotubes on a n-doped silicon substrate and a MIS junction placed on the opposite surface. This study extends the work done by the SinPhoNIA group for the development of a novel large area detector featuring low noise, high quantum efficiency in a wide spectral range from the infrared to ultraviolet and great surface uniformity. The device has been modelled and simulated in order to understand the main parameters that characterize the performances of the photodetector. In order to simulate the device behavior, we started from a dual-diode-based approach: one diode placed back to back to one photodiode. Once the equivalent circuit parameter values are fixed we are able to reproduce the current-voltage characteristics of new photodetector both in dark conditions and under illumination for different light intensities.
Patterning of thin film surfaces:
effect of misfit stress on the morphology of ring-shaped and bilayer islands

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The effect of misfit stress has been first theoretical studied onto the location of adatoms in the neighbourhood of a square notch introduced onto the surface of a thin film deposited on a substrate. From an energy variation calculation, it is found that the self-organized formation at constant volume of a two-dimensional ring-shaped island can be favoured along the periphery of the pre-existing notch with respect to the notch shrinking.

The equilibrium shapes of a bilayer island have been then investigated under misfit stress. When this stress is isotropic, an energy variation calculation has shown that both square and rectangular shaped bilayer islands may coexist depending on the island volume and stress level. When the misfit stress is anisotopic, the possibility of formation rectangular islands along both perpendicular directions is finally discussed.
Breaking the diffusion limit of nanosensors through super hydrophobic and nano plasmonic structures


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The detection of few molecules from highly diluted solution is of extreme interest in different fields such as biomedicine, safety and eco pollution from rare and dangerous chemicals. Nanosensors based on plasmonic structures are promising devices that combine high sensitivity, label free detection and miniaturization [1]. However, plasmonic based nanosensors, and more in general sensors whose sensitive area is in the nanometer scale, cannot directly be used for detecting molecules dissolved in femto/atto molar solutions. In other words, they are diffusion limited and their detection time becomes impractical at those concentrations. In this work we demonstrate that few molecules can be localized and detected even at atto molar (10^{-18} mole/litre) concentration.

The basic idea is to exploit super-hydrophobic surfaces to drive molecules toward those positions where nanosensors are placed. Molecules of interest, initially dispersed in solution of few mm^3 in volume, are guided toward the active area of the sensors with an accuracy of few µm. We designed and fabricated a plasmonic nanosensor in the barycentre of the hydrophobic surface, and we were able to observe a detailed Raman signature of less than 10 molecules of lysozyma starting from 1 fM solution [2]. In our knowledge, this is the lowest number of molecules from 1 fM concentration solution ever detected by physical methods. This work faces radically the “diffusion limit” and proposes a way out to treat highly diluted samples.

Moreover, by varying the dilution is possible to create a suspended regular λ-DNA network. In the next future, the possibility of having isolated suspended DNA, or more in general elongated macromolecules, will allow novel biochemical and physical insights.

Cu_2S thin films: main properties and device application

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Cu_2S thin films, 30 nm thick, are deposited at room temperature by vacuum thermal evaporation of sulfur-rich powder mixture, Cu_2S:S (50:50 wt.%). The Cu_2S films are deposited at very low deposition rates (0.1-0.3 nm/s) to avoid the formation of Cu or S-rich films. The evolution of Cu_2S films main properties (optical, electrical and surface morphology) under mild post-annealing treatments in air, at 270 °C and time span of 255 up to 345 s, is studied.

The as-deposited Cu_2S films are found to be very conductive and the annealed films found their electrical resistivity increased with annealing time, from ~10^{-3} to ~10^{-2} ohm.cm. Although, the as-deposited films show inconclusive type of carriers (n or p-type, at random), the annealed films exhibit a conclusive p-type conduction.

Visible transmittance, conductivity versus temperature and mainly SEM characterization to verify possible changes in the surface morphology of the films due to annealing treatments will be made.

The application of these Cu_2S films in a TFT structure is also made and, consequently, the type of electrical conduction analysed. The I(V) characteristics of the Cu_2S based TFTs show that the conductivity of these films are mainly due to the presence of majority p-type charge carriers.

References
Emissive properties of dye-doped polymer thin films containing metallic nanostructures

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The fabrication of complex micro and nano-scaled architectures attracted a great interest during the last decades. The devices that are based on polymers are gaining attention considering the possible applications, especially the ones requiring the processing on large areas with low costs. Polymer thin films doped with dyes or metal particles were studied [1, 2]. Polymers doped with dyes are successfully used as modern light sensing materials, white light diodes [3, 4], light amplifiers [5] or waveguides [6]. Our purpose is to produce polymer thin films doped with different dyes and codoped with metallic nanowires that present controllable optical properties. Thus, thin films of polyvinylpyrrolidone (PVP) doped with dyes from blue-green and orange-red domains of the spectrum were produced by spin coating. The dye-doped polymer films are codoped with nickel nanowires obtained by template method (electrodeposition in polycarbonate foils obtained by ion-irradiation and subsequent chemical etching) and their optical properties were investigated.

Preparation and Characterization of Nanosized Zinc Oxide on Zinc Sulfide and study of photocatalytic activity

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Abstract

In recent years, nanosized ZnO in different morphologies have considerable interest for scientific research due to their importance in mesoscopic physics and their potential applications. So far various morphologies of ZnO such as nanospheres, one-dimensional structure (nanorods, nanowires and nanotubes), fractal shape (flower and prism) etc as well as their photocatalytic applications have been reported. In this process, the surface chemistry and charge trapping characteristics extends the lifetime of photogenerated electrons and holes and decreases their recombination rate. This is a desired effect because it enhances the quantum yield of the photocatalyst. In the other way, surfaces and defects associated with the surface have a major impact on the physical properties of polycrystals, when they get a few nanometers in size since the surface-to-volume ratio is large. Therefore, the crystal size control of ZnO as a support material is crucial to monitor adequately the catalytic activity or enhancement of the photocatalytic activity of zinc sulfide and seems to be attractive in use of zinc sulfide fixed materials on this benign supports for practical applications. In this work, nano-sized zinc oxide was fabricated from precursors containing zinc acetate as zinc source and loaded on the sulfide zinc that synthesized by sulfide sodium. As prepared material, nanosize zinc oxide loaded on the sulfide zinc was investigated by using X-ray diffraction (XRD), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR). Photocatalytic activity of the samples, zinc oxide loaded on the sulfide zinc were finally evaluated by degrading of the methyl orange under irradiation of UV light. The results showed that the nanosized zinc sulfide enhances the photocatalytic activity of zinc oxide when loaded on it.

Key words: Nanosized zinc Sulfide; Photocatalytic activity; semiconductor
Si Nanowires Organized Growth for Band Gap Engineering


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Nanowires (NWs) are considered as promising building blocks for photonics and electronics devices. They display original properties and can be produced on large scales with low cost and simple fabrication process [1-2]. Nevertheless, a lack of reproducibility limits the development NWs formed by bottom-up technologies. In this context, a deep understanding of the fundamental growth process of NWs must be investigated.

Various methods such as vapor-liquid-solid (VLS), solid-liquid-solid (SLS), oxide-assisted growth, or vapor-solid-solid (VSS), are used for NWs production. For each method, a large number of studies reports the modification of NWs morphology considering the influence of the growth parameters: nature of the ambient gases, ambient pressure, nature and size of the catalyst clusters, etc. However most of the processes lead to inhomogeneous diameters and lengths, with random positioning and orientation.

In this study, we focus on the VLS process, which is mainly used for Si and Ge NWs growth. We developed two original ways for the self-organization of gold catalysts by Focused Ion Beam (FIB) induced clustering. The two ways produce well ordered arrays of Au clusters that serve during the subsequent deposition step, as seeds for the nucleation of Si and Ge NWs. We show that the temperature range for the growth of NWs is extremely restricted in MBE growth conditions. Moreover, the effect of epitaxial strain on the growth direction of NWs is also revealed. We highlight the strain-driven evolution of the energy requested to create new facets at the trijunction between solid, liquid, and vapor. As a consequence, on Si (100) substrates, after a first vertical growth step, the Ge NWs rapidly kink and crawl along (110) directions of the substrate (see Fig. 2). Such a directional change was not observed during the growth of Si NWs.

The combination of FIB patterning and MBE NWs growth, enable to gain fundamental understanding of the physical laws that govern NWs properties and how these laws can be harnessed to dramatically improve the future devices characteristics.

Raman scattering studies of Ni-coated ZnO nanorods

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Owing to a direct and wide band gap and a large exciton binding energy, ZnO has attracted considerable attention worldwide as a high desirable electronic material for a wide variety of applications. Utilization of one-dimensional (1D) ZnO nanostructures, such as nanowires (NWs) is foreseen to further improve device performance as compared with their planar counterparts. Realization of such devices often requires controlled doping and also coating of ZnO with various elements. For example, it has been recently suggested that doping or coating of ZnO NR with Ni could be employed in spintronic devices to achieve spin functionality. However, detailed understanding of Ni –induced effects on material properties is still lacking.

In this study we employ Raman spectroscopy to characterize effects of Ni-coating on structural properties of ZnO core-shell NWs. The structures were fabricated via 3 steps process: (I) NW synthesis using thermal chemical vapor deposition; (II) room temperature Ni coating using an e-beam evaporator; (III) annealing in vacuum at 200-600 °C for 5 minutes. It is found that Raman spectra of ZnO NRs differ significantly from that of bulk ZnO and are affected by both coating and annealing process. The obtained results of resonant and non-resonant Raman measurements are interpreted in terms of degradation of surface quality of ZnO upon Ni coating.
THREE-DIMENSIONAL BROADBAND EPSILON-NEAR-ZERO NANOSTRUCTURED METAMATERIALS

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In terms of the effective medium theory, we consider a problem of designing nanostructured metamaterials with the real part of the permittivity very close to zero (the so-called epsilon-near-zero, or ENZ metamaterials) over a frequency band – materials of unquestionable practical interest due to their numerous potential applications (see, e.g., [1] and references therein). In particular, we show that this problem can be solved when dealing with metallodielectric composites under the condition of properly chosen constituents and geometry. Mathematically, the problem reduces to minimizing an objective function on the frequency band. The objective function, in its turn, involves the effective (macroscopic) dielectric function of the composite. If both the constituents and basic geometry of the composite are specified, geometrical parameters can be found using a proper optimization technique. Earlier, we have dealt with one-dimensional and quasi-one-dimensional cases [1,2]; now we consider a generalization of our previous techniques to three-dimensional broadband epsilon-near-zero metamaterials.

We develop the effective medium theory for the problem under study and provide a means to specify the basic geometry of the composite. Then, we determine the needed geometrical parameters by solving the inverse problem. The results obtained with the use of the effective medium theory are validated by using ab-initio numerical simulation. The effect of different material parameters on the performance of designed metamaterials and the range of applicability of our technique as well as its limitations are discussed.

References
The effect of dielectric constant on electrochemical properties of copolymer 3,4-Ethylenedioxythiophene and p-TSP

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Electrically conducting polymers have been regarded as excellent materials to be applied to electronic devices, electrolytic capacitors, actuators, sensors, artificial muscles and light-emitting diodes (LEDs) [1]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a relatively new member in the family of conducting polymers. The development of biosensor devices requires the achievement of an efficient interface between the biomolecules and the electronic transducer. Conducting polymer interfaces are particularly suitable for localizing biomolecules onto micron-sized surfaces.

p-Tolylsulfonyl pyrrole (p-Tsp) is a new type of monomer, which contains sulfonyl groups. The combination of these high-performance polymers can be used in aero spatial, chemical, drug, and food industries, due to their resistance to high temperature, impact, fire, as well as to their electrical properties.

Recently, self doped copolymers were prepared [2] for a wide variety of potential technological applications, i.e., electro catalysis, fuel cell electrodes, biosensor microelectrodes, and biomedical applications.

In this study, we electro synthesized copolymer of EDOT and p-Tsp on a single carbon fiber in solvent systems having different dielectric constants. The inclusion of the p-Tsp to the polymer structure was changed the capacitive properties of PEDOT. These changes were observed in 41.7 of dielectric constant having solvent system (PC-ACN: 20-80). With a low frequency capacitance of $C_{LF}$ 43.94 mF for copolymer of EDOT-p-TSP, which is 17.41 mF for PEDOT. The $C_{DL}$ of copolymer of EDOT-p-Tsp is 93.44 mF, and the double layer capacitance was found to be 63.83 mF for PEDOT. The characterization of resulting copolymers were performed by using Fourier Transform Infrared (FTIR-ATR) spectra and further analysis by Scanning Electron Microscopy (SEM), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The results indicated that it is possible to obtain frequency dependent capacitive and sensitive microelectrodes can be obtained.

Key words: 3,4-ethylenedioxythiophene, p-tolylsulfonyl pyrrole, electrosynthesis, copolymerization, biosensor.

References
In$_{2-(x+y)}$Sn$_x$Zn$_y$O$_{3.8}$ thin films for transparent electronics

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It was established that up to 40% of indium in the indium oxide bixbyite structure can be co-doped by zinc and tin (ZITO) and that ZITO phase solid-solutions exhibit compositionally tailored properties, such as n- and p-type conduction [1,2]. Thin films in the system In$_{2-(x+y)}$Sn$_x$Zn$_y$O$_{3.8}$ (x+y=0.36-0.40, y=0.10-0.30) were obtained through a process which implied the total evaporation, in vacuum, of a certain metallic mixture (In, Sn, Zn) and an oxidation process in air (380 °C, 600°C). The structural characteristics were examined by using X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy. All the studied thin films evidenced a nanocrystalline bixbyite type structure. A dependence of XRD patterns, grain sizes and surface morphology on y value was established. EDX and XPS spectra confirmed the projected thin film elemental composition and the presence of Sn and Zn in the bixbyite structure. The studies of I/V characteristics of some heterojunctions, evidenced the n and p type of studied thin films. The carrier concentration, Hall mobility and resistivity of the films were measured at room temperature using Hall effect measurement. The temperature dependence of thin film electrical conductivity evidenced the influence of substrate nature (glass, quartz, ITO/glass, n-Si(111), p-Si(111)) and oxidation process on the electrical conductivity mechanism.

Structural Studies on Layered Silicone - Silver Composites

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Two silicone-silver composites were prepared by mixing methyl-trimethoxy-silane, dimethyl-diethoxy-silane and 3-amo-no-propyl-triethoxy-silane, after which silver nitrate was added dissolved either in dimethylformamide-water mixture or in water only. X-ray diffraction, X-ray photoelectron spectroscopy, electron paramagnetic resonance and electrical investigations evidenced that the nature and the size of formed nanoparticles are influenced by the reaction mixture.

According to the literature, the location of the XPS peaks of silver depends on the chemical state of the silver element and the size of the nanoparticles [1, 2]. Both size and chemical effects are evidenced in the XPS spectra, not only for Ag 3d but also for O1s and N1s. XPS analysis indicates places that prevent Ag nanoparticles from being oxidized and others that favour the oxidation process.

The effect of UV irradiation on the structure and properties of layered silicone-silver composites is investigated. It is established that a long UV irradiation process (16 h) determines an increase in the XPS signal corresponding to Ag\textsuperscript{0} and the apparition of a new XPS spectrum belonging to Ag\textsuperscript{3+}. The increase in the silver XPS spectrum and the decrease in the silicon XPS spectrum suggest the migration of silver nanoparticles on the layer surface. UV irradiated samples show electron paramagnetic signals at g = 2, attributed to silver nanoparticles.

The quantum heterobimetallic zigzag chains and isolated centers with bridged Re(IV) and Cu(II) or Ni(II) magnetic complexes

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An anisotropic quantum Heisenberg model is proposed [1] and thoroughly analyzed within the numerical density-matrix renormalization group approach and exact numerical diagonalization. The model takes into account the site-dependent alternating directions of the local coordination system for the Re(IV) ions and both the axial and the rhombic single-ion anisotropy terms. Thermodynamic properties of a simpler collinear model without the rhombic term and its Ising counterpart as well as some previous approximations for Re(IV)-ion containing compounds are discussed to point out the importance of quantum effects and deficiencies of classical approaches. For the non-collinear model with the alternating uniaxial local z axis tilted by the angle θ from the global chain axis formed by copper ions, some symmetries for the single-crystal susceptibilities are found. In the strong anisotropy limit some striking maxima in the corresponding single-crystal χT products are revealed and their relation to the experimental determination of the anisotropy parameters is emphasized. Some cases to which the collinear model for zigzag chains is fully applicable are indicated. Finally, fitting the reference experimental data for a powder sample of given chloro- and cyano-bridged zigzag chains, the new weaker magnetic coupling and the uni-axial single-ion anisotropy term parameters have been found. The corrected value of the ferromagnetic interaction parameter implies that for the cyano-bridge compound the record of the highest superexchange through cyanide has not been beaten. The single-molecule magnet NiRe₂₃ found among the tetra-nuclear Re(IV) containing centers [2] is reanalyzed to get rid of some discrepancies and to reveal its energy structure and thermodynamic properties observed in a number of experiments.

References:
Thermal stability and charge loss mechanism of V₃Si nano-particles memory device

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The vanadium silicide (V₃Si) has a bcc structure and its work function is approximately 4.63eV. Therefore, the V₃Si nano-particles can be improved the electrical properties of nonvolatile memory device by work function difference.[1,2] In this study, the V₃Si nano-particles memory was fabricated on p-type Si (100) wafers. After cleaning of p-type Si wafers, in-situ phosphorus doped poly-Si layer with a thickness of 100 nm was deposited on isolated active region to confine source and drain. The 5-nm-thick SiO₂ tunneling layer was grown by dry oxidation at 1000 °C for 30 min under O₂ ambient after confining the gate region of transistor by using reactive ion etching. Then, V₃Si layer with a thickness of 4~6 nm was deposited on the tunnel oxide layer by sputtering. To create the nano-particles structure, the post-annealing process of sample was carried out at 800 °C for 5 sec by rapid thermal annealing system. Then, the 50-nm-thick control SiO₂ layer was deposited by ultra-high vacuum sputter. Finally, the aluminum gate electrode of 200-nm-thickness was evaporated by using thermal evaporator. The channel length and width of the transistor were ranges from 2 μm to 10 μm. Then, the electrical properties of V₃Si nano-particle memory device were characterized and the thermal stability and charge loss mechanism of memory device will be discussed.

References
Self-assembly of gold nanoparticles covered with rod-like, H- and Π-shaped liquid crystal ligands

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The long-range large scale arrangement of nanoparticles is an important issue in the development of nanostructured materials with new electronic, magnetic, and photonic properties. However, in most cases only amorphous aggregates are formed spontaneously, due to large dispersity of size and shape of building blocks. Rational design of functional nanomaterials can overcome this limitation by ‘chemical’ approaching in which metal nanoparticles are grafted with organic molecules with strong tendency for self-assembling i.e. mesogens.

The aim of the research was to synthesize new potentially liquid crystalline compounds: rod-like and with atypical molecular architecture: H- and Π-shaped dimeric thiols and used it in surface modification of small gold nanoparticles.

Figure 1. Cooling isotropic phase to smectic phase made of gold nanoparticles modified with rod-like liquid crystals.

Figure 2. Example of new H-shaped dimeric ligands, n = 1,3,4,5,6.

Figure 3. Small angle XRD patterns of smectic (a), columnar rectangular (b) and columnar hexagonal (c) phases observed on heating of hybrid material based on 2 nm gold clusters.

Systematic studies let to determine the relationship between the morphology of the organic compounds, the nature of metallic core and the physicochemical properties of obtained hybrid organic-inorganic materials. The phase structures were confirmed by x-ray studies.
Power-law decay of quantum dot photoluminescence

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The experimentally well known effect of a slow decay of the photoluminescence is studied theoretically in the case of quantum dots with indirect gap. The slow decay of the photoluminescence is considered as a time decay of the luminescence intensity following the excitation of the quantum dot electronic system by a short optical pulse. In the presented theoretical treatment the process is studied as a single dot property. The interaction of the excited electrons with longitudinal optical phonons is considered in the self-consistent Born approximation. The theory is built on the nonequilibrium electronic transport theory. The relation of the numerical results to the experimental data is also discussed. A possible connection of the presently considered effect to the blinking property of the quasi-zero dimensional nanostructures is also to be discussed.
Metalomesogens modified by electronoaccepting and electronodonering groups, used for functionalize metal nanoparticles.

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Our bout is to obtain hybrid materials containing inorganic nanoparticles and mesogenic metal complexes which are for assembling nanoparticles into long-range 3D structures. Liquid crystals, which are used for cover nanoparticles of rhutenium and gold, have nonsymmetrical (Series I) or symmetrical (Series II) structure.

To analyze the exact nature of the specific behavior of these hybrid systems will be taken into account such aspects as nanoparticles type and size, length of simple alkyl thiol, mesogen structure and of course the segregation tendency of nanoparticles surface ligands.

Bottom-up method will be used for synthesis of metal nanoparticles, it’s an approach to a problem that begins with details and works up to the highest level.

The combination of metal nanoparticles from organometallic compounds makes it possible to create hybrid materials that combine properties of both components, with new, potential applications in optics, electronics and magnetism. The resulting hybrids are made of a metallic core - nanoparticles of gold or ruthenium functionalized by mesogenic nickel complexes. Specific arrangement of molecules on spherical nanoparticles creates new geometries of interaction for metalomesogenes, which has so far not been studied.

Structure of obtained metalomesogenes is confirmed by spectroscopic studies (1H NMR spectra and 13C NMR). The identification of phases is done by observing textures under polarizing microscope Zeiss Jenapol-U. The results corroborate by X-ray studies using a Bruker D8 GADDS. Temperatures of phase transitions and volume thermal effects will be determined in a differential calorimeter TA DSC Q 200. Instrumentals SAXS and TEM methods are to analyze the size of metal nanoparticles.

References

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Hydrogel contact lenses as the nanodetector of free radicals

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Free radicals play an important role in a number of biological processes, some of which are necessary for life. The study of free radicals has become of extreme interest because of the role of free radicals in a large number of diseases and pathological states for example cancer, aging, heart failure, stroke and diabetes. Free radicals are also implicated in inflammatory states.

The aim of this study was to find out if hydrogel contact lenses can be used as the nanodetector of free radicals. From this reason etafilcon A contact lenses, which are highly hydrated polymer materials based on hydroxyethyl methacrylate (HEMA) and methacrylic acid (MAA), were used. DMPO (5,5-dimethyl-pyrroline N-oxide) spin trap was sorped by contact lenses and such complex was used to detect free radicals. Iron (II) sulfate heptahydrate was used to carry out the Fenton reaction to produce hydroxyl radicals (•OH).

Etafilcon A was measured using Electron Paramagnetic Resonance from Bruker working at 9.4 GHz frequency. Low temperatures were maintained by a Bruker temperature controller ER 4131VT. Contact lenses soaked in a solution of DMPO then dried and immersed in a solution containing •OH radicals formed by Fenton reaction. Using EPR method it was found the occurrence of spin trap radicals with •OH attached to the ring of DMPO.

It can be concluded that the contact lenses soaked in a solution of DMPO spin trap can be used as a detector of free radicals (•OH radicals).

References
Nanoscale p/n Junction Depth Control by Emitter Pre-deposition at Room Temperature

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Shallow p/n crystalline silicon junctions are required for both CMOS and solar cells technologies. In the former, scaling down transistor dimensions lead to a problem known as the short channel effect. To overcome this problem, shallow, but highly conductive source/drain layers are needed. In the latter, shallow emitters present less recombination losses than deep emitters.

However, shallow p/n junctions are quite difficult to achieve when c-Si conventional diffusion technology is used. The well known two-step diffusion sequential procedures, pre-deposition and drive-in, are both carried out at high temperatures. As the solid solubilities of common dopants normally increase with temperature, to obtain high surface dopant concentration, temperatures in the range of 900-1100°C are needed. At such temperatures, high diffusion coefficients are involved and shallow junctions become unpractical. Even when using ion implantation, the crystalline network needs a high temperature annealing after bombardment damages, which leads to some migration of a very shallow junction.

In this work we propose to use a pre-deposition layer of a-Si:H deposited by PECVD at low temperatures as a dopant source and, subsequently, to promote a controlled drive-in of dopant from the amorphous layer to the crystalline wafer in order to form shallow pn junctions. After a dehydrogenation phase at moderate temperatures (300-450°C), finely controlled drive-in steps were done in order to control the junction depth for different times and temperatures. Dopant profiling in c-Si wafers as well as dopant concentration in a-Si:H prior to diffusion, both measured by SIMS, will be presented.
Determination of Majority Carriers Type in Semiconductors Via TFT Structure

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The knowledge of majority carriers type in semiconductors is essential to their application in devices. The usual technique to determine the type of carriers is based on Hall-effect. This technique needs an expensive and sophisticated apparatus which needs to be adapted to the characteristics of the material being tested, namely, the conductivity.

This work shows that Thin-Film Transistors (TFTs) can be used to make this determination. TFTs have been made using different materials, such as a-Si:H and ZnOx as n-type semiconductors, and CuOx and CuxS as p-type semiconductors. A series of I(V) characteristics was measured in all TFTs regardless the semiconductor used. For testing a TFT as a p-type (“p-tests”) two sets of measurements were made: sweeping Vgs and keeping constant Vds (transconductance curve) and sweeping Vds for different Vgs voltages (conductance curve). Accordingly, for testing a TFT as n-type (“n-tests”) the same sweeping procedure was made using symmetrical values.

Results show that, in all cases, the absolute Ids current values (|Ids|) increase with the absolute Vgs voltages (|Vgs|), when the measurement agreed with the type of semiconductor used, “p-tests” on p-type materials or “n-tests” on n-type materials.

On the other hand, when “p-tests” were made on n-type TFTs and vice versa, a decrease in |Ids| is observed when increasing |Vgs|.

These results will be discussed and related to the electrical field effect on majority charge carriers of the semiconductor material.
Studying the growth of single wall carbon nanotubes by Transmission Electron Microscopy and computer simulation

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Selectively growing single wall carbon nanotubes with designed diameter and chirality is still challenging but would have a major impact since their (opto-)electronic properties directly depend on these structural parameters. Combining experimental information from Transmission Electron Microscopy and atomistic computer simulation [1,2,3], we try and understand the relation between the tube diameter and the metallic nanoparticle (NP) from which it grows. We identify two nucleation and growth modes - tangential when both diameters are almost equal, perpendicular when the tube diameter is smaller than the nanoparticle’s one - and we show that the first mode is favored under slow growth conditions [4, 5, 6]. This tangential growth mode enables one to control the tube diameter and is thereby a first step towards chirality control.

Our second step is to numerically study the growth of tube butts with different chiralities. We observe three regimes that correspond to experimental situations: aborted growth by encapsulation of the metal NP with carbon, growth termination by detachment of the tube from the NP and continuous growth under mild carbon chemical potential, temperature and feeding rate conditions. We then try and refine these conditions in order to preserve the initial (n, m) structure. In the present contribution, we will report the results of this ongoing work.

Ultra-small Ge Quantum Dots with positional regularity on FIB patterned Si(001) substrates


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In this presentation, we demonstrate that Focused Ion-Beam (FIB) nanopatterning can be used for manipulating self-assembled Ge nanodots in epitaxy on Si substrate. In order to fabricate spatially regular arrays of nanostructures, we combined the patterning of 2D arrays of nanoholes in the substrate and the MBE growth of Ge on the patterned areas. We show that the non traditional FIB nanopatterning which utilizes a direct writing process, has unique advantages for these nanofabrication processes such as the absence of mask to produce the grating, the capability to produce patterns with ad hoc geometry and the ultimate resolution of the patterns (∼15 nm) with a very high density resulting from the 5 nm beam spot size. In this work, we patterned either ultra-thin SiO2 layer on Si substrates or directly the Si substrate. In the first situation, the SiO2 layer is used as a sacrificial layer which enables to decrease the size of the patterns and increase their density. It also allows the complete removal of the atoms incorporated into the Si substrate during patterning. We fabricated 2D arrays of nanoholes using several FIB experimental conditions. The effect of atoms incorporated into patterns from the ion beam on the Ge islands nucleation, was investigated by comparing the growth of Ge on areas patterned by Ga+, Au++ and Ge+ and also on patterned areas after the complete removal of the incorporated atoms. Highly aligned Ge QDs arrays with various periodicities were grown by solid source MBE on FIB-nanopatterned areas. The Ge QDs grown on the patterns have a mean size almost 20 times smaller than those on unpatterned areas. Their shape, size and density depend on the nature of the ion source and are not related to the nanoholes topographic effect, while their placement is mainly related to the surface curvature. They exhibit a remarkable order and an homogeneous size (Fig. 1a). When the distance between patterns is large, a bi-modal distribution of Ge nanodots can be obtained (Figs. 1b,c).

Such self-organization process combining ALMIS-FIB patterning and QDs self-assembly could be used to produce nanostructures of several materials with quantum size effects and ultra-high density.

Figure 1: Ge QDs grown on Si(001) areas patterned with: (a) Ga+ and D=130 nm using oxide sacrificial layer; (b) Ga+ and D=300 nm on clean; (c) with Au++ and D=500 nm
The Influence of the Nb Content on Some Physical Properties of the Titania Thin Films

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TiO₂ and TiO₂/Nb amorphous thin films were grown on glass substrates by a sol-gel technique (spin coating). Films’ surface composition, structure and morphology were derived from X-ray Photoelectron Spectroscopy, X-ray Diffraction and Atomic Force Microscopy data. The investigated films showed a smooth surface (roughness RMS values below 5nm). A separate surface wettability investigation showed that, by increasing the Nb amount in pristine titania films, results in a decrease of contact angle values from 40º to nearly 0º, thus indicating a super-hydrophilic conversion under UV illumination. This conversion rate is greatly enhanced by increasing the Nb content, the surface super-hydrophilic behavior occurring after a couple of minutes in the TiO₂/Nb samples, but after 4 hours in the pristine titania specimen. The current results are discussed in terms of the optical band gap shift towards higher energies, by increasing the Nb content in the films, a process explained based on small polaron hopping model.
Tailoring the properties of zinc oxide nanowire arrays by pulsed electrodeposition

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Electrochemical deposition proved itself as an interesting method to produce zinc oxide with various morphologies ranging from hexagonal prisms to hollow tubules or nanowires [1-3]. Experimental conditions such as the composition of the electrochemical bath, deposition overpotential or temperature are factors which strongly influence the process results in terms of morphology, structure optic or transport properties. In most reports, the conditions used for depositing zinc oxide were either constant potential or constant current. In this report we present our results regarding the deposition of zinc oxide nanowire arrays employing pulsed overvoltage. This approach allows one to better control materials characteristics in order to achieve the desired functionality.

A Unified Formulation Of Homoepitaxial Growth, Droplet Formation And Crystallization For Compound Semiconductors

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We present a unified KMC model of compound semiconductor growth. Two crucial features of this model is that it explicitly takes the different species into account and is not bound by the typical solid-on-solid constraint. Although this work is generally applicable to many systems, here we focus on GaAs. The model was calibrated with our experiments of homoepitaxial growth. For example, the model was validated by tuning the parameters such that the transition Ga-terminated to As-terminated surfaces obeyed the experimentally observed behavior. This simple model also faithfully captures liquid Ga droplet formation under reduced As overpressure and subsequent crystallization when As over pressure is restored. In addition, it reproduces the range of morphologies observed in droplet epitaxy, thus provides key insight into the mechanisms behind their appearance. The model shows that there are three key processes that control the recrystallization of liquid droplets: (a) crystallization of the droplet at the vapor-liquid-solid interface (b) diffusion of Ga out of the droplet, and (c) homogeneous nucleation of GaAs at the vapor-liquid interface. The competition of these three processes at various growth conditions (substrate temperature and As flux) gives rise to all of the nanostructures reported for droplet epitaxy, including compact islands and rings. In addition, the simulations show that for high growth temperatures and very high As fluxes, a liquid core is trapped as a result of fast nucleation of GaAs at the vapor-liquid interface.
Nanostructured films of metal particles obtained by laser ablation

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In the past 20 years we have assisted to a very fast development of matter manipulation techniques down to the nanoscale. Actually, nanostructured materials exhibit physical and chemical properties that largely differ from those of bulk. In particular, metal nanoparticles represent one of the most significant class of particulate, which find applications in several research fields of environmental, catalytic and biological interest. Different chemical methods allow preparing metal colloidal particles with wide versatility of sizes and shapes [1], but the presence of reaction products deriving from the procedure to obtain the metal suspensions can impair important applications like those biomedical. This problem, however, can be overcome adopting the laser ablation method of metal targets in pure liquids [2-4]. In this work we obtained colloidal dispersions of different metals (Ag, Au, Cu, Pd) by ablation with picosecond or nanosecond pulsed lasers. Then, by filtration of the metal particles we fabricated nanostructured films, whose surface morphology was examined by atomic force microscopy. These metal platforms exhibited a giant Raman amplification of the adsorbed molecules by SERS (surface-enhanced Raman scattering) effect, ensuring important perspectives of applications in biomedicine and heterogeneous catalysis.

References
Self-Assembly of Flat Organic Molecules on Metal Surfaces Subtitle: A Theoretical Characterisation of STM Images.

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The phenomenon of self-assembly of atomic and molecular superstructures on crystal surfaces has attracted an increasing interest in nanotechnology. Self-organised nano-templates where the self-assembled monolayer traps other molecules with selected functional properties, can be used as building blocks for larger nanoscale structures. Self-assembled superstructures can form chiral domains ranging from 1D chains to 2D monolayers.

In particular, there have been many scanning tunneling microscopy (STM) studies of self-assembly of melamine, perylene tetra-carboxylic di-imide (PTCDI) or perylene tetra-carboxylic di-anhydride (PTCDA) molecules on the Au(111) and Ag/Si(111) surfaces [1],[2],[5]. STM images of these networks do not reveal the exact details of the intermolecular bonding and process of network growth. It is therefore the task of theory to determine the exact atomic structure of these networks.

We present a theoretical study of self-assembly of flat organic molecules (such as melamine, PTCDA, PTCDI, NTCDA, NTCDI and DNA derivative molecules) on the Au(111) metal surface. In order to describe in detail the assembly of the molecules, we propose a systematic approach to building molecular superstructures based on the notion of binding sites. First, we identify all possible sites for hydrogen bonding between molecules. Then we form molecular pairs and larger structures using all possible combinations of these binding sites. In this way, we constructed all possible dimers, chains and 2D monolayers of melamine, dimers and chains of PTCDA and PTCDI molecules. The energies of these structures are calculated using the density-functional theory SIESTA code. The strength of hydrogen bonding in various molecular arrangements is analysed. The theoretically predicted monolayer structures are in very good agreement with the results of STM measurements [4][5].

References:
Co-sputtering and analytical characterization of ZnO nanoparticles-fluoropolymer thin films for antimicrobial applications

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Zinc oxide (ZnO) is a promising material for a wide variety of applications, due to its peculiar property of forming various nanostructures suitable for antimicrobial treatments of industrial products. Deposition of ZnO nanoparticles (NPs)-fluoropolymer thin antimicrobial coatings on different kind of manufactured goods via ion beam co-sputtering (IBS) of a ZnO target and a Polytetrafluoroethylene (PTFE) one offers an alternative method in all those contexts in which wet-impregnation techniques [1] with aggressive solvents cannot be used.

The main advantages of using ZnO-NPs, embedded in a polymer matrix, compared with its bulk oxide is its improved efficiency and reactivity in several fields [2]. IBS allows to produce antibacterial coatings with controlled chemical-physical properties, enabling to change the NPs loading and, as a consequence, the release of bioactive ions [3]. As a result, a control on the proliferation of microorganisms is achieved in an operating regime which prevents toxicity for humans.

The morphology and surface chemical composition of all the samples were investigated by means of Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). Biological tests were performed in order to study the coatings’ bioactivity.

TEM images have revealed the nanoclusters size, as a function of the increasing loading of dispersed ZnO NPs in the composite, and their homogeneous in-plane distribution in the coatings. XPS has been used to control the stoichiometry of the NPs and the chemical changes in the polymer matrix.

Biological tests have shown the marked bioactive action of ZnO-PTFE coatings on the tested microorganisms.

References
The features of morphology and surface fracture in 100G13L steel with high impact strength

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Fig.1. Scanning electron microscopy image of sample 110G13L steel fracture with high impact strength after shock loading

The aim of this work is to study the processes of structure formation in the samples 110G13L were exposed to shock loads, and to explain of the processes from the perspective of the theory of shear transformation zones.

The experimentally observed particles with a high content of manganese in the conical craters viscous fracture in the samples were 110G13L subjected to impact loads (Fig.1).

The process of structure formation in the shock waves can be explained from the standpoint of the theory of shear transformation zones (STZ) [1] which may be applicable to a wide range of materials.

Structural and optical properties of ZnO films deposited on graphene by sputtering method

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Heteroepitaxial growth remains as one of the continuously growing interests, because the heterogeneous crystallization on different substrates is a common feature in the fabrication processes of many semiconductor materials and devices, such as molecular beam epitaxy, pulsed laser deposition, sputtering, chemical bath deposition, chemical vapor deposition, hydrothermal synthesis, vapor phase transport and so on [1,2]. By using the R.F. sputtering system, ZnO thin films were deposited on graphene 2 and 4 mono layers, which were grown on 400-nm and 600-nm-thick SiO₂ substrates, respectively. In this experiment, the working power and pressure during sputtering were 3x10⁻³ Torr and 50 W, respectively. The base pressure of the chamber was kept at a pressure around 10⁻⁶ Torr by using a turbo molecular pump. The oxygen and argon gas flows were controlled around 5 and 10 sccm by using a mass flow controller system, respectively. The structural properties of the samples were analyzed by XRD measurement. The film surface and carrier concentration were analyzed by an atomic force microscope and Hall measurement system. The optical properties were investigated by using the photoluminescence spectra obtained with a 325 nm wavelength He-Cd laser. The surface morphologies were observed using field emission scanning electron microscope (FE-SEM).

References
Exchange Bias in Fe@Mn nanocomposites

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We have studied the Exchange Bias (EB) effect in nanocomposite films consisting of Fe nanoparticles (mean size ~ 2 nm) embedded, with different Fe volume filling fractions (2.2% and 24.8%), in an antiferromagnetic Mn matrix[1]. They were produced by co-deposition through a gas aggregation cluster source and molecular beam epitaxy. The exchange field, higher in the sample with higher Fe concentration (at T = 5 K, $H_{ex} \sim 460$ Oe for 24.8% and ~310 Oe for 2.2%), in both samples decreases with increasing T, finally disappearing at T ~ 40 K. The results of zero-field-cooled and field-cooled magnetization, the thermal dependence of the coercivity and thermoremanence have been discussed. The different Fe content strongly affects the magnetothermal properties, featuring superparamagnetic relaxation in the diluted sample and a reentrant ferromagnet-type transition in the concentrated one. The effect of interparticle interactions and the role of the Mn matrix on the EB properties has been discussed.

References

Novel piezoelectric ceramic-polymer nanocomposites for optical components

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This research presents a new group of piezoelectric nanocomposite coatings based on integrating piezoelectric material poly(vinylidene fluoride) (PVDF) structures and nanoparticles of silver and barium titanate (PZT) into organic polymer poly(methyl methacrylate) (PMMA) matrices [1]. Different analytical techniques were used to characterize the structure and properties of obtained thin-film nanocomposites. Piezoelectric properties were analyzed with respect to applied frequency. Results imply that novel nanostructures exhibit good dielectric, surface and mechanical properties, and allow independent control of tribological properties. Formed nanocomposite systems were integrated in designing optical components, which may be employed in medicine for in-situ monitoring of wounds and broken bones healing. Mathematical modeling was performed to predict the behavior of these optical components for observing dependence of diffraction efficiency on deformation of the structure.

Synthesis  Nano-copper chromite catalysts (CuCr₂O₄ )
for employ in several organic reaction

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Abstract:
The copper chromite (CuCr₂O₄ ) is one of the most efficient materials, has wide commercial application as catalysts being used in the unit processes of organic synthesis such as hydrogenation, dehydrogenation, hydrogenolysis, oxidation, alkylation, cyclization, etc. It can be used in the pollution abatement as the catalyst to remove aqueous organic wastes, volatile organic compound (VOC) and vehicular primary emissions such as CO, unburned hydrocarbon, NOx and soot[1]. In addition it has been used in various composite solid propellants as one of the efficient combustion supporting catalysts in the domain of space vehicles (rockets) and weapon industries (high explosives, ballistic missiles). Furthermore, copper chromite has been proved as promising catalyst for the production of H₂ a clean energy carrier, by photo-catalytic phenomena, conversion of alcohols, water gas shift reaction, through sulphur based thermo-chemical water splitting cycles, etc. The next application of CuCr₂O₄ is catalyst for alternative fuels preparations[2], synthesizing methanol, an important hydrogen carrier; high alcohol synthesis (HAS) by hydrogenation of CO or CO₂[3] , and fast pyrolysis of biomass to bio-oil products[4]. The catalyst is also helpful in the production of drugs and agro chemicals. In fine chemicals industry for perfumery and synthesis of fragrances[5]. In this article we present the synthesis of Cu-Cr-O nanocomposites via a citric acid (CA) complexing approach. Techniques of thermo-gravimetric/differential thermal analyzer (TG/DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM) as well as scanning electron microscopy (SEM) have been employed to characterize the thermal decomposition procedure, crystal phase, microstructural morphologies and grain size of the as-synthesized materials, respectively. The results show that well-crystallized Cue Cr e O nanocomposites can be produced by using a temperature as low a s 600 °C. Phase structure of the as-obtained Cu-Cr -O nanocomposites depends on the Cu/Cr molar ratio in the starting reactants.

References
CuO/TiO₂ heterojunction for photocatalytic H₂ evolution under simulated sunlight irradiation

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Spinel copper oxide (CuO) is a versatile catalyst, widely applied in the oxidation, hydrogenation, dehydrogenation, dehydrocyclization, decomposition of organic compounds, pollution treatment [1] furthermore CuO has also been proved as promising catalyst for the photocatalytic H₂ production [2]. Several preparation methods have been established to prepare CuO for instance sol-gel state reaction, coprecipitation, and sol-gel [3]. Crystallinity, surface properties, and specific surface area, three of the most important parameters determining the catalytic activity of the product are highly dependent on the synthesizing routes [4]. Citric acid (CA)-assisted sol-gel method (namely Pechini approach) is a facile method for producing homogeneous nanocomposites, in which the using of citric acid as chelating agent ensures the formation of homogeneous transparent metal-citrate gels, and the intimate mixing of components ensures homogeneity of the final product. As catalyst for the photo electrochemical water-splitting to produce hydrogen. CuO/TiO₂ heterojunction has been successfully synthesized via a facile citric acid (CA)-assisted sol-gel method. Techniques of X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV–vis spectrum have been employed to characterize the as-synthesized nanocomposites. Furthermore, photocatalytic activities of the as-obtained nanocomposites have been evaluated based on the H₂ to TiO2 evolution from oxalic acid solution under simulated sunlight irradiation. Factors such as CuO molar ratio in the composites, calcination temperature, photocatalyst mass concentration, and initial oxalic acid concentration affecting the CuO/TiO₂ heterojunction photocatalytic hydrogen producing have been studied in detail. The results showed that the nanocomposite of is more efficient than their single part of CuO or TiO2 in producing hydrogen. The optimized composition of the nanocomposites has been found to be CuO 0.7 TiO2 And the optimized calcinations temperature and photocatalyst mass concentration are 500 °C and 0.8 g l, respectively. The influence of initial oxalic acid concentration is consistent with the Langmuir model.

References
N-Alkylation of poor nucleophilic anilin and derivatives with alcohols by a hydrogen autotransfer process catalyzed by Copper oxide nanoparticles

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Anilin and their derivatives are of fundamental importance as naturally occurring bio-active compounds such as alkaloids, amino acids and nucleotides contain amino groups, which are particularly useful for the development of new pharmaceuticals and agrochemicals [1]. Consequently, the development of improved methods for the synthesis of amines continues to be an intense focus of research [2]. Traditionally, the alkylation of amines is achieved using conventional alkylating agents, such as alkyl halides. There can be selectivity problems in such reactions when control of multiple alkylation can be difficult and many alkyl halides have toxic or even mutagenic properties and an alternative to using such reagents is therefore advantageous [3]. Alternatively, in recent years a number of reports on the hydroamination [4] or hydroamino-methylation of olefins or alkynes [5] for the synthesis of anilin derivatives have been reported. Compared to the frequently applied N-alkylations with alkyl halides and reductive aminations, an economically and environmentally attractive method is the N-alkylation of anilin and their derivatives using primary and secondary alcohols. This domino reaction sequence involves in situ dehydrogenation of the alcohol to give the corresponding carbonyl compound, which on subsequent imination followed by reduction with the initially produced hydrogen leads to the formation of the N-alkylated anilin and their derivatives. The advantages of this method are the ubiquitous availability of alcohols and high atom efficiency, for example no salt formation and water as the only by-product. Moreover, compared to reductive aminations, it is possible to run these reactions in the absence of hydrogen pressure [6]. Typical procedure for the N-alkylation of anilin and their derivatives with alcohols: A mixture of amine (3 mol) alcohol (1.5 mol), K2 CO3(2.5 mol) and CuO NPs (5 mol %) in toluene (8 mL) was stirred at 140 °C temperature for 6 h. After completion of the reaction as indicated by TLC, the reaction mixture was centrifuged to separate the catalyst, the solid residue was washed with ethanol to make the catalyst free of organic matter, and the reaction mixture was diluted with water and then extracted with ethanol. All products were characterized by IR, 1 H NMR, 13 C NMR and mass spectroscopic techniques.

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Enhancing the sensitivity of carbon nanotube arrays for the detection of sub-ppm concentrations of ammonia in urban environments

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Carbon nanotubes (CNTs) are known to interact with many gas molecules that, depending on their reducing or oxidizing properties, may inject or extract electrons from the CNTs, resulting in a detectable electrical signal. These effects could be exploited to prepare gas sensors for polluting or hazardous molecules. With respect to commercial electrochemical sensors for environmental monitoring (mostly based on metal oxides), CNTs show a higher physical and chemical stability, better transport of charge to the electrodes and a wide range of possible architectures and operational features that make them a unique system for gas detection [1,2]. The possibility to use these architectures for a realistic monitoring of the air quality in, e.g., a urban environment, is based on the capability to monitor sub-ppm concentrations of polluting gases. This limit has been so far virtually neglected.

In this study, we present several strategies to enhance the sensitivity to NH3 of single-wall CNT arrays operating at RT. The lower limit of 150 ppb is reached, which is little above the average NH3 concentration in a urban environment and well below the sensitivities so far reported. This sensitivity improvement is achieved by minimizing the film thickness, aligning the CNTs during the thin film deposition and curing the CNTs with UV light. Control over these effects is reached by a thorough characterization based on scanning electron microscopy, Raman spectroscopy, and X-ray photoemission, which also allowed us to discuss the effect of alkali impurities on the response characteristics.

References
Heat and erosion resistant nanostructured coatings for the gas turbine engines

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The increase of gas turbine engine effectiveness is related to the growth of parameters of their gas-dynamic cycle and, first of all, to the growth of gas turbine entry temperature and compressor pressure ratio.

This paper analyses the characteristics of functional coatings created by vacuum ion-plasma deposition. These coatings represent double- and triple-layer multi-phase multi-component structures, which are made by condensation of aluminium and titanium according to the given technology. The thickness of coatings is 20…40 µm. They were deposited on compressor blades and vanes manufactured from titanium alloy and chrome-nickel steel. In order to provide the necessary coating properties, the spraying was carried out in argon and nitrogen medium. During the first stage of the research, the analysis of microstructure and microhardness distribution was carried out. It gave the opportunity to confirm the qualities and structure of the coating. In particular, the microhardness of coating external layer exceeded 10 000 MPa, which provides high erosion resistance of a coating.

Then the comparative heat resistance tests for compressor blades and vanes with and without the given coating were carried out. The tests were carried out under the temperature of 780°C and up to the moment when first symptoms of blade surface destruction occurred, i.e. when corrosion products started to separate. These tests showed, for instance, that the time, during which the first symptoms of coated blade surface destruction had occurred, increased by 2…3 times when compared with blades without the coating. The test data made it possible to assert that the developed coatings can be used for a long time under the temperatures of 600…750°C (see Fig.1).

![Fig.1 Mass gain depending on temperature](image)
Synthesis and applications of hierarchical ZnO – CNT hybrid architectures

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Chemical vapour deposition (CVD) carried out on vertically aligned ZnO nanorod (NR) templates allowed us to synthesize different carbon nanostructures, whose morphology is driven by the ZnO NRs and whose dimensions and shapes change as a function of the CVD temperature. The carbon nanostructures span from amorphous carbon cups, covering continuously the ZnO NRs, to high density and defective CNTs. During CVD at 630-710°C, the NRs result to be partially etched, while they are completely etched at higher temperatures (>800°C) CVD. Control over these effects is reached by a thorough characterization based on scanning electron microscopy, X-ray photoemission and Raman spectroscopy. These systems, having enhanced and new functional properties, may be used in many technological applications, such as the detection of polluting gases. Indeed, we have recorded an enhanced sensitivity and selectivity to the NH3 detection with respect to the bare ZnO nanorods. We finally remark that this simple method can enable the production of different carbon architectures, using cheap templates (ZnO) and industrial processes (CVD).
Nanostructured $\text{Pb}_{1-3x/2}\text{La}_x\text{Zr}_{0.2}\text{Ti}_{0.8}\text{O}_3$, ferroelectric thin films for electro-optical applications

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The quadratic electro-optic behavior and optical properties of nanostructured PLZT ($\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)_{1-x/4}\text{O}_3$) thin films has been studied by means of variable angle spectroscopic ellipsometry (VASE) method. Thin films of ferroelectric relaxor PLZT deposited by pulsed laser deposition assisted by a radiofrequency oxygen plasma, have been integrated in a full oxide heterostructure for electro-optical investigations. An improvement of the birefringence values up to $\delta \Delta = 0.25^\circ$ have been obtained for quadratic compositions at $\lambda=540$ nm and $65^\circ$ angle of incidence. Different systems of electrodes and substrates (AZO/PLZT/Nb:STO, Pt/Si etc.) have been employed in the deposition, with the purpose to improve the dielectric constant, the dielectric loss and the electrooptical properties. PLZT films with different textures and orientations have been obtained. Structural and morphologic properties of PLZT thin films have been investigated by XRD and AFM techniques. Dielectric spectroscopy measurements have been performed at room temperature by using an HP 4194A impedance analyzer in the frequency range from 100 Hz up to 1 MHz. Ferroelectric measurements evidenced typical relaxor properties. Measurements of ac conductivity as a function of the ac driving field frequency and dc bias field amplitudes have been also performed.

References:
Morphological studies on the noble metal nanoparticles-multiwalled carbon nanotube composites

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A simple method to decorate the multiwalled carbon nanotubes (MWCNTs) with Au, Ag and Cu nanoparticles is illustrated. The method consists in directly depositing the selected metals by thermal evaporation on the carbon nanotubes. Comparative measurements carried out on samples that differ in the quantity and type of the deposited metal, reveal that isolated discrete particles form on the nanotube outer wall for all three metals. The CNT-based composites have been investigated by scanning and transmission electron microscopy to determine the size, shape and distribution of the nanoparticles. The results indicate that the quantity of evaporated metal only affects the nanoparticle size and not the average particle density. Particle composition was determined by X-ray photoelectron spectroscopy study. The results are discussed in terms of metal nanoparticle-tube interactions, an important issue for the fundamental and practical applications of similar MWCNT based composites.
Optimization of conditions to fabricate high sensitive non-enzymatic Hydrogen peroxide sensor

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Abstract

This work described a straightforward and new effective approach to construct a sensitive amperometric enzyme-free sensor toward detection of hydrogen peroxide. This novel sensor relied on electropolymerization of 3,4-ethylene dioxythiophene (EDOT) on a multi-walled carbon nanotubes (MWCNTs) modified glassy carbon electrode (GCE), The factors affecting the performance of the resulted sensor were also studied such as the concentration of MWCNT, the number of cycles at electro polymerization of EDOT as well as the operate potential for amperometric detection. Carbon nanotubes have been widely used in the preparation of sensors and biosensors [1-3], owing to their high surface area, high electrical conductivity and good chemical stability. The introduction of MWCNTs not only enhanced the surface area of the modified electrode but also facilitated the electron transfer rate, resulting in a high sensitivity of the sensor. Moreover, the proposed sensor possessed a good stability and reproducibility.

References

Control of Discotic Liquid Crystals monolayer self-assemblies by molecular engineering

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Recently, Shimizu et al. have demonstrated that discotic mesogens functionalized with photoswitchable azobenzene units switches from discotic liquid crystalline to smectic with temperature [1] or under irradiation with a laser pulse [2]. Now we demonstrate that this molecule self-organizes in an ordered network on Au(111) or graphite with particularly large crystallographic cell, thanks to the large size of the molecule (Fig.1). The origin of the order can be essentially ascribed to intermolecular interactions between neighbouring azobenzene groups which may be also the case in bulk liquid crystal phases. For this reason the nature of group linking azobenzene moieties with triphenylene core (ether or ester group) plays a fundamental role in determining interactions between the two azobenzene groups belonging to neighbouring molecules. Consequently it also plays crucial role in determining the geometry of the entire adsorbed network. We indeed demonstrate that modifying it from ester to ether lead to formation of only quasi-hexagonal network, associated with stabilization of molecules pairing.

It would be now important to test how this adsorbed geometry impacts the one in bulk liquid-crystal phases.

Fig.1. Schematic representation of one of the analogues under investigation: 2,3,6,7,10,11-hexakis(4-n-dodecylphenyl)azophenyl-4-propylene carboxy)triphenylene (left) and the STM picture showing its hexagonal packing at the 1,2,4-trichlorobenzene/Au(111) interface (right). Scan size: 9.7 × 9.7 nm²; tunneling current: Iᵣ = 3.93 pA; tip-sample bias: Vᵣ = 315.3 mV.

References
CVD graphene on silicon dioxide influence of hydrophobic interlayer

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Graphene demonstrates fascinating electrical, optical and mechanical properties. Cheap and reliable production of large area monolayers is a precondition of an industrial use of graphene in nanoelectronics. In recent years graphene has been prepared by mechanical exfoliation, by chemical vapor deposition (CVD) and by thermal decomposition on silicon carbide. Real graphene parameters especially carrier mobility do not reach theoretical prediction. We investigated properties of graphene monolayer produced by CVD growth on copper strip where a presence of graphene monolayer and its crystallinity is confirmed by Raman spectroscopy. The crucial role plays an interaction with substrate underneath the graphene monolayer. We used standard silicon substrates with high quality silicon dioxide (SiO₂) 65 nm thick. We focused on few different ways how to treat a surface of SiO₂ substrate to obtain lower influence of hydrophilic silanol (SiOH) groups on the graphene transport properties. The hydrophobic interfacial monolayer is generally used for this purpose. We analyzed several methods of hexamethyldisilazane (HMDS) deposition on the SiO₂ surface. Subsequently graphene field-effect transistors (GFET) were prepared by combination of standard electron beam lithography and optical lithography. Characterization of GFET was performed. Channel conductivity is measured in four-point arrangement at different temperatures. Hall measurement is realized at low temperature in magnetic field up to 6T.
Yeast Cytochrome C monolayers on gold substrates: an UV-Vis investigation by spectroscopic ellipsometry

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Yeast Cytochrome C (YCC) is a relatively small protein belonging to the class of Heme-proteins which plays a key role in electron transfer between two membrane-bound enzyme complexes, through a reversible Fe (III) ↔ Fe (II) process. Adsorption of YCC on well-defined, flat gold substrates has been studied by Spectroscopic Ellipsometry (SE) in the 245-1700 nm range. We applied methods successfully tested to study the growth of alkanethiols and other thiolate SAMS on the same type of substrates [1-3]. In practice we have considered differences between spectra taken after and before the molecular layer formation (δΨ and δΔ patterns) in order to put spectral features related to the protein SAM in the greatest evidence. The SE investigation was carried out in situ in buffer solution, at room temperature during protein deposition. SE data have been obtained at submonolayer and monolayer coverage. Ex situ SE spectra and AFM measurements on dried samples are also presented. Difference spectra (both ex-situ and in situ) showed well defined, sharp features at about 410 nm, related to an intense YCC-related absorption (the so-called Soret or B band typical of HEME group). The position of these features didn’t change with coverage. Experimental δΨ and δΔ spectra have been quantitatively reproduced by combining a suitable number of Lorenz oscillators, accounting for molecular absorptions. These simulations allowed to determine with great accuracy the position of the Soret absorption peak of adsorbed molecules. The Soret peak occurred at the same position found in transmission measurements for the molecule in its buffer, suggesting that the molecules have preserved their native structure upon adsorption. SE features possibly related to the molecule-surface bond are finally discussed with the aid of results obtained by synchrotron-based high resolution XPS.

References
Nanostructured surface changes of aluminosilicate microspheres immersed in simulated body fluid

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Abstract:

Aluminosilicate microspheres obtained by spray drying were investigated in prospect of their potential biomedical applications. The as-prepared microspheres are amorphous. Transmission electron microscopy (TEM) was used to examine the morphology of the samples before and after immersion in simulated body fluid (SBF). The local structure of the samples and the effect of aluminum and yttrium on the biodegradability process were evaluated by $^{29}$Si and $^{27}$Al MAS–NMR, Fourier Transform Infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). After SBF immersion, the silica network partially depolymerised by hydration/hydroxylation and the completely changed aluminium environment suggest a phyllosilicate-like structure [1-3]. $^{31}$P MAS–NMR analysis evidenced phosphorus ions incorporated in a new crystalline phase developed during SBF immersion.

References:

Optical and structural properties of organic-inorganic hybrid perovskite (C$_{12}$H$_{25}$NH$_3$)$_2$PbI$_4$ quantum wells embedded in porous anodic alumina

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Porous anodic aluminum oxide (PAA) has long been considered a viable material for template growth of nanomaterials for electronic, magnetic and optical applications due to the ability to form self-organized, high aspect-ratio nanochannels [1]. More recently these porous materials have been incorporated with fluorescent molecules to create a template for nanostructured materials [2–3]. However, there has been no investigation into how pore growth is affected by confining the pre-anodized aluminum dimensions to the nanometer scale. The photoluminescence (PL) from organic-inorganic perovskite quantum well colled C$_{12}$PbI$_4$ embedded in the pores of anodic alumina thin films on glass and aluminum substrates was investigated in detail. It was found that the PL was strongly dependent on the diameter and depth of the pores. A photoluminescence blue shift with a maximum value of 30 nm was observed when the organic-inorganic quantum well were embedded into 50 nm pores of the alumina film compared to the corresponding spectrum on glass substrate. The results have shown the penetration of the molecules into the pores.

Figure 1. 3D AFM images of a PAA/Glass with 10 nm pore diameter. (a) before and (b) after the impregnation of the perovskite C$_{12}$PbI$_4$ multiple quantum well.

Tailoring of domain wall dynamics in amorphous microwires

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Last few years studies of current and magnetic field driven domain walls (DW) propagation in different families of thin magnetic wires (planar and cylindrical) attracted considerable attention[1-3]. Considerable attention has been paid to achieve controllable and fast domain wall (DW) propagation in thin magnetic wires (planar and cylindrical) taking into account possibility to use it for high density data storage devices (magnetic random memory MRAM devices, logic devices). We studied effect of magnetoelastic anisotropy and local inhomogeneities on domain wall (DW) dynamics and remagnetization process of magnetically-bistable Fe-Co-rich microwires with metallic nucleus diameters (from 1.4 µm till 22 µm). We manipulated the magnetoelastic anisotropy applying the tensile stresses, changing the magnetostriction constant and strength of the internal stresses. Microwires of the same composition of metallic nucleus but with different geometries exhibit different magnetic field dependence of DW velocity with different slopes. Application of stresses resulted in decrease of the DW velocity, \( v \), and DW mobility \( S \). Quite fast DW propagation (\( v \) till 2500 m/s at \( H \) about 30 A/m) has been observed in low magnetostrictive magnetically bistable Co₅₆Fe₈Ni₁₀Si₁₀B₁₆ microwires. Consequently, we observed certain correlation between the magnetoelastic energy and DW dynamics in microwires: decreasing the magnetoelastic energy, \( K_{me} \), DW velocity increases. On the other hand, nucleation of additional DWs on local defects limits single DW regime.

Magnetic and transport properties of Co-Cu microwires with granular structure

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Granular materials consisting of ferromagnetic nano-sized grains embedded in a nonmagnetic metallic matrix attracted considerable attention mostly owing to giant magnetoresistance (GMR) [1]. For obtaining of the granular structures, melt spinning technique is quite suitable [2]. On the other hand last years great attention has been paid to the studies of glass-coated microwires produced by Taylor- Ulitovski technique allowing to achieve high quenching rate and therefore producing amorphous, nanocrystalline and granular microwires [3].

We studied magnetic, transport and structural properties of Coₓ-Cu₁₋ₓ (5 < x < 40 at %) glass-coated microwires, exhibiting considerable magnetoresistance (MR) effect. For x=5 % we observed the resistivity minimum at 40 K associated with the Kondo effect. For x > 10 % evidence of granular structure has been observed. For x ≥30 anisotropic contribution to MR has been observed giving rise to nonmonotonic field dependence of MR. Temperature dependence of magnetization measured during cooling without external magnetic field (ZFC) and in the presence of the field (FC) show considerable difference at low temperatures, attributed by us with the presence of small Co grains embedded in the Cu matrix. By X-ray diffraction we found, that the structure is granular consisting of two phases: fcc Cu appearing in all the samples and fcc α-Co presented only in microwires with higher Co content. For low Co content (x≤10%) Co atoms are distributed within the Cu crystals. The quantity and the crystallite size of the phases depend on the geometry of the microwire: the glass coating induces the internal stresses and affects the quenching rate.

**JUNE 27 WEDNESDAY**

**NAUTILUS ROOM**

**8:30 - 10:00** **Si-Ge NANOSTRUCTURES**

8:30 - 8:45 **Smereka, Department of Mathematics, University of Michigan, USA**  
Kinetic Monte Carlo Simulation of Heteroepitaxial Growth: Wetting Layers, Quantum Dots, Capping, and NanoRings

8:45 - 9:00 **Bollani, IFN-CNR, L-NESS laboratory, Como, Italy**  
Lithographically-defined low dimensional SiGe nanostripes as silicon stressors

9:00 - 9:15 **Fromherz, Institute of Semiconductor and Solid State Physics, Johannes Kepler University, Linz, Austria**  
SiGe island growth on (001) Si substrates: quantitative determination of shape-dependent Ge capture rates by modeling of the Ge surface diffusion

9:15 - 9:30 **Chrastina, L-NESS Politecnico di Milano, Polo di Como, Como, Italy**  
Ge/SiGe Superlattices for Nanostructured Thermoelectric Modules

9:30 - 9:45 **Etzestorfer, Institute of Semiconductor and Solid State Physics, Johannes Kepler University, Linz, Austria**  
X-ray scattering studies of SiGe/Ge superlattice interfaces

9:45 - 10:00 **Escoubas, IM2NP – AMU – CNRS, Campus de St Jérôme, Marseille, France**  
Enhanced critical thickness of epitaxial SiGe layers on porous Si stressor layer

10:00 - 10:30 Coffee break

**10:30 - 12:30** **MAGNETIC NANOSTRUCTURES**

10:30 - 11:00 **Laureti, ISM-CNR, Area della Ricerca Roma1, Monterotondo Scalo (Roma), Italy**  
Interface exchange coupling in magnetic nanostructures

11:00 - 11:15 **Dobosz, Medical Physics Division, Faculty of Physics, Adam Mickiewicz University, Poznan, Poland**  
Electron Paramagnetic Resonance of magnetite nanoparticles coated with dextran

11:15 - 11:30 **Peddis, Dipartimento di Scienze Chimiche, Università di Cagliari, Italy & ISM-CNR, Monterotondo Scalo, Roma, Italy**  
Magnetic properties of CoFe2O4 nanoparticles: Influence of the nanoparticles arrangement and of the synthesis method

11:30 - 11:45

11:45 - 12:00 **Ognev, Laboratory of Thin Film Technologies, Far Eastern Federal University, Vladivostok, Russia**  
Manipulation of spin configurations in patterned 3D magnetic nanostructures
12:00 - 12:15  **Rumpf**, Institute of Physics, Karl Franzens University Graz, Graz, Austria  
Iron oxide nanoparticles dispersed in porous silicon

12:15 - 12:30  **Seyedsajadi**, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran  
Room Temperature Superparamagnetism Evaluation of Cobalt Doped ZnO nanoparticles

**ASTREA ROOM**

8:30 - 10:00  **MOLECULAR SELF ASSEMBLY**

8:30 - 9:00  **Keynote**  
**Gautier**, CNRS, CEMES (Centre d’Elaboration des Matériaux et d’Etudes Structurales), Toulouse, France  
Charge effects in adsorbed molecules characterized by UHV STM and non contact-AFM

9:00 - 9:15  **Barth C**, CINaM-CNRS, Aix-Marseille University, Marseille, France  
Two-dimensional growth of nanoclusters and molecules on Suzuki surfaces

9:15 - 9:30  **Della Pia**, Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, United Kingdom  
Using charge transfer at metal-organic interfaces to control supramolecular self-assembly

9:30 - 9:45  **Riello**, Department of Physics, King’s College London, London, United Kingdom  
Modeling the self-assembly of charged molecules on metallic surfaces

9:45 - 10:00  **Boarino**, INRIM, NanoFacility, Division Electromagnetism, Torino, Italy  
Nanofabrication by supramolecular self-assembly and mediated laser ablation

10:00 - 10:30  Coffee break

10:30 - 12:30  **MOLECULAR SELF ASSEMBLY**

10:30 - 11:00  **Keynote**  
**Barth J**, Physik Department E20, TU München, Garching, Germany  
Porphyrin nanochemistry – a 2D perspective

11:00 - 11:15  **Morgado**, Instituto de Telecomunicações and Technical University of Lisbon, Lisboa, Portugal  
Self-assembly of a zinc-porphyrin on HOPG studied by STM at the liquid-solid interface and stepwise growth of molecular wires

11:15 - 11:30  **Melis**, Dipartimento di Fisica, Università di Cagliari and Istituto Officina dei Materiali CNR Ricerche, Cagliari, Italy  
Diffusion and self-assembling of Zinc Phthalocyanines on the ZnO (10-10) surface: a combination of Metadynamics and Metropolis Montecarlo simulations

11:30 - 11:45  **Riele**, Università di Roma Tor Vergata, Rome, Italy and TU Berlin, Berlin, Germany  
Thin layer growth of differently shaped Phthalocyanine molecules on reconstructed GaAs(001) surfaces
11:45 - 12:00 Sheremet, Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany
Size and Gap Dependent SERS and TERS Measurements of Phthalocyanine Molecules on Specially Designed Substrates

12:00 - 12:15 Winkler, Institute of Physical Chemistry PAS, Warsaw, Poland
Stable and Efficient SERS Platform Produced by Hierarchical Self Assembly

CYPRE A ROOM

8:30 - 10:00 CARBON NANOTUBES

8:30 - 9:00 Aramo, INFN e Dipartimento di Scienze Fisiche, Università degli Studi di Napoli
“Federico II”, Napoli, Italy
A new Silicon-CNT photodetector

9:00 - 9:15 Capasso, School of Engineering Systems, Faculty of Built Environment and Engineering, Queensland University of Technology, Brisbane, Australia
Carbon nanotubes-enhanced electrodes for organic and dye-sensitized solar cells

9:15 - 9:30 Grossi, Dipartimento di Fisica, Università degli Studi dell’Aquila, Aquila, Italy
Photocurrent from planar strips of multi wall carbon nanotubes

9:30 - 9:45 Melisi, INFN– Sezione di Bari, Bari, Italy
Fabrication and characterization of UV detectors with multiwalled carbon nanotubes using spray technique

9:45 - 10:00 Scarselli, Dipartimento di Fisica, Università di Roma Tor Vergata, Roma, Italy
Effects of the deposition of noble metal nanoparticles on the multiwall carbon nanotube photo-electrochemical response

10:00 - 10:30 Coffee break

10:30 - 12:30 CARBON NANOTUBES

10:30 - 11:00 Battie, Loiseau, Laboratoire d’Etudes des Microstructures - ONERA-CNRS - Chatillon France
Using carbon nanotubes for a selective gas sensing

11:00 - 11:15 Umemura, Faculty of Science, Tokyo University of Science, Shinjuku, Tokyo, Japan
Study of dispersed single-walled carbon nanotubes by atomic force microscopy

11:15 - 11:30 Lefrant, Institut de Matériaux de Nantes, Nantes, France
Carbon nanotube nanostructures: Resonance and Anti-Stokes Raman effects

11:30 - 11:45 Gautron, Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, Nantes, France
Characterisation of iron nanoparticles in carbon nanotubes grown on stainless steel substrate used as catalyst
11:45 - 12:00  Pagliara, Interdisciplinary Laboratories for Advanced Materials Physics and Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, Brescia, Italy
Relaxation dynamics in vertically aligned Single- and Multi-Wall Carbon nanotubes

12:00 - 12:15  Giri, Department of Physics, Indian Institute of Technology Guwahati, Guwahati, India
Defect Engineering in Carbon Nanotubes and Its Application for Efficient Fluorescence Quenching in Single Walled carbon Nanotubes

12:15 - 12:30  Gaillard, GREMI, Université-CNRS, Orléans, France
Electrical and thermal characterization of next generation nanoscale porous materials for 3D integration schemes

Afternoon  EXCURSION
A new kinetic Monte Carlo algorithm that efficiently accounts for elastic strain is presented and applied to study various phenomena that takes place during heteroepitaxial growth. For example, it is demonstrated that faceted quantum dots form by the layer-by-layer nucleation of pre-pyramids on top of an apparent critical layer; faceting then occurs via anisotropic surface diffusion. It is also shown that the dot growth is enhanced by the depletion of the apparent critical layer which leaves behind a wetting layer. Capping simulations provide insights into the mechanisms behind dot erosion and ring formation. The algorithm used for the simulations presented here is based on the observation that adatom and dimer motion is essentially de-coupled from the elastic field. This is exploited by decomposing the film into two parts: the weakly bonded portion and the strongly bonded portion. The weakly bonded portion is taken to evolve independent of the elastic field. In this way the elastic field need only be updated infrequently. Extensive validation reveals that there is little loss of fidelity but the algorithm is 15 to 20 times faster.

Lithographically-defined low dimensional SiGe nanostripes as silicon stressors

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Uniaxially-strained silicon has become dominant in high-speed microprocessing applications, since it allows for a greater increase in mobility with lower level of stress applied with respect to biaxial strain [1]. Investigation of the strain relaxation as induced by the patterning of a continuous SiGe layer is thus of scientific and technological importance [2]. By varying the Ge content it is possible to maximize the strain in the Si without inducing plastic relaxation. In the present work, Ge content and strain in unpatterned samples grown by low-energy plasma-enhanced chemical vapour deposition [3] has been characterized by high-resolution x-ray diffraction and µRaman.

Following electron-beam lithography, strain maps in lithographically-defined low dimensional SiGe structures obtained by µRaman spectroscopy.

We found that our nano-patterning approach induces an anisotropic strain relaxation in the SiGe stripe respect to continuous SiGe film, in accordance with Finite Element Method modelling. We show how the SiGe stripes can induce a local compressive strain in the Si below, and that we are able to induce strong uniaxial compressive strain in the Si substrate of around -0.9% (1.6 GPa). Our results suggest that lithographically-defined low dimensional SiGe nanostripes are effective and valuable stressors for mobility engineering in next generation electronic devices.

SiGe island growth on (001) Si substrates: quantitative determination of shape-dependent Ge capture rates by modeling of the Ge surface diffusion

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For properly chosen growth parameters extremely homogeneously ordered SiGe island ensembles were demonstrated over macroscopic substrate areas [1]. However, at both sides of the border between patterned and un-patterned substrate areas, regions with spatially varying island volumes are usually observed [2], which result from Ge diffusion between un-patterned and patterned substrate areas.

Here, we model the influence of these diffusion processes on the observed spatial dependence of island volumes and shapes. We quantitatively extract the rates at which Ge is incorporated into growing SiGe islands for the different island evolution stages (pre-pyramids, pyramids, transition domes, domes) together with a Ge surface diffusion constant of 4.2 \( \mu \text{m}^2/\text{s} \) for a growth temperature of 650 °C in a solid source MBE system.

By comparing the diffusion constant and the Ge incorporation rates, we show that a Ge add-atom on average approaches several 1000 pits before being incorporated. These findings clearly indicate that secondary island nucleation between pits [3] is not a consequence of the inability of a Ge atom to reach a nucleation site during its life time as a diffusing surface atom (as assumed in capture-zone models [4]). Instead, we quantitatively explain secondary island nucleation consistently with our model by the interplay between the wetting-layer between the ordered island sites and a mismatch of the incorporation- and deposition rates. In agreement with our model, we experimentally show that perfect island ordering can be achieved for pit periods beyond 1 \( \mu \text{m} \) with properly chosen Ge deposition rates.

References
Ge/SiGe Superlattices for Nanostructured Thermoelectric Modules


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Thermoelectrics are presently used in a number of applications for both turning heat into electricity and also for using electricity to produce cooling. Mature Si/SiGe and Ge/SiGe heteroepitaxial growth technology would allow high $ZT$ materials to be engineered which would be compatible and integrable with CMOS micropower circuits used in autonomous systems.

$ZT$ can be improved with respect to bulk thermoelectric materials using low-dimensional structures [1], such that electrical conductivity can be maintained while thermal conductivity is reduced, by enhancing the density of states near the Fermi level and through phonon scattering at heterointerfaces.

We have grown and characterized Ge-rich Ge/SiGe/Si superlattices and dot multilayers for nanofabricated thermoelectric generators. Low-energy plasma-enhanced chemical vapour deposition [2] has been used to obtain nanoscale-heterostructured material which is several microns thick. Crystal quality and strain control have been investigated by means of high resolution X-ray diffraction.

High-resolution transmission electron microscopy images confirm the material and interface quality. Electrical and thermal conductivity measurements indicate the viability of this material for the realization of thermoelectric devices. Seebeck coefficients for p-Ge/SiGe superlattices of 150±13 µV/K with electrical conductivity of 118500±15000 S/m have been demonstrated at 293 K producing a power factor of 2.67 mW/K²m.

X-ray scattering studies of SiGe/Ge superlattice interfaces


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High resolution synchrotron X-ray scattering techniques are used to study micro-/nano-fabricated SiGe/Ge superlattices intended for integrated on-chip harvesting of thermoelectric energy.

The efficiency of thermoelectric materials is improved by enhancing the electrical conductivity while simultaneously blocking the thermal energy transport [1]. Therefore, nanostructures with a large number of interfaces are designed to introduce barriers for phonon transport, in order to efficiently reduce the thermal transport, while maintaining a good electrical transport.

X-ray reflectivity (XRR) and grazing-incidence small-angle X-ray scattering (GISAXS) methods are employed to characterize the interface roughness and its correlation, which play important roles in the transport characteristics both in lateral and vertical designs. Measured reciprocal space maps are compared with simulated ones in order to determine the total width, the integral r.m.s. roughness, the Hurst parameter and the lateral and vertical correlation lengths of the interfaces.

Small roughnesses are found together with duty cycle changes in the layer thicknesses within one period along growth direction. Additionally, the influence of dislocations on period fluctuations, which affect especially vertical transport devices, is shown.

These studies are correlated with transmission electron microscopy studies and electrical and thermal transport measurements in order to optimize design and growth.

Enhanced critical thickness of epitaxial SiGe layers on porous Si stressor layer

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The microstructure of highly porous Si films (PSi) obtained by electrochemical processes was investigated by HRXRD and HRTEM. The results show that the crystalline PSi lattice is distorted and expanded in the direction perpendicular to the substrate plane. This expansion was attributed to the influence of the chemisorbed OH in the Si lattice. In this presentation we will study the effect of the temperature of annealing on the morphological and structural changes: the pores diameter increases with the annealing temperature while the lattice parameter decreases. The investigation allows determining the optimal experimental conditions to produce a compliant template PSi layer. We show that the compliant PSi layer can be used to epitaxially grow Ge and SiGe layers with larger critical thickness and flat surface morphology.

In the case of Ge, 40 nm and 80 nm layer thickness were deposited by MBE on the top of 270 nm thick PSi at different temperatures. The layers obtained are fully relaxed by misfit dislocations. For the two thicknesses, the layers exhibit a quite smooth surface morphology and a large penetration of most of the Ge atoms inside the pores of the PSi layer. At low growth temperature (T_G~400°C), we obtain a pure Ge layer with an almost negligible interdiffusion. At temperatures ≥ 600°C, the small and dense porosity of the PSi layer is fully destroyed; the pores coalesce and form large bubbles with dimensions in the sub-micrometer range. At these temperatures, a strong interdiffusion is observed and the Ge penetrates almost fully through the PSi layer to form a SiGe layer.

For the deposition of Si_{1-x}Ge_x layers with low x, we used a double PSi structure composed of a thin (200 nm) PSi layer with a small porosity about 25% deposited on a thick (7 µm) highly porous PSi layer. The PSi double layer is first in situ annealed at 900 °C in order to expand the lattice parameter of the PSi layer in the direction parallel to the substrate plane. This expansion is caused by the desorption of –HO which creates a large density of dangling bonds (which produce a lateral expansion of the lattice parameter). In these conditions, the PSi layer has a larger lattice parameter than the Si substrate and can serve as a template stressor for the epitaxial growth of the SiGe layers. In these conditions, we can deposit Si_{1-x}Ge_x layers with x = 0.2 (x = 0.3) as thick as 250 nm (70 nm), fully strained and totally free of extended defects. Such SiGe/PSi structures produce high PL efficiency and are very promising for optoelectronic applications.
Interface exchange coupling in magnetic nanostructures

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The exchange coupling between two different magnetic phases, modulated on the nanometric scale, has led to the discovery of novel magnetic properties of great technological impact [1, 2]. The two main classes of exchange-coupled systems are the FM-soft/FM-hard, which shows the so-called Exchange Spring (ES) effect [3], and FM/AFM interface, which exhibits the Exchange Bias (EB) effect [4]. The results on three systems will be presented.

In FM-soft/FM-hard Fe/FePt exchange-coupled bilayers with perpendicular anisotropy, the reversal mechanism shows a strong dependence on the FM-soft thickness moving from a rigid-magnet like regime to the ES behaviour [5].

FM (Co, Fe) nanoparticles embedded in a AFM (Mn) matrix were investigated as a function of the FM volume fraction, Vf. EB was observed, due to interface exchange coupling between the FM particles and the surrounding AFM shell. With increasing the FM Vf, the low temperature behaviour moves from blocking of superparamagnetic particles to super-spin-glass like freezing [6-8].

The EB effect was studied in assemblies of Co/CoO nanodots vs Co thickness (thCo). At small thCo (<10 nm), a strong increase in the bias field and the associated coercive field are found as the dot size is reduced. This indicates that the characteristic length, DAF, within the AFM which governs the EB effects, is the nanostructure size. By contrast, at larger thCo (23 nm) the EB field does not depend on the size implying that DAF is smaller than the size [9].

References
Electron Paramagnetic Resonance of magnetite nanoparticles coated with dextran

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Iron oxide nanoparticles are very interesting as applicable in nanotechnology due to their properties like superparamagnetism, high saturation fields and anisotropy contributions attributed to finite size and large surface area. They are also applied in biomedicine, including drug delivery and hyperthermia cancer treatment. These nanoparticles are also used in image contrast agents in magnetic resonance imaging (MRI).

Magnetite nanoparticles coated with dextran were investigated using Electron Paramagnetic Resonance (EPR) from Bruker working at 9.4 GHz frequency. The aim of this study was to perform the behaviour of these nanoparticles in different temperature and solvent conditions. From this reason they were investigated in the dependence on their orientation in an external magnetic field and in the dependence on the temperature in the region of 120-300 K. Low temperatures were maintained by a Bruker temperature controller ER 4131VT. For all recorded EPR spectra the spectroscopic parameters like g-factor and line width were determined. The relations between these parameters, temperature of the measurement and sample orientation were plotted.

It was found a step change of g-factor and line width at temperatures above 240K. Perhaps this is due to melting of the solution and the loss of dipolar interactions between molecules. Measurements of changes in line width and g-factor for a sample cooled to a temperature of 115K without a magnetic field and for a sample cooled in a magnetic field of 5000G were done. Magnetic orientation of nanoparticles in investigated samples has been identified. The anisotropy of spectroscopic parameters for frozen samples was determined in the dependence on the orientation in magnetic field.

References
Magnetic properties of CoFe$_2$O$_4$ nanoparticles: Influence of the nanoparticles arrangement and of the synthesis method

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This paper focuses on the magnetic properties of CoFe$_2$O$_4$ nanoparticles, analyzing the influence of nanoparticles arrangement and of the synthesis method. Using synthesis procedures based on direct micelle (DM) and high thermal (HTD) decomposition of metalorganic precursors, three samples of CoFe$_2$O$_4$ nanoparticles with the same average particles size were prepared ($<D_{TEM}> \sim 5$ nm). The DM method results appropriate to prepare either secondary spherical iso-oriented nanoporous assemblies with a high surface area (ACoFe$_{DM}$, figure a) or individual primary CoFe$_2$O$_4$ nanoparticles (CoFe$_{DM}$, figure b).

The comparison between ACoFe$_{DM}$ and CoFe$_{DM}$ samples shows as the ordering of nanocrystals at the mesoscopic scale in 3D superstructure induces an increase of the coercive field ($H_c$ 1.17 T $\rightarrow$ 1.29 T) and of the reduced remanent magnetization ($M_r/M_s$ 0.4 $\rightarrow$ 0.5). HTD method allows to obtain high crystalline nanoparticle coated by oleic acid and self-assembled in hexagonal close packing (CoFe$_{HTD}$, figure c). Magnetic characterization of CoFe$_{HTD}$ shows as, despite the same particle size, this synthetic approach allows to obtain nanoparticles with tendency towards cubic anisotropy ($M_r/M_s \sim 0.7$) with respect to uniaxial anisotropy ($M_r/M_s \sim 0.5$) observed in CoFe$_{DM}$ sample. Finally, a detailed study of magnetic interparticle interactions have been carried out, highlighting the influence of molecular coating (CoFe$_{HTD}$/CoFe$_{DM}$ samples) and of the formation of 3D superlattices (ACoFe$_{DM}$/CoFe$_{DM}$).

References

Manipulation of spin configurations in patterned 3D magnetic nanostructures

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In the last two decades the technological development in science has led to the intensive study of nanoscale magnetic elements as a prospective basis for nanoelectronics. The main advantages of magnetic nanoelements are nonvolatility and a presence of the stable micromagnetic states. Hereby, manipulation of micromagnetic states is an important trend of the fundamental and applied physics. In this context the most interesting test object is a nanodisk with the vortex ground state characterized by two parameters: chirality and polarity [1]. As a disk is an object with high order of symmetry the control of these parameters is a difficult task. One of the robust approaches to manipulate the micromagnetic state is a disk’s deformation. It has been shown that in structures as a truncated disk [2], disk with a hole [3] or a “packmen-like” disk [4] the vortex parameters can be precisely controlled. However, the disadvantage of this is a breakdown of structure’s magnetostatics leading to changes in magnetization reversal. To avoid this we consider 3D nano-architectural approach for creation magnetic nanostructures with tailored magnetic properties.

Our samples were fabricated on the naturally oxidized silicon substrates using a two-stage process. At the first stage we prepared a polymeric pattern of a disk with diameter 600 nm by electron-beam lithography following the magnetron sputtering of 30 nm thick Py. At the second stage on the top of 600 nm disk we fabricated a Py disk with 200 nm in diameter. We called this 3D system as “disk on the disk”. We prepared a series of samples with distances between disks’ centers in a range from S=50 to 230 nm.

The study of the “disk on the disk” system has shown that its magnetization reversal has strong difference from the remagnetization process of an individual disk. The comparison of hysteresis curves allows concluding of the vortex ground state in both systems. The conclusive proof of this is characteristic steps on the hysteresis curves matching a nucleation and annihilation of a vortex. The difference consists in a vortex core movement in a big disk caused by an interaction with a small disk playing a role of a magnetic defect.

As result we have demonstrated the possibility of using 3D nano-architectural approach for creation of the patterned nanostructures with high inverse remanent magnetization. The orientation of an external magnetic field is defined the vortex chirality and the spin configuration in a small disk. Thereby we have proposed a novel type of magnetic nanoelements with 3D architecture allowing the robust control of micromagnetic configuration in nano-sized disks considering for a wide range of practical applications.

References
Iron oxide nanoparticles dispersed in porous silicon

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Iron oxide nanoparticles (NPs) of 3.8, 5 and 8 nm have been infiltrated into the pores of porous silicon. The aim is to create a superparamagnetic (SPM) nanocomposite system with maximized magnetic moment. Therefore the particle size versus the superparamagnetic behaviour has been figured out. The blocking temperature $T_B$ which indicates the transition between SPM behaviour and blocked state is not only dependent on the particle size but also the magnetic interactions between them which can be varied by the distance between the particles. Thus a modification, on the one hand of the pore-loading and on the other hand of the porous silicon morphology results in a composite material with a desired $T_B$. Because both materials, the mesoporous silicon matrices as well as the Fe$_3$O$_4$-NPs offer low toxicity the system is a promising candidate for biomedical applications as e.g. magnetic field guided drug delivery.
Room Temperature Superparamagnetism Evaluation of Cobalt Doped ZnO nanoparticles

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Magnetic Zinc oxide semiconductors, doped with 1–10% of magnetic 3d transition metal ions such as Mn, Fe, Co, V, etc. are promising for the emerging field of spintronics. Since the spin and charge of the carriers in this materials can be coupled separately with an external magnetic field. In conventional electronic devices, the electrons carry both charge and spin and the processing of information is based only on the charge of the electrons. Whereas, spin electronics or spintronics, uses the spin of electrons, as well as their charge, to process information. In order to develop spintronics technology, it is necessary to explore potential materials and their magnetic properties and obtaining a thorough understanding of the spintronic phenomena. The theoretical prediction of such materials, “so-called diluted magnetic semiconductor (DMS),” operational at RT was firstly performed by Dietl et al. [1] and has been lead to the production of magnetic semiconductors in the various host semiconductor materials such as ZnO, TiO₂, and In₂O₃, by doping with 3d transition metals [2-4]. In this work we report synthesis and magnetic characterization of cobalt doped ZnO nanoparticles (with different percent of cobalt oxide). Synthesis of the materials was carried out at room temperature by polyacrylamide-gel method, using zinc sulfate and cobalt nitrate as source materials, acrylamide as monomer and N,N-methylene bisacrylamide as a lattice reagent. Characterization of the samples were performed using XRD, SEM, TEM, UV and photoluminescence (PL) studies. The X-ray diffraction patterns obtained showed formation of wurtzite ZnO structure with no secondary Co phases. The EDS measurements were employed to investigate the composition of the samples and showed the presence of Zn and cobalt elements detected. The optical absorption spectra showed internal d–d transitions related to Co²⁺ incorporated on the Zn lattice site of ZnO structure. Low temperature photoluminescence measurements confirm these results. The magnetic behavior of the cobalt doped samples investigated at room temperature using vibrating sample magnetometer (VSM) and will be reported in this work.


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Charge effects in adsorbed molecules characterized by UHV STM and non contact-AFM  
(invited talk)

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It is now possible to image single molecules adsorbed on insulating surfaces, due to the recent progress in Atomic Force Microscopy in the non-contact mode (nc-AFM) [1,2]. This is particularly useful for applications in molecular electronics, where the decoupling of the molecule from the electrons of the substrate is mandatory. But charges are easily trapped on the surface of insulators and the influence of these charges should be taken into account in the experiments.

Two experiments will be discussed in the talk.

- In the first experiment [3], it will be shown how the switching behavior of a molecule adsorbed on a NaCl thin film deposited on Cu(111) can be monitored by a combined use of STM and nc-AFM. In particular, it will be demonstrated that the conformational switch of the molecule is triggered by the injection of an electron in a molecular orbital and that the sign of the resulting charge species can be determined unequivocally by nc-AFM.

- In the second experiment [4], we will show how the molecular structures formed by depositing a specially designed derivative of triphenylene on the bulk insulator KBr(001) can be imaged by nc-AFM and electrically characterized by Kelvin Force Probe Microscopy (KPFM). We will use these results to discuss the difficulties in interpreting the KPFM signals on bulk insulators.

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Two-dimensional growth of nanoclusters and molecules on Suzuki surfaces

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Nanostructured surfaces are used for confining the growth of molecules and clusters into specific surface regions, which finds nowadays many applications in nanotechnology. In this contribution it is shown that the nanostructured surface of Cd doped NaCl crystals [1] (Suzuki surface) can be used to confine the growth of palladium clusters and functionalized brominated pentahelicene molecules [2] into the Suzuki regions of the surface. It is shown that especially the combination of noncontact AFM (nc-AFM) and Kelvin probe force microscopy (KPFM) in ultra-high vacuum (UHV) greatly helps in the characterization of the structure and morphology but also the electrostatics of the considered surfaces [3]. The growth of palladium onto the Suzuki surface results into nanometre sized clusters, which form two-dimensional cluster arrays inside the Suzuki regions. The clusters exhibit a high cluster density, are uniform in size, and due to the specific Suzuki structure the clusters are polarized or charged. Brominated pentahelicene molecules perfectly decorate the Suzuki regions and form two-dimensional islands whereas no molecules can be found inside the pure NaCl regions. The molecules are in a flat configuration, which finds strong support from first principle calculations. Due to the specific adsorption of the molecules, the surface dipole of the Suzuki regions is modified by the molecules. It is shown that changing the functional group of the helicene molecules leads to different adsorption characteristics, self-assembly phenomena and different surface dipoles [4].

(a) The Suzuki surface is composed by regions of pure NaCl and regions, which contain the impurities and vacancies (Suzuki regions). (b) The interface NaCl-Suzuki is well-defined at the atomic scale. (c) Pd clusters can be found almost only in Suzuki regions. (d) Structure of the functionalized helicene molecules used for the experiments.

Using charge transfer at metal-organic interfaces to control supramolecular self-assembly

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Surface engineering through molecular adsorption is emerging as one of the most powerful technologies for the fabrication of advanced nanostructured materials. With the almost unlimited capabilities of modern synthetic chemistry, the real limiting factor for the development and practical use of this technology is the restricted ability to control molecular adsorption and organisation, in particular over length scales where it can be integrated with top-down nanofabrication techniques.

We demonstrated that the use of long-range interactions generated by charge transfer at metal-organic interfaces can be used as a novel method for regulating 2D molecular assembly. Specifically designed donor molecules were deposited at various coverages on different metal substrates and characterised by low temperature scanning tunnelling microscopy (STM). The resulting supramolecular assemblies were analysed by comparing the experimental data with density functional theory (DFT) calculations. Energy level alignment at the metal-organic interface and substrate polarisability appear to regulate the interfacial charge transfer and therefore the development of induced dipoles. These have a profound influence on the supramolecular assembly which is further rationalised by kinetic Monte Carlo simulations taking into account the competition between Van der Waals attraction and electrostatic repulsion among the adsorbed molecules.

A coherent picture emerges where long-range forces between charged molecules drive the spontaneous formation of a novel classes of supramolecular structures. Conversely, these can be used to obtain crucial information on the electronic properties of metal-organic interfaces.
Modeling the self-assembly of charged molecules on metallic surfaces

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The configuration and functionalities of a molecule adsorbed on a metallic surface, together with the value of its ionization potential/electronic affinity and the substrate work function, are crucial in the definition of supra-molecular self-organized patterns on the substrate, especially when charge transfer occurs.

In this contribution we will illustrate the design and realization of metal-organic systems characterized by charge transfer, focusing on the self-assembly of rubrene [1] and tert-butylphenil pyrene at the Au(1,1,1) surface.

We will outline how a metal-organic interface can be modeled by classical molecular dynamics and Monte Carlo simulations. In particular, we will introduce a model for the electronic polarization effect in a classical potential [2] and a model Hamiltonian suitable to describe the tiling of adsorbed organic charged molecules [3]. We will show how the proposed models represent a way to establish whether the molecule/substrate interface is subjected to charge transfer and a valuable tool to describe the self-assembly experimentally observed via STM measurements and the charge transfer predicted from DFT calculations.

The work has been done in close collaboration with experimental groups at the University of Warwick (STM measurements) and the University of Namur (molecular synthesis).

NANOFABRICATION BY SUPRAMOLECULAR SELF-ASSEMBLY AND MEDIATED LASER ABLATION

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Supramolecular self-assembly of colloidal nanoparticles allows today a variety of fabrication methods for periodic nanostructures on large area. These methods are commonly termed Colloidal Lithography (CL) or Nanosphere Lithography (NSL). Among these methods, hexagonal close packed (hcp) ordered nanospheres can be used as an optical masks for near-field lithography, each sphere behaving like a microlens, producing sub-wavelength light spot when illuminated by a planar wave. The process works with irradiation of deep UV laser pulses, (DUV) in this way local writing or also ablation occurs on almost any type of solid substrate supporting the spheres. In this work, laser structuring of silicon dioxide is performed, and pores can be optically drilled underneath each particle by the so-called optical nanojets produced by the spheres.

Silica nanospheres with diameters ranging from 117 to 568 nm were obtained with a modified Stöber process and characterised by scanning electron microscope and dynamic light scattering. Silica nanospheres self-assembly is achieved by depositing silica ethanolic suspensions either by spin-coating (900 rpm) or drop coating on an oxidized silicon substrates (oxide layer thickness: 90 nm). The substrates are then subjected to deep UV (DUV) laser exposure (λ = 193 nm) (Fig.1).

![Fig. 1 Process scheme to obtain arrays of nanoholes with DUV laser nanofocalization.](image)

Scanning Electron Microscopy analysis has been performed by a Field Emission Gun Inspect F FEI microscope. Periodicity of the arrays is determined by the size of the assembled spheres. While the local field enhancement is strongly dependent on the sphere size, the morphology of the produced features can be maintained for all tested situations by balancing the change in local fields with the laser pulse energy. This work demonstrates the fabrication of 100-nm thick porous membranes with pore size of about 100nm and periodicity ranging from 250 to 650 nm.

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Porphyrin nanochemistry – a 2D perspective

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The comprehensive characterization and engineering of low-dimensional nanostructures on surfaces is of significant current interest, both from a scientific and technological point of view. Specifically, the fabrication of molecular nano-architectures on metal surfaces, applying self-assembly protocols inspired from supramolecular chemistry, is a maturing and rapidly advancing field of research. Here we present recent insights putting particular emphasis on results elaborated with porphyrins. Given their intriguing variety of functional properties, which are exploited in both biological and artificial systems, porphyrins are ideally suited both as individual functional units and versatile building blocks in surface-confined nanosystems. Using scanning tunneling microscopy (STM) we determine the order characteristics and inspect or manipulate the interior of these molecules. High-resolution scanning tunneling spectroscopy (STS) allows to determine the pertaining electronic characteristics (frontier orbitals, energy level alignment). Supported with complementary theoretical modeling and space-averaging techniques we address key questions related to their functionality: How does the molecular conformation respond to surface anchoring and what are the consequences for the self-assembly? How to control metalation pathways on surfaces? What determines the reactivity of adsorbed metalloporphyrins towards small gas molecules? Can we achieve and control conductance switches or molecular rotors?

Four-level conductance switch based on single proton transfer. The atomically sharp tip of an STM is used to selectively remove one of the two hydrogen atoms from the central cavity of a free-base porphyrin molecule adsorbed on a metal surface. The position of the remaining hydrogen atom can be switched between the four different positions giving rise to four distinct electric current levels (nnano, in print).
Self-assembly of a zinc-porphyrin on HOPG studied by STM at the liquid-solid interface and stepwise growth of molecular wires

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Controlling the ordering and the properties of single molecules and their aggregates is of increasing importance, not only from a fundamental point of view but also when aiming at the development of unimolecular electronics.

In this communication we report on the assembly of a zinc-porphyrin (ZnOEP) on HOPG from a tetradecane droplet, using STM to image the various stages of the self-assembly process, until a close packing arrangement is attained. At the early stages of ZnOEP assembly on HOPG we observe a polymorphic monolayer with the presence of a metastable phase ($\alpha$), which, over two hours, is converted into the thermodynamically stable one ($\beta$) (Figure 1).

Once the fully packed ZnOEP monolayer is formed, we proceeded to the fabrication of molecular wires anchored on such monolayer.

The process is based on the alternating combination of bipyridine (BP) and ZnOEP, being the binding between units due to the formation of Zn-N bonds [1]. We used STM to follow the growth at each step, confirming the high ordering of the molecular wires up to 25 units. Preliminary measurements of their electrical properties will be presented and discussed.

Figure 1 – STM image of a ZnOEP monolayer on HOPG obtained by STM at liquid/solid interface. The two polymorphic phases are indicated ($\alpha$: $a = (2.64 \pm 0.23)$ nm, $b = (1.41 \pm 0.06)$ nm and $\gamma = (83 \pm 4)^\circ$ and $\beta$: $a = (1.39 \pm 0.05)$ nm, $b = (1.36 \pm 0.08)$ nm and $\gamma = (115 \pm 1)^\circ$). The inset shows an incomplete BP monolayer on the ZnOEP monolayer, where the bright points correspond to BP molecules.

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Reference
Diffusion and self-assembling of Zinc Phthalocyanines on the ZnO (10-10) surface: a combination of Metadynamics and Metropolis Montecarlo simulations.

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Phthalocyanines (Pc’s) molecules are commonly used as dyes for photovoltaic applications. Recently, they have been used in combination with metal oxides (e.g., ZnO, TiO2) showing sizable photocurrents that are nevertheless affected by many factors, including temperature and actual amount of surface coverage. The surface morphology is as well expected to drive the performances of the corresponding device. In particular, it has been recently shown that the assembling of Pc molecules on top of the inorganic surface is detrimental for the optoelectronic properties [1]. This scenario suggests that any further technological improvement toward hybrid photovoltaics does require, among other issues, a better fundamental understanding of the role played by temperature and molecular assembling at the metal oxide surface. To these aims we have investigated the diffusion and the self-assembling of Zinc-Phthalocyanine (ZnPc) molecules on a ZnO (10-10) surface, by combining atomistic simulations. In particular, the diffusion at room temperature has been studied by Metadynamics. Simulations provide evidence that ZnPc diffuses on the metal oxide surface along well-defined crystallographic directions with a free energy barrier as small as 0.4eV [2]. By combining this information with the quantitative estimation of the adsorption energy we developed a simple coarse grained model then used to perform Langevin molecular dynamics and Metropolis Montecarlo simulations. Present results show that the molecular assembling only takes place at given temperatures and coverages. Finally, we prove that the most favorable surface configurations consists in ZnPc stripes oriented along well defined crystallographic directions [3].

Thin layer growth of differently shaped Phthalocyanine molecules on reconstructed GaAs(001) surfaces

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The electric conductivity of organic layers depends crucially on the orientation and ordering of the molecules within the respective layers.[1] Depending on the specific application in optoelectronic or electronic devices, e.g. organic solar cells [2], a controlled growth of well-ordered organic layers on inorganic substrates is therefore of major significance.

In this work, we present a combined study of Reflectance Anisotropy Spectroscopy (RAS) and Raman spectroscopy to determine ordering and orientation within Phthalocyanine (Pc) layers (up to 20 nm thick) on GaAs(001) surfaces. For these experiments two differently shaped Pc molecules, the non-planar PbPc and planar CuPc, were deposited on c(4x4) and (2x4) reconstructed surfaces of GaAs(001).

The growth of the molecular layers was monitored by RAS revealing molecular contributions to the optical anisotropy. For 20 nm thick PbPc layers, these investigations showed a strong influence of the GaAs(001) atomic surface structure on the molecular arrangement, resulting in an isotropic or anisotropic arrangement of the molecules on the (2x4) and c(4x4), respectively. [2] For CuPc, on the other hand, an in-plane optical anisotropy was observed within layers on both surfaces, and the layers apparently possess the same crystalline structure.

The influence of the surface reconstruction on the molecular ordering was furthermore analyzed by measuring the intensity of the Raman peaks as a function of sample rotation. We observe periodic intensity changes of the Pc vibrational modes with the rotation angle for both CuPc/PbPc molecules. These periodic changes exhibit a fixed relation to those of the GaAs substrate phonons. [3] On the basis of DFT calculations, we could assign the respective symmetry of the vibrational modes (A1, B1, B2, etc.) and we could perform model calculations with the different Raman tensors.

Our observations therefore indicate well-ordered Pc layers with a fixed geometrical relation to the substrate. We will discuss the epitaxial-like growth mode which will also be tested by XRD measurements.

To test the potential use of these ordered organic layers in organic solar cells, photocurrent measurements were carried out.

Size and Gap Dependent SERS and TERS Measurements of Phthalocyanine Molecules on Specially Designed Substrates


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During the past years the growing demand for reliable, ultrasensitive and non-destructive analysis of materials has fueled the development of new techniques in Raman spectroscopy. Notably, the coupling of Raman with plasmonics leads to new exciting methods such as tip-enhanced Raman spectroscopy (TERS) and surface-enhanced Raman scattering (SERS). We combine these techniques to experimentally realize the so-called gap-mode TERS [1]. In this contribution specially designed SERS substrates composed of dimers of gold nanoclusters (Fig. 1) are fabricated using nanolithography. In order to maximize the electromagnetic field enhancement, SERS performance is evaluated as a function of nanocluster size (from 30 to 100 nm) and distance between centers (from 100 to 150 nm). For this purpose a submonolayer of manganese phthalocyanine (MnPc) is deposited on the structures and the SERS effect is studied using a micro-Raman setup at different excitation wavelengths and polarization directions. For TERS a customized setup is developed with side illumination/collection optics by coupling a Horiba LabRam spectrometer with an Agilent AFM 5420. Special all-metal tips are fabricated for this purpose. The TERS spectra are recorded at different points of the structure in order to determine local enhancement efficiency for gap-mode TERS for MnPc molecules in the vicinity of the gold nanoclusters (Fig. 2).

![Fig. 1. SEM image of a dimer of gold nanoclusters.](image1)

![Fig. 2. Schematic diagram of the gap-mode TERS experiment.](image2)

References

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Stable and Efficient SERS Platform Produced by Hierarchical Self Assembly


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We report a new “bottom-up” method for fabricating efficient platforms for surface enhanced Raman spectroscopy (SERS). In our procedure, the following three consecutive steps are performed (Fig.1): (i) First, two-dimensional networks of gold nanoparticles (AuNPs) in a liquid crystal matrix are formed in a Langmuir trough and are transferred onto solid substrate with the Langmuir-Blodgett technique [1]. (ii) Next, the surface decorated with the nanoparticles is applied as a substrate in the chemical vapor deposition process of growth of gallium nitride (GaN) nanowires. (iii) Finally, the obtained array of GaN nanowires is covered with gold micro-flowers (AuMFs). The AuMFs are metallic particles of expanded nano-structured surface. Their synthesis is a one-pot method based upon the reaction of chloroauric acid and hydroxylamine hydrochloride in an aqueous solution [2]. The AuMFs are formed at the top of the GaN “scaffolding” and are not present in the cavities in between the nanowires.

Our method offers an easy control over morphology of the product (2D network of AuNPs, GaN nanowires, and AuMFs) at each step of the procedure. Moreover, the obtained SERS platforms provided the enhancement factor higher than 10⁶, were mechanically stable, exhibited excellent reproducibility, and retained their SERS properties over a period of more than six months of storing at room temperature.

Fig.1 Three-step procedure of obtaining SERS platform by hierarchical self-assembly.

References
A new Silicon-CNT photodetector
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The realization of a Silicon Carbon Nanotube heterojunction obtained by growing multiwall carbon nanotubes on a n-doped silicon substrate opens the door to a new generation of photodetector (Silicon-CNT detector) based on the coupling between this two materials. The obtained device presents a low dark current, high photoresponsivity, high linearity and a wide voltage range. The junction barrier is about 3.5 V in reverse polarity with a breakdown limit at more than 100 V. The photosensitivity properties appear only where CNT are deposited. This process is very cheap and easy, and permits to obtain large sensitive areas with the desired shape and extension.
Carbon nanotubes-enhanced electrodes for organic and dye-sensitized solar cells

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New-generation photovoltaic cells still provide low power conversion efficiency, mainly due to limited absorption spectra and poor charge mobility. Carbon nanotubes (CNTs) have been proposed by many groups as a suitable material for OSC, due to excellent charge transport properties combined with high aspect ratios [1]. We report on the direct synthesis of CNTs on two transparent conductive oxides commonly used as electrodes in organic photovoltaics: indium tin oxide (ITO) and fluorine-doped tin oxide (FTO). The addition of an intermediate layer of CNTs is beneficial for the charge collection and extraction at the electrode, by providing additional and highly-conductive percolation paths for the charges [2]. A specific set of parameters for a fast chemical vapour deposition (CVD) synthesis has been established which allows a good degree of control on the CNT properties without decreasing the conductivity and the optical transmittance of the oxide film. The created CNT-enhanced electrodes contribute to a significant increase in the open circuit voltage and in the short circuit current of both organic and dye-sensitized solar cells, mainly due to the increased and nano-structured superficial area of the electrodes.

References

Photocurrent from planar strips of multi wall carbon nanotubes

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We report a study of photocurrent generation [1] from a planar devices made by growing simultaneously different strips of multi-wall carbon nanotubes (MWCNTs) onto quartz substrates. MWCNT have been synthesized at 500°C and 750 °C by thermal chemical vapour deposition (CVD) of acetylene (C₂H₂) gas, in ammonia (NH₃) atmosphere, onto nickel (Ni) catalyst nanoparticles. Gold electrodes have been evaporated on the ends and in the middle of each strip overlapping the nanotube film for about 1 mm. The whole surface of the sample, included gold electrodes, and each MWCNT strips, have been illuminated using a tungsten lamp and an halogen lamp by means of an optical fiber, respectively. High photocurrent measurements have been obtained for the two samples and compared. We have shown that the photocurrent of all strips depends on the light spot position [2]. The highest photo-response has been obtained when the light spot was close to the electrode negatively biased. No experimental evidence can be found that the Schottky barriers have been formed at the contact regions (nanotube-metal heterojunctions). We have also investigated photoconductivity properties of MWCNTs under ultraviolet, visible and near-infrared radiation. The spectral photoresponse of all devices increases with increasing photon energy and very interesting agreement is found between the trends of the photoconductance and the absorbance. These preliminary photocurrent measurements have demonstrated the ability of our devices to work as large area detector for white light as well as monochromatic incident radiation.

References
Fabrication and characterization of UV detectors with multiwalled carbon nanotubes using spray technique

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The nanotechnology process allows the realization of devices that have finely submicron dimensions. Between the materials suitable for this technology, carbon nanotubes (CNT) are more interesting for the development of photodetectors. Actually the more used technique is Chemical Vapor Deposition (CVD) that requires high temperatures of the substrate. This last limits the substrate materials that can be used [1].

In this paper we present a study of multiwalled carbon nanotubes (MWCNTs) films deposited at room temperature by spray technique [2] on different substrates, starting from a nanodispersion of nanotube powder in a non-polar 1,2-dichloroethane (DCE) solvent [3]. Transmission Electron Microscopy (TEM) images are reported to show the morphological and distribution properties of the deposited MWCNTs.

UV detectors have been prepared by spray method of the MWCNTs on silicon substrates. The nanotubes layer has been covered by means of a indium tin oxide (ITO) layer to obtain ohmic contact. Electrical device analysis, both in dark and on light irradiation, have been performed and characteristics of the samples are reported [4].

References should be listed as below
Effects of the deposition of noble metal nanoparticles on the multiwall carbon nanotube photo-electrochemical response

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It is now well established that carbon nanotubes (CNTs) have so remarkable electronic and structural properties that can be used as active building blocks for a large variety of nanoscale devices. To really disclose CNT true nano-technological potential, they have been incorporated in a variety of composite materials that showed even more attractive properties and possible applications. In this research field, an interesting class of derivatives rises from the controlled deposition of metal nanoparticles (NPs) on the CNTs. Here we present a simple method to decorate the multi wall CNTs (MWCNTs) with Au, Ag and Cu nanoparticles and demonstrate the ability of such hybrid composites to generate photocurrent in the visible and near ultraviolet photon energy region. The selected metals were deposited in-situ by thermal evaporation on the CNTs grown by chemical vapour deposition. The CNT-based composites morphology has been investigated by transmission electron microscopy that reve al for all three metals, the formation of isolated discrete particles on the nanotube outer wall. The photocurrent response from the MWCNT composites was measured with an electrochemical cell and a remarkable increase with respect to the bare MWCNTs was observed in all the spectral range studied. We attribute the effect to the presence of an electronic charge transfer behaviour in the NP-CNT interface. Recently we found a similar trend for Cu-MWCNTs, although MWCNTs are not expected to show low dimensional effects, due to their close similarity to metallic graphite [1]. These findings have encouraged our research on MWCNT composites for photovoltaic and solar energy conversion applications.

A single walled carbon nanotube (SWCNT) is a one dimensional structure only composed of surface atoms. The SWCNT electronic properties are known to be extremely dependent on the chemical environment, which makes it an ideal candidate for the development of ultra-sensitive gas sensors. However, the development of selective SWCNT gas sensors remains a great challenge because the origin of the sensing mechanism is still unclear. Two physical mechanisms are invoked: the charge transfer between the adsorbed gas molecules and the p-doped SWCNT and the modification of the Schottky barrier between the semiconducting nanotubes and the electrical contacts.

In this talk, we proposed to investigate the influence of the metallic / semi-conductor tubes ratio and of the film thickness on the detection mechanism with the objective to highlight the SWCNT film/gas molecule interaction. Using a dedicated measurement device coupled to a theoretical conduction model to analyse the I(V) characteristics, we have extracted the film resistance as well as the Schottky barrier height at the interface between the film and the electrical contacts. Enrichment of the films in semi-conducting tubes up to 95% could be achieved using an optimized DGU technique [1]. Sensing detection and selectivity were tested on two model gases: NO$_2$ and NH$_3$ [2]. We demonstrate that the percolation of metallic SWCNTs plays a crucial rule on the gas detection mechanism. Below the metallic SWCNT percolation threshold, sensing is dominated by the modulation of the Schottky barrier while above this threshold, it is only attributed to a charge transfer between SWCNT and gas molecules. Both mechanisms are discussed in terms of sensitivity and resolution leading to routes for the optimization of gas sensor architecture [3].

Based on this investigation, we proposed a new strategy to achieve gas selectivity by covering the SWCNT network with a mesoporous silica film elaborated by sol–gel process. This thermally stable film was considered as a diffusion barrier, which traps polarized molecules like water vapour. Other molecules like NO$_2$ can diffuse easily in the mesoporous silica layer to reach the SWCNT network without increasing the response time [4].

Study of dispersed single-walled carbon nanotubes by atomic force microscopy

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Hybrids of single-walled carbon nanotubes (SWNT) and organic molecules, such as DNA and sodium dodecyl sulfate (SDS), were investigated by atomic force microscopy. Such hybrids have been intensively studied, as they constitute an important technique for the solubilization of SWNTs; however, preparing the hybrids such that they have well-controlled, uniform structures remains difficult. In this work, we prepared hybrids with several different types of SWNTs and organic molecules and compared the results to determine a better way of preparing the hybrids. Characterization of the prepared hybrids was mainly carried out by atomic force microscopy (AFM), and was supported by Raman spectroscopy, UV-vis spectroscopy, and electrophoresis. We found that the sequential dialysis of SDS-SWNT hybrids effectively realized stable AFM imaging of the hybrids, although the dialysis was not necessary for the DNA-SWNT hybrids. $1 \times 10^2$ times dilution of excess SDS molecules was sufficient to obtain clear images of the SDS-SWNT hybrids, although this was not the case when the solvent was replaced completely. In addition, even in the case of $1 \times 10^6$ times dilution, the hybrids were stable for at least 14 days after the dialysis. Further, when DNA was employed as an absorbent, the morphology of the hybrids was mainly influenced by the types of SWNTs, rather than the types of DNAs. We hope our results will form the basis for various applications of SWNTs in areas such as nano- and biodevices. This work was supported by a Grant-in-Aid for Scientific Research (23540479) from Japan Society for the Promotion of Science (JSPS).
CARBON NANOTUBE NANOSTRUCTURES: RESONANCE AND ANTI-STOKES RAMAN EFFECTS

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Since the discovery of single-walled carbon nanotubes (SWNTs), Raman scattering has been used for their characterization and the understanding of their electronic properties. Functionalized materials have also been prepared and the different steps of the chemical treatments followed via this non-destructive technique. Moreover, in the case of arc-discharge SWNTs, a systematic study of the Raman response, as a function of the excitation wavelength, showed changes in radial breathing mode frequencies and transition energies for both semiconducting and metallic tubes. For a particular family of tubes clearly identified in the Kataura plot for which we continuously tune the excitation energy from 704 to 752 nm, we could quantify the energy shift occurring in the spacing of the van Hove singularities. We demonstrate that, independently of the functionalization technique, the type of chain covalently bound to the tubes plays an important role, notably when oxygen atoms lie close to the tubes, inducing a larger shift in transition energy as compared to that of other carbonaceous chains. The study shows the complexity of interpreting Raman data and suggests that many interpretations in the literature may need to be revisited. The use of SERS (Surface Enhanced Raman Scattering) is also currently used to investigate for example interfaces when SWNTs are deposited on rough metallic substrates. Initiated firstly to amplify the Raman signal, it has more recently revealed peculiar properties such as an abnormal anti-Stokes Raman emission. This effect, reminiscent to a Coherent anti-Stokes Raman Scattering (CARS) emission, results from a wave mixing process between the incident laser light and Stokes Raman light, generated by the SERS mechanism. This phenomenon has been demonstrated to occur mainly at high frequencies whereas resonance effects dominate at low frequencies. This was demonstrated by a careful investigation varying several parameters including the observation temperature, the environmental conditions, the dilution in solvents, etc. Composites based on carbon nanotubes and conjugated polymers exhibit also interesting properties. This is the case of several conjugated polymers for which one observes a strong amplification in the anti-Stokes branch of the modes located around 1500 cm⁻¹, generated by the plasmon excitation of metallic tubes. An anti-Stokes luminescence excited in the low energy tail of the absorption band of PPV and PPV/SWNTs composites has even been observed for the first time. The effect is explained through a phonon-energy up-conversion mechanism that, in the case of PPV/SWNT composites, is improved by the increase of the carbon nanotube content.
Characterisation of iron nanoparticles in carbon nanotubes grown on stainless steel substrate used as catalyst

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Continuous and large-scale production of multiwall carbon nanotubes (MWCNT) implies the use of a substrate that can act both as support and catalyst source so as to be rapidly reused. In this context, stainless steel is a substrate that fulfils the mentioned requirements and for this reason it has been used for the MWCNT growth performed by chemical vapour deposition (CVD).

The present contribution aims at investigating the metallic particles found inside the MWCNTs. The core of the study is based on transmission electron microscopy (TEM). Electron energy loss spectroscopy (EELS) experiments clearly show that the particles are made of unoxidized iron, while neither Cr nor Ni, which are the other major components of the substrate, are detected in most of them. X-ray diffraction, electron diffraction and extended electron loss fine structure (EXELFS) analysis prove that both \( \gamma \) (face-centered cubic structure, fcc) and \( \alpha \) (body-centered-cubic structure, bcc) iron phases are present inside the CNTs, while Fe contained in the starting alloy has only a fcc structure, due to the presence of Ni stabilizer.

All those data can be explained as follows: \( \gamma \) iron is extracted selectively from the surface of the substrate during MWCNT growth; at this stage, in absence of Ni, some of the iron particles transform in \( \alpha \) phase which is stable at room temperature up to 900°C. Moreover, we find that the studied iron particles are not oxidized due to their encapsulation inside the MWCNTs.

Relaxation dynamics in vertically aligned Single- and Multi-Wall Carbon Nanotubes

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Multi-Wall Carbon Nanotubes (MWCNT) and Single-Wall Carbon Nanotubes (SWCNT) can be grown in different architectures, as unaligned or vertically and horizontally aligned ensembles. The alignment strongly affects the tube-tube interaction by changing the relaxation dynamics and the charge transfer channels occurring inside these systems [1].

The understanding of the charge dynamics is of great importance for improving the performance of several devices based on Carbon Nanotubes (CNTs), in particular the efficiency of a CNT-based solar cell [2,3]. Here, performing transient optical measurements (in a pump-probe experimental set-up) we are able to investigate the charge dynamics in vertically aligned SWCNT and MWCNT and to compare them with the relaxation dynamics previously investigated in unaligned SWCNT [1].

The results allow to correlate the SWCNT Raman spectrum with the transient reflectivity measurements. An excitonic behavior is evidenced and the linear and the non-linear exciton response is analyzed. Moreover, a comparison between the SWCNT and MWCNT dynamics contributes to shed light on the MWCNT electronic structure, not yet completely understood.

This work points toward a deeper understanding of the relaxation dynamics in heterogeneous systems (CNT plus nanoparticles or organic molecules), that are revealing good performances in the photovoltaic field [4].

Defect Engineering in Carbon Nanotubes and Its Application for Efficient Fluorescence Quenching in Single Walled carbon Nanotubes

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Once thought to be a perfect tubular structure, the carbon nanotubes (CNTs) are far from being perfect in reality. However, nondestructive evaluation and manipulation of defects in CNTs have remained a great challenge. Further, defects in CNTs are thought to be usually detrimental to the device performance and hence unwanted. However, engineering of defects and its possibility of its useful applications are least explored in the literature. In this talk, I shall present our recent findings on the manipulation and nondestructive evaluation of defects in SWCNTs and MWCNTs with special emphasis on spectroscopic signature of defects, and its beneficial applications in fluorescence quenching of common fluorophores. Commercially procured SWCNTs and MWCNTs of wide range of diameters (1-100 nm) have been systematically studied for identifying structural defects using several complimentary techniques. In particular, use of Raman, photoluminescence, electron spin resonance, thermogravimetry, X-ray photoelectron spectroscopy will be demonstrated to understand the nature and role of defects in CNTs structures and its thermal stability [1,2]. Our studies reveal that several intermediate frequency Raman modes observed from the CNTs indeed arise from defects in the nanotubes, instead of the commonly assigned combination modes of perfect nanotubes [3]. Direct observation of defects under high resolution transmission electron microscopy will be presented [4]. Controlled introduction/ elimination of defects and engineering the structure of CNTs by energetic ion irradiation and vacuum annealing will also be shown [5]. Finally, the role of defects in the ultrahigh efficiency fluorescence quenching of several fluorescent dyes by CNTs will be presented [6]. Nature of molecular interactions in the observed high efficiency quenching has been studied in details using Langmuir and Freundlich isotherms [7]. Implications of these results will be discussed for futuristic applications of defects in CNTs.

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Eletrical and thermal characterization of next generation nanoscale porous materials for 3D integration schemes


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For integrated circuits industries, the 3D integration (to stack components one above another) solution leads to difficulties when electrical interconnections between different levels must be achieved. Parallelly, the need of heat evacuation around active zones becomes critical. The emergence of porous material like carbon nanotubes (CNTs) based materials has already brought fundamental changes as they are good conductive media for heat and current simultaneously.

A demonstrator is realized with CNTs covered by metallic contacts. The CNTs films are obtained by PECVD deposition technique. Study of the growth process parameters allow the control of internal structure, morphology and length of CNTs. The metal is deposited by magnetron PVD process and is chosen with respect to the requirements of the characterization techniques used. The four-probe technique allow to measure the electrical conductivity: gold electrical contacts are necessary and are deposited according to the probes size. To identify the thermal properties, nanosecond pulsed photothermal pyrometry experiments are done in the IR range. In this case, Ti, W or Ni have been tested to answer the stringent conditions demanded by the pyrometry technique. The metal deposition process parameters have been studied in order to control the layer properties in terms of adhesion to the porous media, effective thickness, density, homogeneity and emissivity.
JUNE 28 THURSDAY

NAUTILUS ROOM

9:00 - 10:30  GRAPHENE

9:00 - 9:30  Sutter P, Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, USA
Growth of 2D Graphene-Boron Nitride Heterostructures

9:30 - 9:45  Hsiang, Department of Chemistry, Center for Nanotechnology, Chung-Yuan Christian University, Taiwan, R.O.C.
Synthesis of Graphene-based Nanosheets via Chemical Reduction using Titanium Metal Powders in Acid Solution

9:45 - 10:00  Caputi, Surface Nanoscience Group, Department of Physics, University of Calabria, Cosenza, Italy
Intraband plasmon dispersion in graphene/Ni(111)

10:00 - 10:15  Strupinski, Institute of Electronic Materials Technology, Warsaw, Poland
Growth of graphene by CVD and Si sublimation methods on SiC substrates

10:15 - 10:30  Coffee break

11:00 - 12:30  METALLIC NANOWIRES

11:00 - 11:15  Chen, Department of Materials Science and Engineering, National Cheng Kung University, Taiwan
Fabrication and Properties of Electrospun Silver Nanofibers as Transparent Conductive Electrodes

11:15 - 11:30  Buatier, Dipartimento di Fisica, Università di Genova, Genova, Italy
Self-organised Ion Beam Synthesis of Transparent and Flexible metal nanowire electrodes with tunable plasmonic functionality

11:30 - 11:45  Respaud, LPCNO (CNRS-INSA-UPS), Toulouse, France
Elaboration and magnetic properties of monocristalline sub-10nm Co nanowires directly grown on metallic surfaces by chemical solution epitaxy

11:45 - 12:00  Samardak, Laboratory of Thin Film Technologies, School of Natural Sciences, Far Eastern Federal University, Vladivostok, Russia
Magnetic properties of amorphous CoP nanowires electrodeposited in alumina template

12:00 - 12:15  Mrzel, Jozef Stefan Institute, Ljubljana, Slovenia
Molybdenum based Nanowires and Nanotubes by a Two-Step Molybdenum/Chalcogenide Halide Approach

12:15 - 12:30  Dzhes, D. Serikbayev East Kazakhstan State Technical University, Ust-Kamenogorsk, Kazakhstan
Computer simulation of deformation martensite three-dimensional intergrowth needles in Fe–Mn–C systems
13:00 - 16:30 Lunch and break

16:30 - 19:30 GRAPHENE

16:30 - 17:00 Vogt, Technische Universität Berlin, Institut für Festkörperphysik, Berlin, Germany and CINaM-CNRS, Campus de Luminy, Marseille, France
Formation of 2D Silicene on Ag(111): growth mode, atomic arrangements and Dirac fermions

17:00 - 17:30 Cadelano, SLACS, CNR-IOM, Cittadella Universitaria, Cagliari, Italy
INVITED
How the mechanical properties of graphene are affected by the hydrogen coverage

17:30 - 17:45 Ricco, Dipartimento di Fisica, Università di Parma, Parma, Italy
Interaction of hydrogen with graphene defects: a muon spectroscopy investigation

17:45 - 18:00 Ruocco, Dipartimento di Fisica, Università Roma Tre, Roma, Italy
INVITED
Electron spectroscopy investigation of Graphene oxide thermal reduction

18:00 - 18:15 Ishii, Tottori University, Koyama, Tottori, Japan
Density functional calculation for various adatom adsorptions on graphene for using graphene as substrate of self-assembled nano structures

18:15 - 18:30 Politano, Dipartimento di Fisica, Università degli Studi della Calabria, Cosenza, Italy
Angle-resolved energy loss spectroscopy experiments on epitaxial graphene on metal surfaces: a powerful tool for investigating vibrational, elastic and electronic properties

18:30 - 18:45 Sindona, Dipartimento di Fisica, Università della Calabria and INFN, Cosenza, Italy
Theoretical and experimental study of collective excitations in graphene/Ni(111)

18:45 - 19:00 Pisarra, Dipartimento di Fisica, Università della Calabria and INFN, Cosenza, Italy
Theoretical and experimental study of the K-edge loss in electron energy loss spectroscopy in Graphene adsorbed on Ni(111) surfaces

19:00 - 19:15 Degli Esposti, CNR-IMM, Sezione di Bologna, Bologna, Italy
Structural properties of folded few-layers graphene sheets: Computational studies versus transmission electron microscopy analysis

19:15 - 19:30 Lee D U, Department of physics and Research Institute for Natural Sciences, Hanyang University, Seoul, Korea
Electrical characteristics of resistive switching memory with metal-oxide nano-particle on the graphene layer

ASTREA ROOM

9:00 - 10:30 NANOMAGNETISM

9:00 - 9:30 Zhukov, Dpto. de Fis. Mater., UPV/EHU San Sebastián, Spain and IKERBASQUE, Bilbao, Spain
Recent advances in soft magnetic properties and magnetooimpedance of thin magnetic wires
<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Institution</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:30 - 9:45</td>
<td>Chizhik</td>
<td>Universidad del Pais Vasco, San Sebastian, Spain</td>
<td>Magnetic properties of sub-micrometric Fe-rich wires</td>
</tr>
<tr>
<td>9:45 - 10:00</td>
<td>Enculescu</td>
<td>National Institute of Materials Physics, Magurele-Bucharest, Romania</td>
<td>Influence of electrodeposition conditions on the magnetic properties of cobalt nanowires</td>
</tr>
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<td>10:00 - 10:15</td>
<td>Prischepa</td>
<td>Belarus State University of Informatics and Radioelectronics, Minsk, Belarus</td>
<td>Structural and magnetic properties of Ni nanowires grown in mesoporous silicon templates</td>
</tr>
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<td>10:15 - 10:30</td>
<td>Kveglis</td>
<td>Siberian Federal University, Krasnoyarsk, Russia</td>
<td>The variable thermoelectric effect in magnetic viscosity alloy Fe86Mn13C</td>
</tr>
<tr>
<td>10:30 - 11:00</td>
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<td>Coffee break</td>
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<tr>
<td>11:00 - 12:30</td>
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<td>NANOSTRUCTURED SOLAR CELLS AND LIGHT SOURCES</td>
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<td>11:00 - 11:30</td>
<td>Escoubas L</td>
<td>Aix-Marseille University, IM2NP, CNRS, Marseille, France</td>
<td>Enhanced absorption of light in organic solar cells by photonic crystals</td>
</tr>
<tr>
<td>11:30 - 11:45</td>
<td>Saba M</td>
<td>Dipartimento di Fisica, Università di Cagliari, Cagliari, Italy</td>
<td>Bi2S3 nanocrystals for non-toxic solar cells</td>
</tr>
<tr>
<td>11:45 - 12:00</td>
<td>Berbezier A</td>
<td>Institute Materials, Microelectronics and Nanosciences of Provence, Marseille, France</td>
<td>Modeling of quantum dot junction for third generation solar cell</td>
</tr>
<tr>
<td>12:00 - 12:15</td>
<td>Salamonczyk</td>
<td>Laboratory of Physicochemistry of Dielectrics and Magnetics, University of Warsaw, Warsaw, Poland</td>
<td>TiO2 Nanoparticles coated with Organic Dyes</td>
</tr>
<tr>
<td>12:15 - 12:30</td>
<td>Faglia</td>
<td>Università degli Studi di Brescia &amp; CNR, Brescia, Italy</td>
<td>Zinc Oxide Nanowires for UV LEDs</td>
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<tr>
<td>16:30 - 17:00</td>
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<td>MAGNETIC SEMICONDUCTORS</td>
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<tr>
<td>16:30 - 17:00</td>
<td>Reinke</td>
<td>University of Virginia, Department of Materials Science and Engineering, Charlottesville, USA</td>
<td>Structure and magnetism in Mn-doped group IV semiconductors</td>
</tr>
<tr>
<td>17:00 - 17:15</td>
<td>Goldfarb</td>
<td>School of Mechanical Engineering and Materials, Faculty of Engineering, Tel Aviv University, Tel Aviv, Israel</td>
<td>Superparamagnetic Self-Organization of Iron-Disilicide Nanoislands</td>
</tr>
<tr>
<td>17:15 - 17:30</td>
<td>Rezvani</td>
<td>School of Science and Technology, University of Camerino, Camerino, Italy</td>
<td>Growth of diluted magnetic germanium nanowires using manganese nano-droplets</td>
</tr>
</tbody>
</table>
17:30 - 19:30  III-V QUANTUM DOTS

17:30 - 18:00  **Arciprete**, Dipartimento di Fisica, Università di Roma “Tor Vergata”, Roma, Italy
Selective Nucleation and Lateral Alignment of Epitaxial InAs Quantum Dots

18:00 - 18:15  **Baskoutas**, Materials Science Department, University of Patras, Patras, Greece
Ionized Donor Bound Exciton Complex in an Inverse Parabolic Quantum Well: Electric Field Effect

18:15 - 18:30  **Hazdra**, Department of Microelectronics, Faculty of Electrical Engineering, Czech Technical University in Prague, Prague, Czech Republic
Light emitting diodes with InAs/GaAsSb self-assembled quantum dot layer embedded in GaAs

18:30 - 18:45  **Kret**, Institute of Physics, Warsaw, Poland
Structural transformation of MOVPE InGaN QDs during capping with GaN at high temperature

18:45 - 19:00  **Moiseev**, Ioffe Institute, Politekhnichestkaya 26, St. Petersburg, Russia
High-density uniform quantum dots in narrow-gap InSb/InAs(Sb,P) system

19:00 - 19:15  **Stoica**, Peter Grünberg Institute, and Jülich-Aachen Research Alliance, Jülich, Germany
Photoluminescence and Raman studies of InN-GaN nano-heterostructures selectively grown in small holes of an oxide mask using Metal-Organic Vapor Phase Epitaxy

19:15 - 19:30  **Milekhjn**, A.V. Rzhanov Institute of Semiconductor Physics, Novosibirsk, Russia and Novosibirsk State University, Novosibirsk, Russia
Micro-Raman phonon scattering by InAs/AlAs quantum dot superlattices

CYPREA ROOM

9:00 - 10:30  NANO OXIDES

9:00 - 9:30  **Li Bassi**, Department of Energy, Politecnico di Milano and Istituto Italiano di Tecnologia, Milano, Italy
Nanostructured Oxide Surfaces for Advanced Applications: from Individual Building Blocks to Functional Films

9:30 - 9:45  **Fleutot**, Institut de Physique et Chimie des Matériaux de Strasbourg, CNRR, Strasbourg, France
Multifunctional arrays of dendronized iron oxide nanoparticles

9:45 - 10:00  **De Renzi**, Dipartimento di Fisica, Università di Modena e Reggio Emilia & Centro S3, CNR, Modena, Italy
Energy Level Alignment and Electronic properties at the dye/ZnO interface: a Ultra-High Vacuum investigation on nitrocatechol adsorption on ZnO(10-10) surface

10:00 - 10:15  **Buyanoiva**, Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden
Cathodoluminescence characterization of ZnO Tetrapod structures
10:15 - 10:30  Lee Hyung Jin, Korea Institute of Ceramic Engineering and Technology (KICET), Seoul, Rep. Korea
Protein coated silica magnetic nanoparticles for environmental and medical applications

10:30 - 11:00  Coffee break

11:00 - 12:30  CARBON NANOTUBES

11:00 - 11:30  Motta, School of Chemistry Physics and Mechanical Engineering Queensland University of Technology, Brisbane, Australia
Microscopic studies of polymer-wrapped nanotubes for solar cells

11:30 - 11:45  Bendoudou, Laboratoire de Recherche sur les Propriétés des Matériaux Nouveaux-Université de Caen, Damigny, France
Development and characterization of polymer nanocomposites using carbon nanotube - silica hybrids as reinforcing fillers

11:45 - 12:00  Camilli, Dipartimento di Fisica, Università di Roma “Tor Vergata”, Roma, Italy
Super-strained epitaxial growth of metal islands on multiwalled carbon nanotubes

12:00 - 12:15  Baruselli, SISSA and CNR-IOM, Democritos Unità di Trieste, Trieste, Italy
Kondo impurities in nanotubes

12:15 - 12:30  Capobianchi, Istituto di Struttura della Materia, C.N.R., Monterotondo, Roma, Italy
FePt(L10)@MWCNTs/Ru(NPs): A smart nanocomposite for catalysis applications

13:00 - 16:30  Lunch and break

16:30 - 19:30  POLYMERS

16:30 - 16:45  Birjega, National Institute for Lasers, Plasma and Radiation Physics, Bucharest, Romania
Layered double hydroxides/polymer thin films grown by matrix assisted pulsed laser evaporation

16:45 - 17:00  Quochi, Department of Physics, University of Cagliari, Cagliari, Italy
Lasing performance of organic heteroepitaxial nanofibers realized by periodic deposition of para-sexiphenyl and sexithiophene on muscovite

17:00 - 17:15  Mallocci, Istituto Officina dei Materiali del Consiglio Nazionale delle Ricerche (CNR-IOM), Cagliari, Italy
Modeling morphology and electronic properties of organic oligomers on ZnO

17:15 - 17:30  Mattoni, Istituto Officina dei Materiali del Consiglio Nazionale delle Ricerche (CNR-IOM), Unità di Cagliari, Cagliari, Italy
Theoretical design of self-assembled interlayers for efficient photoconversion at polymer/metaloxide interfaces
17:30 - 17:45  **Saba M. Ilenia**, Dept. of Physics, University of Cagliari and CNR-IOM Unità Cagliari, Cagliari, Italy
Atomistic investigations of the P3HT/ZnO interface by including solvent effects

17:45 - 18:00  **Paczesny**, Institute of Physical Chemistry, Warsaw, Poland
Layering transition in thin films of partially fluorinated bolaamphiphiles at the air-water interface

18:00 - 18:15  **Manca**, Dipartimento di Fisica, Università di Cagliari, Cagliari, Italy
Thermoelectric force-extension behavior of polymers with elastic bonds

18:15 - 18:30  **Yerlikaya**, Istanbul Technical University, Nano Science & Nano Engineering, Istanbul, Turkey
Nanofibers and Characterizations of Polypyrrole / Poly(acrylonitrile-co-Methacrylate) Composites

18:30 - 18:45  **Ivas**, NCCR Nanoscale Science and Department of Physics, University of Basel, Basel, Switzerland
Confinement effects of a nanoporous network on the Copper surface

18:45 - 19:00  **Caddeo**, Department of Physics, University of Cagliari and Istituto Officina dei Materiali del CNR, Cagliari, Italy
Nanoscale effects on polymer-ZnO hybrids for photovoltaics

19:00 - 19:15  **Rudko**, Institute of Semiconductor Physics NAS of Ukraine, Kiev, Ukraine
Nanocomposites properties variation under UV-exposure

19:15 - 19:30  **Dolas**, Department of Chemistry, Polymer Science and Technology, Istanbul Technical University, Istanbul, Turkey
The Voltage Effect on Impedance of Polythiophene Obtained from Boron Trifluoride Diethyl Etherate Solution
Growth of 2D Graphene-Boron Nitride Heterostructures

P. Sutter, J. Lahiri, R. Cortes, and E. Sutter
Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973 (USA)
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Heterostructures, integrating different materials to achieve novel properties, have long been a focus of crystal growth and epitaxy. The advent of graphene and related 2D materials has paved the way for novel types of heterostructures based on atomically thin membranes. Apart from stacks of alternating 2D sheets, similar to quantum wells and superlattices grown by conventional epitaxy, one can envision monocrystalline materials consisting of different, tightly interfaced components within a single 2D membrane. Such materials raise questions on interface formation, intermixing and phase separation, strain, etc. in a new context of reduced dimensionality.

Among the known 2D materials, the integration of graphene and hexagonal boron nitride is particularly interesting, as it combines two nearly lattice-matched systems with identical structure but very different electronic properties. Here we consider the fundamental mechanisms underlying the controlled synthesis of graphene-boron nitride monolayer heterostructures on metal substrates, utilizing methods developed recently for graphene [1,2] and boron nitride [3] growth. We discuss the fundamental growth mechanisms, studied by a combination of in-situ surface microscopy methods. Real-time observations by low-energy electron microscopy provide a detailed mesoscale view of nucleation and growth, while related in-situ methods such as micro-diffraction and micro-ARPES [4,5] give unique insight into structure and electronic properties. Scanning tunneling microscopy is used to probe the atomic-scale structure of interface boundaries. Combining real-time and atomic-resolution imaging, we identify successful methodologies for the controlled formation of single layer graphene-boron nitride heterostructures.

Synthesis of Graphene-based Nanosheets via Chemical Reduction using Titanium Metal Powders in Acid Solution

*Kai-Hsiang Hung, Hong-Wen Wang*

Department of Chemistry, Center for Nanotechnology, Chung-Yuan Christian University, Chungli, 320, Taiwan, R.O.C.

*E-mail: hongwen@cycu.edu.tw*

Highly conductive graphene-based nanosheets were fabricated by chemical reduction from graphene oxide (GO) using titanium metallic powders in acid solution. The reduced materials were characterized by Field emission scanning electron microscopy (FESEM), Energy dispersive dpectrometer (EDS), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), Thermo-gravimetric analysis (TGA) and Atomic force microscopy (AFM). UV-vis spectroscopy and four-point probe method were employed to characterize the transparency and conductivity of the graphene films, respectively. The present method offers a scalable and facile process to synthesize dry grphahene-based nanosheets powders. The synthesized graphene materials were in good quality and could be applied to the applications of dye-sensitized solar cells.

Reference

Monolayer graphene (MG) has been obtained on Ni(111) by ethylene dissociation in ultra-high vacuum. MG isolation has been achieved by Cs intercalation. Angle-resolved electron-energy-loss spectroscopy has been used to study the intraband plasmon (also called sheet plasmon), on both the MG/Ni(111) and MG/Cs/Ni(111) systems. The dispersion curve obtained on MG/Ni(111), showing a square-root behavior, has been fitted within the framework of the non local response theory using RPA [1]. The results of the fitting allowed us to conclude that the fluctuating charge density close to the Fermi level is strictly two-dimensional, with a Fermi velocity about half the value assumed in ideally isolated graphene. In the presence of intercalated Cs atoms, the sheet plasmon shows a similar square-root dispersion, which still indicates a two-dimensional charge density. The plasmon overall energy is reduced, indicating a lower MG/substrate charge transfer.

Growth of graphene by CVD and Si sublimation methods on SiC substrates

W.Strupinski (1)*, K.Grodecki (1,2), R.Bozek and J.M.Baranowski (1,2)

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(2) Faculty of Physics, University of Warsaw, Hoza 69, 00-681 Warsaw, Poland
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Graphene, a single sp²-bonded carbon atomic sheet has great potential for microelectronics applications, including conventional components such as high frequency analog devices, and devices in emerging fields such as spintronics, terahertz oscillators, and single-molecule gas sensors. However, a major factor hindering the development of technology for the large-scale production of graphene-based nanoelectronic devices is the lack of access to high-quality uniform graphene layers grown on large SiC substrates. Graphene produced by sublimating Si from SiC heated to high temperatures (1200-2000°C) is sensitive to the surface quality of the SiC substrates. Concurrently, the CVD epitaxial growth of graphene on metal substrates has lately received much attention. Unfortunately, epitaxial growth on metals suffers from the disadvantage that electronic applications require graphene on an insulating substrate, and although wafer-scale transfer is possible, it is a difficult process. In this paper, we report the CVD of epitaxial graphene (CVD-EG) on SiC substrates using propane gas as the carbon precursor. Graphene layers were grown using a commercially available horizontal CVD hot-wall reactor (Aixtron VP508). This new technique involves controlling the dynamic flow of argon in the reactor, which stops Si sublimation. The CVD-EG approach offers numerous potential benefits in comparison to S-EG, including the reduction of substrate surface influence on graphene thickness uniformity, graphene doping during the growth, modification of substrate surface prior to the growth, etc. To provide information at the atomic scale, samples were characterized by scanning tunneling microscopy (STM), micro-Raman spectroscopy and transmission electron microscopy (TEM). The thickness of the graphene films were estimated by ellipsometry, the position of the σ and π electronic energy bands were evaluated by angle-resolved photo-emission spectroscopy (ARPES). The transport parameters of the graphene samples were measured with the van der Pauw method at room temperature. The micro Raman histograms revealed that CVD growth of graphene produces much less strained layers in comparison with S-EG.
Fabrication and Properties of Electrospun Silver Nanofibers as Transparent Conductive Electrodes

Hung-Tao Chen, Hsiu-Ling Ling, Changshu Kuo, In-Gann Chen*

Department of Materials Science and Engineering, National Cheng Kung University, Taiwan
*E-mail: dragoner0616@gmail.com, ingann@mail.ncku.edu.tw

Silver nanofibers were fabricated via a polymer-assisted electrospinning technique. Silver trifluoroacetate precursor was dissolved and mixed with poly(methyl methacrylate) (PMMA) as the electrospinning solution. Silver/polymer composite nanofibers were electrospun and deposited on glass or polyimide substrates, followed by a post thermal treatment. Formation of silver nanoclusters inside polymer nanofibers successfully constructed the continuous silver nanofiber networks. Sheet resistance of these silver nanofiber depositions were measured to be less than 300 ohm per square. And, the optical property revealed the transmittance as high as 80% in the visible wavelength. In addition, the polymer-based electrodes also exhibited excellent flexible stability, showing < 5% resistance change after over 100 bending cycles. Electrospun silver nanofibers demonstrated a cost-effective/high-throughput fabrication and a promising alternative to indium tin oxide (ITO) as the transparent conductive electrodes.
Self-organised Ion Beam Synthesis of Transparent and Flexible metal nanowire electrodes with tunable plasmonic functionality

F. Buatier de Mongeot, D. Chiappe, A. Toma, M. Giordano, C. Martella

Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy
Email: buatier@fisica.unige.it

Here we report on a self-organised approach based on defocused Ion Beam Sputtering (IBS) for the synthesis of laterally ordered arrays of noble metal nanowires supported on transparent substrates (glass slides or flexible polymer films) which feature a dual functionality [1]: (i) they exhibit anisotropic conductivity along the nanowire axis, with sheet resistances comparable to the best transparent conductive oxides (TCOs), (ii) the noble metal nanowires support localised plasmon resonances which can be tuned by modifying the nanowire morphology. The nanowire network appear thus as alternatives to TCO’s endowed with the additional plasmonic functionality in view of Plasmon enhanced photon harvesting applications [2].

The formation of periodic metal nanostructures is induced by self-organized IBS patterning of polycrystalline Ag and Au films supported on soda lime glass slides or on flexible polymer films. A defocused broad beam ion source destabilizes in a self-organised way the surface with the formation of a regular nanoscale pattern extended over a macroscopic scale (cm^2 range). Regular arrays of ripples with a wavelength in the 100 nm range are formed by the competition of a smoothing term induced by thermally activated diffusion and by the destabilising erosive action of the ion beam [3]. By increasing the ion dose, the rippled metal film decomposes into an array of disconnected nanowires when the troughs of the valleys reach the supporting glass substrate [4]. The metal nanowire arrays exhibit anisotropic resistivity along the nanowire direction, with low sheet resistances in the 3-5 Ohm/square range [2]. Given their low sheet resistances, and high optical transparency in the 80 % range, the nanowire arrays appear as promising alternatives to the best TCOs employed in photovoltaic or OLED applications. Additionally, far-field optical characterisation demonstrates that the nanostructured surfaces exhibit a tunable plasmonic response which matches the solar spectrum [2,4], a crucial issue in view of photovoltaic applications [1].

The plasmonic properties of the nanowire arrays are intriguing since the substrates show evidence of strongly polarized enhancement of the SERS signal [5], of interest in view of bio-sensing applications, as well as the amplified generation of the Second Harmonic signal of interest in non linear optical applications [6].

References:
Elaboration and magnetic properties of monocrystalline sub-10nm Co nanowires directly grown on metallic surfaces by chemical solution epitaxy

N. Liakakos (1,2), K. Soulantica (1), T. Blon (1), C. Achkar (1), B. Warot-Fonrose (2), E. Snoeck (2), O. Benamara (1,2), B. Chaudret (1), M. Respaud* (1)

(1) LPCNO (CNRS-INSA-UPS), 135 avenue de Rangueil, 31077 TOULOUSE, France
(2) CEMES-CNRS, 29 rue Jeanne Marvig, 31055 TOULOUSE, France
E-mail: respaud@insa-toulouse.fr

Some years ago we have presented the solution synthesis of monocrystalline Co nanorods (NRs) by decomposition of a coordination cobalt precursor in the presence of hexadecylamine (HDA) and lauric acid (LA) [1]. These NRs spontaneously form well organized super-lattices over limited areas, and their magnetic properties are very interesting with high remanence and high coercive fields [2]. These ferromagnetic NRs (diameter of 5-6 nm) are promising candidates for high density data storage devices provided that they can be organized over large areas [3]. We present here for the first time the directed chemical solution epitaxy of sub-10nm Co NRs perpendicularly organized side by side on flat substrates and describe their magnetic properties [4]. The method includes two steps: first, a 20 nm layer of Pt(111) is epitaxially grown by sputtering on an α-Al2O3(0001) substrate and then introduced into a reactor containing a solution of a cobalt precursor and organic ligands (HDA and LA). After 4 days reaction, 130 nm length NRs have grown perpendicular to the substrate surface, with a density of 2.2×1012 NRs/inch² and uniform diameter (8 nm) (fig. 1). High resolution TEM studies demonstrate the metallic hcp monocrystalline structure of the NRs grown along the c hcp axis. The NRs have grown epitaxially on Pt according to the relationship: Co(0002)[1-100] // Pt (111)[2-1-1]. After deposition of a 100 nm thick Al2O3 layer to avoid oxidation, the magnetic properties measured at 300 K by SQUID reveals an out-of-plane anisotropy (1.81×10^6 erg/cm³) with a 0.15 T coercive field (0.4T at 5K) (fig. 2). This is a result of the magnetocrystalline and shape anisotropies along each NR axis, which dominate the collective demagnetizing field. No exchange bias has been measured after field cooling indicating that our nanorods are oxide-free. We presently extend our study to the Co NR growth on substrates of different crystallographic orientations, as for instance on a Pt(001) which leads to a tilted growth of NWs. This new bottom-up approach opens new routes for the integration of magnetic nanoparticles in functional devices.

References
15 January 2012

Magnetic properties of amorphous CoP nanowires electrodeposited in alumina template

*F. Nasirpour* (2)

(1) Laboratory of Thin Film Technologies, School of Natural Sciences, Far Eastern
Federal University, Vladivostok, Russia
(2) Department of Materials Engineering, Sahand University of Technology,
Tabriz, Iran
(3) Department of Physics, University of Bath, Bath, UK

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The controlled production of magnetic nanowire arrays with outstanding characteristics is attracting much interest recently owing to their applications in emerging technologies related with magnetic information storage, high sensitive GMR sensor devices, thermoelectric cooling system and photonic crystals [1,2]. Various templates have been used to electrodeposit nanowires, but anodic aluminium oxide (AAO) template method has been applied widely due to its self-organized nanopore structure, convenience and flexibility of fabrication [3,4]. There are two main factors determining the magnetic properties of the nanowire arrays: (1) the magnetic character of individual nanowire, which is determined by its magnetic anisotropy, such as magnetocrystalline anisotropy and shape anisotropy, and (2) the periodicity or the symmetry of nanowire arrays, which determines the strength of the magnetostatic interaction among nanowires [5]. If the microstructure is amorphous in nature, then the magnetocrystalline anisotropy can be neglected.

In this abstract we report on the fabrication of amorphous CoP alloy nanowires by means of alternative current (ac) electrodeposition in highly ordered anodic aluminum oxide (AAO) template. An ac voltage with sinusoidal waveform at a distinct frequency of 400 Hz at room temperature was applied to electrodeposit nanowires from aqueous solutions with different phosphorous content. Current transients demonstrate the general four-stage nucleation and growth behavior of nanowires into nanoporous template and scanning electron microscopy confirms the formation of CoP nanowires in AAO. Results show that electrolyte phosphorous content influences the growth, microstructure and magnetic properties of nanowires. The increase of phosphorus content reduces the growth rate of nanowires. The crystalline structure of cobalt nanowires electrodeposited in AAO changes significantly to amorphous by the incorporation of phosphorous as an alloying element in the structure, as X-ray diffraction patterns show. The main influence of the P exists for coercivity values, as is increases with decreasing P content in the electrolyte. Because the domain walls are wide in amorphous alloys and the defects are narrow, there is little pinning of domain walls on defects in amorphous materials and coercivity decreases.

References
Molybdenum based Nanowires and Nanotubes by a Two-Step Molybdenum/Chalcogenide/Halide Approach

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Transition metal based nanotubes, and nanowires find several applications, especially as ultra-low friction materials, catalysts and in nanoelectronic devices. Here we report on an efficient two-step synthetic route that enables efficient, large-scale production of these one-dimensional nanostructures based on molybdenum [1]. First, by optimizing the reaction conditions M₆SyIₓ (8,2<y+z≤10) nanowires (MoSI nanowires) were grown directly from the elements very efficiently. The nanowires with the diameters less than 1 nm are self-assembled into bundles of different sizes and orientation. Several different types of nanowires and nanotubes are obtained by annealing of bundles in different gas mixtures. The controlled annealing of Mo₆S₂I₈ nanowires in N₂/O₂ gas mixture resulted in the production of the MoO₂ or MoO₃ nanowires [2]. Transformation of bundles in argon-H₂S mixture leads to the MoS₂ nanotubes with split walls [3]. These nanotubes keep many technological advantages, like mechanical strength and better tribological properties (up to 40 % lower friction coefficient) in comparison to typical MoS₂ crystals. Heating of bundles in argon/H₂ mixture enables quantitative formation of pure molybdenum nanowires still grouped in starting morphology. The oriented molybdenum nanowires with similar length and diameters and very porous nanowires composed of molybdenum nanograins were obtained by hydrogenation of suitable precursor bundles. Finally, bundles of MoSI nanowires are transformed into novel superconducting MoN nanowires by annealing in the presence of NH₃/argon gas mixture. Two types of MoN nanowires were prepared- the first type has a typical diameter of 100-200 nm and length of up to several mm and the second type has a characteristic diameter from 30 to 50 nm and typical length of several μm. SQUID measurements were performed to verify the superconductivity of these nanowires at low temperatures similarly as the bulk specimen. We have found that roughly ten percent of the produced material goes to superconductive phase below 12.4 K. X-ray diffraction, scanning electron microscopy with wave dispersive analysis, and transmission electron microscopy were used to characterize the starting nanowires and all the final products.

References

Computer simulation of deformation martensite three-dimensional intergrowth needles in Fe–Mn–C systems

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The object of this research is the analysis of austenitic-martensitic structure (see fig. 1) and properties of the Hadfield steel with help of computer simulation.

The topicality of Fe–Mn–C system alloys research [1] connected with the set of unique mechanical and physical properties: impact strength, self-reinforcement under shock loading, unusual high durability under friction, invar effect (from –100 to 250°C), electrical– and magneto–resistance.

Figure 1 – The phase of spreading martensite in needle form. Figure 2 – The computer model of deformation martensite structure.

Computer simulation of deformation martensite structure allows to understand the nature of structure formation in crystal boundaries in Fe–Mn–C system under shock loading. Combination of antiferromagnetic austenite structure in the intergrowth needles form and ferromagnetic deformation martensite structure create unique electrical and magnetic properties of Fe–Mn–C system.

Formation of 2D Silicene on Ag(111): growth mode, atomic arrangements and Dirac fermions

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Due to its unique physical properties graphene [1] has attracted tremendous attention over the last years. Silicene, the graphene equivalent for silicon, could follow this trend, opening new perspectives for applications, especially due to its compatibility with Si-based electronics. Free standing silicene has been theoretically predicted and is conjectured to have a buckled honeycomb atomic arrangement of sp³/sp²-like hybridized Si-atoms [2]. Still, silicene would share essentially the same electronic properties as graphene, i.e. an electronic dispersion resembling that of relativistic Dirac fermions at the K points of the Brillouin-zone [2]. An inevitable proof of the synthesis and the existence of 2D silicene is thus a scientifically important issue.

We will discuss the formation and growth of 2D silicene layers on the Ag(111) face. Depending on the growth conditions we observe different 2D silicon arrangements that form on Ag(111). The Si layer at lower growth temperatures gives rise to triangular structures situated in a honeycomb arrangement with a (4×4) coincidence symmetry with respect to the Ag(111) surface. Angle-resolved photoemission data identify a downward-dispersing conical branch resembling that of relativistic Dirac fermions at the Si K points. The results demonstrate that both structural and electronic properties of the 2D Si ad-layers are very similar to the ones observed for graphene and in agreement with all related expectations for silicene. Another 2D Si structure forms at slightly higher growth temperatures, giving rise to a (√13×√13) periodicity. This structure shows a very regular, wide range ordered Moiré-like surface pattern in STM, which, however, is related to surface areas of well-ordered and less ordered arrangements within the Si sheet. We will discuss the formation of this structure and how it could refer to the rotated (4x4) silicene.

How the mechanical properties of graphene are affected by the hydrogen coverage.

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The hydrogenated form of graphene [1-3] (also referred to as graphane) has been systematically investigated by Wen et al. [4], proving that in fact there exist eight graphane isomers. They all correspond to covalently bonded hydrocarbons with a C:H ratio of one. Four isomers have been found to be more stable than benzene, indeed an intriguing issue.

As far as the elastic behavior is concerned, it has been proved that hydrogenation largely affects the elastic moduli as well. By blending together continuum elasticity theory and first principles calculations, we have determined [5] the linear and non linear elastic moduli of three stable graphane isomers, namely: chair- (C-), boat- (B-), and washboard- (W-) graphane. The resulting picture is very interesting; in particular, B-graphane is found to have a small and negative Poisson ratio, while, due to the lack of isotropy, C-graphane admits both softening and hardening non linear hyperelasticity, depending on the direction of applied load.

Although full hydrogen coverage is possible both in ordered and in disordered configurations of the hydrogen sublattice [4], it is more likely that a typical experimental processing procedure generates samples with a C:H ratio larger than one. In other words, we must admit that graphane could exist not only in a large variety of conformers, included an amorphous (A-) configuration of the hydrogen sublattice, but also in several forms characterized by different stoichiometry.

In this work, we present results about the variation of the linear elastic moduli of graphane versus the hydrogen coverage, in three stable conformers and in the amorphous one. The goal is establish whether an incomplete sp3 hybridization affects the elastic behavior and which is the trend (if any) of variation of the Young modulus versus hybridization. Our approach benefits of continuum elasticity (used to define the deformation protocol aimed at determining the elastic energy density of the investigated systems) and first principles atomistic calculations (used to actually calculate such an energy density and the corresponding elastic moduli).

We will discuss how hydrogenation generally leads to a smaller longitudinal extension upon loading than for pristine graphene.

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Interaction of hydrogen with graphene defects: a muon spectroscopy investigation

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Polarized muons have proved to be reliable and sensitive probes of local magnetic fields in matter and an important tool for the investigation of hydrogen reactions in low electron density materials such as carbon1. In defective graphene, muon spectroscopy (μSR) could thus help to address two open and well-debated questions: the possible onset of magnetism[1,2] and the interaction with hydrogen[3,4].

Here, we present the first μSR investigation of graphene, focused on chemically-produced, gram-scale samples, appropriate to the large muon penetration depth. We have observed an evident muon spin precession, usually the fingerprint of magnetic order, but here demonstrated to originate from muon-hydrogen nuclear dipolar interactions[5]. This is attributed to the formation CHMu (analogous to CH₂) groups, stable up to 1250 K where the signal still persists. The relatively large signal amplitude is correlated to defects concentration and demonstrates an extraordinary hydrogen capture cross-section of CH units. These results also rule out the formation of ferromagnetic or antiferromagnetic order in chemically synthesized graphene samples.

Electron spectroscopy investigation of Graphene oxide thermal reduction

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Graphene oxide (GO)[1] is emerging as a versatile material for applications in nanoscience and nanotechnology because of its easier production and processability as well as simple chemical functionalization respect to graphene. The electrical and the optical properties of GO are easily controlled by reductive processes.[2] The annealing in ultra high vacuum (UHV) is an effective free-contaminant process to obtain the progressive elimination of oxygen from the single GO sheet.[3]

In this paper we present the evolution of the electronic structure of GO single sheets as a function of the temperature in the range 150 – 750 °C in UHV. We studied a GO layer corresponding to a partial coverage of 90% of single sheets spin-coated from aqueous solutions on single crystal silicon substrate covered by a silicon oxide film. The electronic structure of the system under consideration is studied by XPS, UPS and EELS. We observe several spectroscopic changes as a function of the temperature. In particular we observe, after annealing at 750 °C, the presence of typical graphite features in the EELS spectrum and the appearance of electronic state at Fermi level in the UPS spectrum indication of the metallization of the system. The reduction of the GO layer and the formation of graphene-like layer is also testified by the intensity reduction of the C-H stretching mode.

Density functional calculation for various adatom adsorptions on graphene for using graphene as substrate of self-assembled nano structures

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The graphene itself is very interesting material to be investigated both experimentally and theoretically. Nowadays, excellent experiments for graphene sheets become possible. However, the graphene is very interesting also for substrates of nanostructure because of its two dimensionality. In order to promote such investigations, the adsorption of atoms and molecules on graphene should be studied, but such studies have not been done so much.

In recent theoretical study [1,2,3,4], the adsorption sites and adsorption energies for some atomic species have been reported. The aim of this investigation is to understand of the general mechanism of the adatom adsorption on a graphene. In this work, we investigate computationally adsorption energies, adsorption sites and migration barrier energies on graphene sheet for a lot of atomic species including transition metals, noble metals, nitrogen and oxygen, from atomic number 1 to 83, using the DFT calculation. We used VASP code. The both magnetic and non-magnetic calculations are done.

We discuss stability of the adatom in the graphene by analysis from the electronic structure. The calculated results show that adsorption at the H-site mainly for simple and transition metal elements. The non-metallic element showed the tendency to be adsorbed at the B-site. Some atomic species have chemisorption adsorption. Many metallic adatoms show ferromagnetic behavior at least for single adsorption on graphene. We found in our DFT calculation that some transition metal atoms adsorb in vertical alignment with spin polarization. Such structure can be applied to some nano-scale magnetic devices. Moreover, magnetic behavior of adatoms on graphene is also reported along the atomic elements table.

The result of this work will be helpful for the choice of material for electrode on graphene or growth of graphene on substrates. This work is supported by JST-CREST project.

References
Angle-resolved energy loss spectroscopy experiments on epitaxial graphene on metal surfaces: a powerful tool for investigating vibrational, elastic and electronic properties

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Angle-resolved electron energy loss spectroscopy has been used to study phonon and plasmon dispersion in monolayer graphene grown on Pt(111). Epitaxial graphene on Pt(111) behaves as an ideal 2D system, sustaining a purely 2D electron gas (2DEG) system whose collective excitations (plasmon modes) are able to propagate along the sheet. The dielectric response of the 2DEG system is determined by plasmon dispersion. We found that the dispersion relation of the low-energy plasmon mode (0-3 eV) confined in the graphene sheet is acousticlike. The linear dispersion relation of its frequency is caused by the non-local screening of the electrons in monolayer graphene due to the presence of the underlying metal substrate.

On the other hand, the elastic properties of a macroscopic graphene sample grown on Pt(111), extrapolated from experiments on phonon dispersion, showed values similar to the theoretical strength for free-standing graphene. Our results indicate that the excellent crystalline quality of graphene grown on metal substrates leads to macroscopic samples of high tensile strength.

Similar experiments have been performed also for periodically rippled graphene/Ru(0001). Results will be compared with the case of graphene/Pt(111).

Theoretical and experimental study of collective excitations in graphene/Ni(111)

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Electron energy-loss spectroscopy (EELS) in reflection mode with an electron beam of low primary energy is a high sensitive method for characterization and investigation of surface-like objects, such as graphene on metal substrates [1-3]. Recent investigations [4-5] have evidenced the high efficiency of this technique in detecting the electronic properties of free-standing graphene layer on Au/Ni(111) and epitaxial graphene on top of Ni(111). The former case is an example of a weak bond, between the graphene sheet and the substrate, where the conical Dirac point in the graphene's electronic band structure is preserved, although small charge exchanges with the metal shift the Fermi level. In the latter case, the strong graphene-metal interaction destroys the conical Dirac points leading to a more complicated picture. The signature of graphene in EELS spectra is clearly manifested in the excitation of a plasmon and its subsequent decay, which is a consequence of the strong Coulomb interaction of the incident electron with the occupied \( \pi \) band states of carbon atoms. The shift of the plasmon peak vs the exchanged parallel momentum has been shown to be directly related to the Dirac point in free standing graphene [6].

In this work, we have combined electron energy-loss spectroscopy (EELS) experiments of graphene/Ni(111), at fixed primary electron energies of 100 eV and varying reflection angles in the range of 35 to 53 degrees, relative to the surface normal, with density functional theory (DFT) simulations. More specifically, we have performed ground state calculations for a single layer of graphene on top of 3,5, and 7 layers of Ni(111), using the local density approximation, a plane-wave basis set (with 425-625 k points in the first Brillouin zone and an energy cutoff of 25 Hartree) and norm-conserving pseudopotentials of the Troullier-Martins type. We have determined the loss spectra within the random phase approximation (RPA) including all valence-electrons from 19-39 occupied bands (as well as 50-100 empty band states). We have computed and observed the reduced dispersion of the \( \pi \) plasmon excitation for parallel momentum transfer along a \( \Gamma K \) line of the first Brillouin zone. We have proved that a square root behavior is the most suitable dispersion of plasmon peak vs the parallel momentum transferred from the incident electron beam to the sample. This result is in contrast with the observations of ref. [4], where a parabolic dispersion was assigned to the same plasmon structure. However, it highlights the two dimensional nature of the electronic structure of the epitaxial layer.

References
Theoretical and experimental study of the K-edge loss in electron energy loss spectroscopy in Graphene adsorbed on Ni(111) surfaces

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The study of the deep core ionization spectrum, induced by either X-Rays or electrons, is a powerful resource to obtain information on the chemical and physical composition of surfaces [1]. For example, it can be used to probe many body shake-up effects induced by the sudden creation of the core hole [2]. These attributes make the study of the core ionization spectrum particularly well suited for surface like systems, like graphene adsorbed on a metal substrate [3].

In this work, we have combined the experimental observation of the Carbon K-level ionization loss spectrum with density functional theory (DFT) simulations of Graphene adsorbed on Ni(111) surfaces. More specifically, we used a 2 keV electron beam to measure the energy loss spectrum near the ionization edge (up to 30 eV from the absorption edge) of the 1s carbon level of graphene/Ni(111), with different scattering configurations, i.e. different incidence and observation angles. We have performed ground state calculations for free-standing graphene and single layer graphene adsorbed on a Ni(111) slab of different thickness. In particular, we have used the local density approximation (LDA) for the exchange and correlation potential, a plane wave basis set (energy cut-off 25 Hartree, and 2500 k-point mesh in the 1st Brillouin zone), and norm conserving pseudo-potentials of the Troullier and Martins type. The one-electron energies and wave-functions, entering the optimized ground state, were used to calculate the first-order transition rate between the Carbon 1s state and the unoccupied band states of the system (up to 30 eV above the highest occupied energy level). The calculated energy distributions show similar peak positions and shapes with the experiments. More insight into the detailed features of the measured spectra stems from the inclusion of many-body electron excitations.

References
Structural properties of folded few-layers graphene sheets: Computational studies versus transmission electron microscopy analysis

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Three-dimensional deformations occur naturally in graphene, and solution-chemistry processes usually yield multiply folded flakes. While it has been argued that fold-induced curvature of graphene sheets without in-plane strain could modify the local chemical reactivity, the electronic transport as well as the mechanical properties, a comprehensive, quantitative, description of folded/bended graphene multilayers is still not well developed. In turn, this perspective is of particular interest in a materials-by-design approach, where tailored membranes could be used as enhanced nano-electromechanical devices or nano-resonators.

In this contribution we will present a joint theoretical-experimental study of folding and bending properties of graphene layers, exploiting continuum elasticity theory, tight-binding and density-functional theory atomistic simulations versus high-resolution transmission electron microscopy and holographic measurements. In particular, we will show that this approach can be successfully applied to the edges of few-layers graphene membranes obtaining a geometrical and physical picture of the local 3D structure of the folds in a non-destructive fashion.

The proposed method proves to be effective in mapping sub-nanometer height variations with superior spatial resolution, and could be easily extended to other classes of 2D crystals.
Electrical characteristics of resistive switching memory with metal-oxide nano-particle on the graphene layer

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The flexible resistive switching memory devices have several potentials for application of a various kinds of electronic device such as a mobile smart phone, a display, an e-paper, and a wearable information technology device. Also, The graphene oxide thin film has reported to use flexible memory device.[1] In recent, the graphene electrode layer is able to improve the electrical properties of memory device due to the reduction of mechanical stress.[2,3] In this study, we demonstrated the resistive switching memory device with metal-oxide nanoparticles on graphene layer. The mono and multi-graphene layers on SiO₂/Si substrate were deposited by using chemical vapor deposition. The metal-oxide nano-particles embedded in the 50-nm thick biphenyl-tertracarboxylic dianhydride-phenylen diamine and poly(N-vinyl carbazole) mixture polymer layer were formed on the graphene layer by using evaporation and spin coating process.[4] After curing process at 400 °C for 1 hr, the metal electrode was fabricated on top of the polyimide layer. Then, the electrical properties of the resistive switching memory device with metal-oxide nano-particle on the graphene layer were characterized and discussed.

References
Recent advances in soft magnetic properties and magnetoimpedance of thin magnetic wires

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Recent trends in the development of magnetic sensors are focused on their miniaturization, significant improvement of their features and on finding of new operating principles based on fundamental studies of new materials. Among new magnetic materials thin wire gained considerable importance [1]. Particularly, studies of giant magneto-impedance (GMI) effect of microwires attracted considerable interest [2].

We present the results on tailoring of soft magnetic properties and GMI effect (GMI ratio, $\Delta Z/Z$, and impedance $Z$) in thin microwires at elevated frequencies (till 4 GHz) paying special attention to achievement of low hysteretic high GMI effect. Both $\Delta Z/Z$ and hysteresis loops of Co-rich low magnetostrictive microwires exhibit strong sensitivity to the internal stresses related with the ratio, $\rho$, of the metallic nucleus diameter to the total microwire diameter. The hysteresis loops exhibit low coercivity (generally below 10 A/m) with well defined magnetic anisotropy field, $H_k$. $H_k$ increases when $\rho$ decreases. Field dependence of the off-diagonal voltage response of nearly zero magnetostriction Co-rich microwires measured in pulsed regime exhibits anti-symmetrical shape. We found, that if the surface anisotropy is not circumferential, then the magnetization and the MI curve $Z(H)$ present hysteresis. This hysteresis can be suppressed by the DC bias current $I_B$ that creates a circumferential bias field $H_B$. The magnetic anisotropy of Co and Fe-rich microwires can tailored by stress or magnetic field annealing. Particularly stress annealed microwires exhibit stress-sensitive GMI effect and hysteretic properties and significantly affects the GMI effect of microwires.

Magnetic properties of sub-micrometric Fe-rich wires

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The investigation of the magnetization reversal has been performed in Fe-rich sub-micrometric glass covered wires. The surface magnetization reversal has been studied using the magneto-optical Kerr effect. The intensity of the light, reflected from the surface of the wire, was proportional to the axial component of the magnetization. The axial tensile stress and torsion stress have been applied during the experiments. Also during the experiment the array of 10 wires has been rotated in the plane perpendicular to the plane of the light. The series of the wires with different values of radius of metallic nucleus (400 nm, 700 nm, 1000 nm) has been studied.

It was found that for the wires of such thin dimensions, surface hysteresis loop has a rectangular shape related to magnetic bistability effect. It confirms the existence of the Surface Large Barkhausen Jump in sub-micrometric glass covered wires which is explained by the magnetization reversal in a large single surface domain.

For the array of 10 wires it was found that the collective jumps of some number of wires take place: 6 wires change the direction of the magnetization during the first jump and then 4 wires change the direction of the magnetization during the second jump. This behaviour could be explained by the very narrow distribution of the switching field in the studied wires.

The performed analysis of the tensile and torsion stresses transformation of surface hysteresis loop demonstrates that about one order decrease of the wire dimension does not abolish the basic effects observed earlier in thicker wires: magnetic behavior of the glass covered wires with such extremely tiny diameter keeps magnetic bistability.

Influence of electrodeposition conditions on the magnetic properties of cobalt nanowires

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Swift heavy ion irradiation of polymer foils and subsequent etching is a flexible approach to produce nanoporous membranes with cylindrical pores and diameters ranging from ten nanometers to micrometers. Further, these porous membranes can be used for obtaining nanowires by filling the pores, this being known as the template method.

Electrodeposition was widely employed for filling these pores with metals or semiconductors. Metallic nanowires with magnetic properties are of high interest for applications ranging from targeted drug delivery to the so called race-track magnetic memories.

In the present report we present our results regarding cobalt nanowires obtained by electrodeposition in polycarbonate membranes. We found that the deposition parameters can influence the structure of the wires, including here the direction of crystallization. This further influences the magnetic properties such as magnetization behavior and magnetoresistance by means of crystalline magnetic anisotropy.
Structural and magnetic properties of Ni nanowires grown in mesoporous silicon templates

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One of the most remarkable progresses of magnetic nanostructures during last decade is related to application of nanotechnology for manufacture the magnetic nanoscale structures. Among them magnetic nanowires grown in mesoporous silicon templates are of special interest [1,2]. In this contribution, we present structural and magnetic properties of Ni nanowires electrochemically deposited into pores of mesoporous silicon template under the stationary galvanostatic regime. We used antimony doped Si (100) wafers with 0.01 Ohm×cm resistivity as the initial substrates. Uniform porous silicon (PS) layers were formed by electrochemical anodization in 1:3:1 = HF:H2O:(CH3)2CHOH solution at current density of 80 mA/cm² for 200 s. This regime provides the formation of the uniform PS layer with thickness of 10 μm, average pore diameter 100 nm and porosity P = 70 %. Ni was grown into the PS template by electrochemical galvanostatic deposition at current density of 3.5 mA/cm² in a proper electrolyte (213 g/l NiSO₄×7H₂O, 5 g/l NiCl₂×6H₂O, 25 g/l H₃BO₃, 3 g/l saccharin) with pH = 2.6 at room temperature. Different samples were fabricated with deposition times ranged in the interval of 5 – 120 min. This allows us to investigate both the crystalline structure and the magnetic properties for different stages of Ni deposition.

X-ray diffraction (XRD) analysis revealed the polycrystalline structure of Ni in PS template with preferential orientation along [111] axis. Also a small amount of Ni₂Si phase is formed, which peak is especially pronounced for low deposition times. The magnetic properties were investigated by studying the temperature dependence of the specific magnetization σ of the samples. Firstly samples were zero field cooled down to the liquid nitrogen temperature, than the field 8.6 kOe was switched on and the sample was heated up to T = 700 K, after that it was cooled down to room temperature. The obtained σ(T) dependencies allows us to estimate the Curie temperature, T_C, of the samples, which for low deposition times of Ni was significantly lower (T_C = 575 K) with respect to the bulk Ni (T_C = 630 K). Also the specific magnetization values of samples were lower with respect to bulk values. This gives us the possibility to conclude that electrons of Ni are partially bounded with silicon electrons. The effect is stimulated by heating. The results of XRD analysis before and after heating as well as the irreversible character of measured σ(T) dependencies confirm this hypothesis.

The variable thermoelectric effect in magnetic viscosity alloy Fe86Mn13C

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The image in scanning electron microscopy of structure Fe86Mn13C specimen after shock loading. There are dark bands of shear deformation in the light austenite grains. The dark bands of shear deformation have the ferromagnetic structure. The light austenite grains have the antiferromagnetic structure.

In this work the thermal electromotive force was detected at various points in the shock-deformed samples of alloy Fe86Mn13C. The electromotive force was established that as a result of long mechanical loading on an austenitic alloy Fe86Mn13C. In its structure, besides known phases of deformation martensite, Frank-Kasper structures can be formed. The structure of the specimen Fe86Mn13C after shock loading (there were dark bands of shear deformation in the light grains of austenite) is shown in the picture.

The variable temperature dependence of thermal electromotive force in samples of alloy Fe86Mn13C has been detected. It has been noticed that at heating of the sample, its property are identical to properties of the thermocouple. If the sample has not been subject to shock strain value the contact potential difference effect was absent. It is determined that in Fe-Mn and Fe-Mn-C alloys there is the complicated magnetic order similar to an order in spin glass, which is installed thanks to coexistence of interacting antiferromagnetic and ferromagnetic phases. Structural studies of alloy Fe86Mn13C may indicate such states and give the answer to the cause of magnetic viscosity. Electronic structure calculations for nanocrystalline Fe87Mn13, by the scattered waves method, were showed the presence of energy gaps in the spectra of the electron density of states of nanocrystalline having a structure of the Frank-Kasper. They are most easily formed from the nonequilibrium state in metallic alloys. Sign thermo electromotive force may vary depending on the temperature. The reason for its appearance is connected with the contact potential difference at the interface of two phases: the antiferromagnetic austenite and ferromagnetic martensite deformation. The nature of the appearance of variable thermoelectric effect can be explained from the standpoint of coexistence in the samples of the inhomogeneous crystal and magnetic structures. The effect of magnetic viscosity in samples of alloy Fe86Mn13C and its change under the influence of long-term impact of mechanical loading was detected.
Organic solar cells (OSC) promise very low cost fabrication processes such as printing, chemical synthesis of materials, low weight flexible and conformable solar cells architectures. OSC may prove useful to deliver electrical power to portable electronics such as mobile phones, PDAs, etc. Main drawbacks are due to the still low conversion efficiency of OSC with a record efficiency on small areas devices (<1.1 cm²) of 9.8%. The efficiency of OSC is limited by several parameters, one of them being the weak optical absorption of organic materials at long wavelengths, thus leading to relatively low current densities. In that context, photonic concepts (bragg mirrors, gratings, plasmons, etc…) need to be considered as potential solutions to improve the photonic absorption of such thin film devices [1-7]. Thus, we have investigated the use of photonic crystals to trap the light inside the OSCs. The aim is to couple Bloch modes with very low group velocities, also called Slow Bloch Modes (SBM), into the active layer. In this presentation, we will explain, using optical dispersion curves of photonic crystals, how SBM can be excited. Then, using a Finite Difference Time Domain method, we will study photonic crystals made of organic semiconductors and their incorporation into the stack of an OSC. We will show that an absorption gain ranging between 4% and 11% is possible according to the band gap of the organic material. Finally, we will present first experimental demonstration by nanoimprint of the organic semiconductor P3HT :PCBM blend in the shape of a photonic crystal able to couple SBMs. In agreement with the model, optical characterizations will demonstrate significant absorption gains.

Bi$_2$S$_3$ nanocrystals for non-toxic solar cells

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A major technology challenge in the exploitation of solar energy is the development of low-cost and high-throughput fabrication techniques for solar cells. Colloidal nanocrystals provide a promising platform, combining solution process with the reliability of inorganic materials. The most efficient solar cells based on colloidal nanocrystals have however been based on toxic compounds as solar absorbers, in particular Cd and Pb chalcogenides, whose commercialization is either severely limited or entirely prohibited because of safety concerns. There is a strong motivation to extend the library of available colloidal materials to non-toxic compounds like Bi$_2$S$_3$ and Fe$_2$O$_3$.

Early attempts on employing such materials have resulted in low efficiencies. The optimization appears to be a non-trivial task, as nanocrystal morphology and composition have complex influences on all the phenomena involved in solar cells, including photoconversion, charge separation and charge transport.

We synthesize and characterize Bi$_2$S$_3$ nanocrystals in composition and morphology. Capping exchange procedures were applied to control the length and polarity of ligand molecules. We used ultrafast optical spectroscopy to demonstrate that their properties, and therefore their suitability for solar cells, critically depend on the fabrication technique and on post-synthesis processing. From our results we deduce a path for rational optimization of non-toxic nanocrystals to be employed in solar cells.
Modeling of quantum dot junction for third generation solar cell

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To improve efficiency, new generation solar cells shall include quantum nanostructures [1]. Very isolated works aimed to analyze the functioning of these new cells [2, 3], we thus relied on the Keldysh formalism to model a quantum wire-dot-wire photovoltaic junction. Using a two-level tight-binding method, we modelled a quantum dot connected to two infinite non-interacting wires. Two hopping parameters, one for each level, characterize contacts to reservoirs in which band offsets control electron/hole selectivity. The structure is designed so that current can only pass under illumination.

The present study focus on the effect of the dot-wire (reservoir) hopping parameter $h$ that characterizes the junction for a fixed monochromatic light resonant with the gap of the isolated dot. But contacts induce resonance shifting and broadening enhanced with $h$, via the amplitude of the reservoir self-energies that similarly shifts and broadens the discrete levels of the dot. Out-of-resonance electron-photon interaction creates a double peaked spectral current. When $h$ increases, peaks decrease and broaden, as the energy levels of the connected dot and the total current and power produced hence decreases. Meanwhile both shunt resistance and series resistance of the equivalent cell circuit increase when $h$ increases.

The dot-wire hopping parameter shows a strong impact on the functioning of the quantum photovoltaic cell and the proposed architecture can thus be designed in order to optimize it.

References:
TiO$_2$ Nanoparticles coated with Organic Dyes

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The titanium oxide spheres (diameter 3.5 nm) are obtained by organic synthesis [1].

\[
\text{TiCl}_4 + \text{C}_2\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{CH}_2\text{OH} \rightarrow \text{TiO}_2
\]

Further, TiO$_2$ nanoparticles surface was modified with organic dyes: porphyrins, metallomesogens or [2]benzothiophene derivatives. The photo-electrical characteristics of the coated TiO$_2$ nanoparticles presents that was made p-type and n-type homojunction. The properties of obtained materials were characterized with AFM, TEM, x-ray and optical measurements (Raman, absorption, fluorescence).


References

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Zinc oxide (ZnO) has recently gathered great interest for optoelectronic applications because of its direct wide bandgap nature (3.37eV) and its large room temperature exciton binding energy (60 meV). Recently, light emitting diodes (LEDs) based on ZnO single crystal nanowires (NWs) have been presented as promising candidates for the next generation of blue/near-UV light sources. However, $p$-type ZnO is not yet a stable material, hence different types of heterojunctions ($n$-ZnO/$p$-GaN) are proposed as an alternative approach. ZnO nanowires have been grown on $p$-GaN thin film on a sapphire substrate by Vapor-Liquid-Solid (VLS) and Vapor-Solid (VSS) methods. Optimization and precise control of the growth parameters to achieve super-saturation condition has led to nanowires aligned perpendicularly to the substrate. Indeed nanowires growth produces grain boundary free and a much less strained and defective interface, which are sources of nonradiative recombination, compared to thin films. Beside nanowires can act as direct waveguides and favor directional light extraction without use of lenses and reflectors. Morphological studies by Field Emission Scanning Electron Microscope (FESEM) as well as the characterization of the emission properties of these heterojunctions are here presented. Photoluminescence (PL) studies at room temperature show a band edge emission at 380nm and defect emission in the visible region (wide band centered at 500 nm). LED device fabrication, then, includes the following steps: (i) deposition of poly(methyl-methacrylate) (PMMA) to isolate electrically each nanowire from its neighbor, (ii) plasma etching to selectively exposed the tip of nanowires, (iii) sputtering of electrical contacts. Photoluminescence, Electroluminescence (EL) and electrical characterization are then presented for the as-fabricated LED structures.

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Structure and magnetism in Mn-doped group IV semiconductors

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The magnetic doping of group IV semiconductors Si and Ge, and Ge-quantum dots with Mn is highly coveted for the integration of charge and spin-based electronics, and poses numerous challenges which are rooted in fundamental materials aspects of the Si-Ge-Mn system. Our research aims to develop a deeper understanding of the structure-property relation by studying bonding, structure and magnetic properties of Mn-doped structures such as monoatomic Mn-wires on Si(100)-(2x1), delta-doped Mn-interlayers in Si and Si-Ge, and Mn-doped Ge-quantum dots. The Mn doping of Ge-QDs is achieved by surface-doping of Mn on Ge-QDs, and by co-deposition of Mn and Ge at T>400°C. The elevated temperatures required to form QDs readily enable the formation of binary and ternary compounds based on Mn-silicides and -germanides.

We present a detailed set of studies with atomic level analysis (STM, TEM) of the formation and growth of the nanoscale structures, their protection with a Si or Ge cap, and combine the growth studies with analysis of the magnetic properties. In the Mn-interlayers the magnetization, and spin-orbit coupling can be directly related to Mn-Si, Mn-Ge and antiferromagnetic Mn-Mn bonding contributions. However, when compounds form they dominate the magnetic properties, and the presence of dilute magnetic semiconduction from substitutional Mn-inclusion in Ge-QDs made by co-deposition of Ge and Mn, remains an open question. A new set of experiments where we observe the transition from Mn$_5$Ge$_3$ to Mn$_5$ (Si,Ge)$_3$ will help to understand the magnetism in mixed silicide-germanide systems, which we suggest is responsible for the diverse Curie temperatures for Mn-Si-Ge systems reported in the literature.

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Superparamagnetic Self-Organization of Iron-Disilicide Nanoislands

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We grew self-organized arrays of epitaxial Fe-silicide nanoislands in UHV, ordered along step-bunch edges of vicinal Si(111) surfaces, and examined their crystal structure and composition by in-situ scanning tunneling microscopy (STM) and surface electron diffraction (LEED and RHEED) and ex-situ high-resolution transmission electron microscopy (HR-TEM) and x-ray photoelectron spectroscopy (XPS). We found that the step-decorating nanoislands had crystallized in a tetragonal $\alpha$-FeSi$_2$ structure, metastable in its bulk form below 1200°C and yet stabilized by a good lattice match at the $\{112\} || \{111\}$ interface with the Si substrate. Although contrary to the Fe-rich silicides, such as Fe$_3$Si, Fe-disilicides in general, and $\alpha$-FeSi$_2$ in particular, are not supposed to be magnetic, our superconducting quantum interference device (SQUID) magnetometry showed considerable superparamagnetism, with in-plane ~ 2.16 Bohr magneton/Fe atom at 4 K. This interesting phenomenon is thought to originate from a highly anisotropic shape of the flat-topped disilicide nanoislands containing excess Fe-cluster defects and elongated along the ordering (and hence the parent step-bunch edge) direction, and may have important implications in the field of nanomagnetism and nanomagnetic devices.
Growth of diluted magnetic germanium nanowires using manganese nano-droplets

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Self-assembled semiconducting nanowires (NW) are promising candidates for applications in nanoelectronics, optoelectronics, solar cells and sensors using carries confinement [1-4]. Although there have been extensive studies on the field recently, progress in designing more complex structures, such as branched or compositionally modulated wires, requires a clear understanding of nanowire growth mechanisms. One-dimensional semiconductor materials have been synthesized using a wide range of approaches with various advantages and limitations [5,6]. However seeded nanowire growth via the vapor-liquid-solid (VLS) [7] and vapor-solid-solid (VSS) [8] mechanisms is broadly exploited to direct the growth of nanowires of controlled morphology and composition [9]. While several reports have been published on the Si nanowire growth, using different NW preparation approaches, the growth of Ge nanowire has been scarcely documented despite quantum size effects are expected to be more prominent in Ge nanowires, considered that the excitonic Bohr radius of bulk Ge is much larger (24.3 nm) than that of Si (4.9 nm) [10]. Furthermore Ge has higher electron and hole mobilities than of silicon in which are expected to exhibit superior performances and are good candidates for nanoelectronic and spintronic applications. In particular, Ge1-χMnχ alloys (a so called diluted magnetic semiconductor: DMS) are considered a promising system for the design and fabrication of spintronic device. In particular, this system has recently attracted a great interest due to its compatibility with the Si based technology and its high Curie temperature (Tc) [11]. It is reported that highly Mn doped Ge alloys with χ>0.7 could be ferromagnetic up to 400 K. [12] while at high Mn dilution in the Ge matrix the system can behaves as a true DMS [13]. However, the synthesis of magnetic Ge NWs is still in its infancy.

In order to get the self assembled growth of magnetic Ge NWs we have been exploring the catalytic growth by using Mn nanodroplets as the growth seed. Several samples have been prepared by molecular beam epitaxy, as a function of the Mn equivalent thickness deposited on a Ge (111) substrate near room temperature, and then annealed at high temperature, in the range 550-650 °C. The size and surface distribution of the manganese nanoparticles on Germanium substrates, have been investigated by Atomic Force Microscopy (AFM). Producing Mn nanoparticles by annealing at high temperature showed nucleation in which the size and distribution of the nano droplets are strongly dependent on the thickness of Mn layer, temperature and duration of annealing. Attempts have been doing to grow Germanium nanowires by using Mn based nanodroplets via VLS and VSS growth methods. Although further studies on VLS growth of Ge ananowires along with the physical properties of these wires are undergoing.
Conversely, nanowires have been provided also by co-evaporation of the Manganese and Germanium at substrate temperatures below 400 °C. Samples have been characterized by several surface sensitive methods such as AFM, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and magneto optical Kerr effect (MOKE). It has been found that in case of co-deposition of the Ge-Mn the produced nanowires are kinetically induced resulting from the formation of a GeMn phase with a low eutectic point, not stabilized at low deposition temperature and which reduces the interfacial free energy of the Ge\textsubscript{1-x}Mn\textsubscript{x}/Ge system and drives the uniaxial growth of Ge NWs along specific crystallographic directions [14-15].

Selective Nucleation and Lateral Alignment of Epitaxial InAs Quantum Dots

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Advances in new generation devices for nanophotonics based on III-V Quantum Dots (QDs) rely on the capability to accurately control their size and lateral position on the substrate surface. In recent years, much experimental effort has been devoted to the search of methods to achieve position control of QDs [1]. For example, standard lithography has been intensely studied, however, albeit selective and flexible, it introduces defects that may severely decrease the emission efficiency of QDs and the performance of the device.

In this work, we present two different Molecular Beam Epitaxy approaches to obtain self-organization of InAs QDs. With the first approach, we demonstrate that the position of InAs islands grown on GaAs can be effectively controlled by exploiting a light anisotropy of the As4 flux, and the mound structures on the GaAs surface originated by growth instabilities. We show that at relatively high temperatures, QDs alignment along step bunching can be deterministically controlled as a function of the As4 flux direction. A true two-species rate equation model, where the two species, In and As, behave quite differently, has been developed to investigate the growth kinetics.

The second method is a bottom-up approach where InAs QDs self-assemble on nanoscale areas of the GaAs(001) surface defined by an e-beam-lithographed SiO2 mask. The SiO2 mask consists of matrices of circular/square shaped holes providing access to the GaAs substrate. The selective growth of a promisingly small number (1-5) of InAs dots inside the holes of the mask has been obtained by a suitable choice of the growth parameters and of the pattern size [2]. Emission from confined single dots has been clearly observed by μ-Photoluminescence (PL) with a radiative decay comparable to that of dots nucleated on the free surface.

Ionized Donor Bound Exciton Complex in an Inverse Parabolic Quantum Well:
Electric Field Effect

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In the present theoretical study, ground-state binding energy and excitonic oscillator strength of the ionized donor bound exciton complex (D+, X) in a GaAs/Al$_{1-x}$Ga$_x$As inverse parabolic quantum well (IPQW) subjected to a growth direction electric field have been investigated. Our numerical calculations are based on the potential morphing method (PMM) in the framework of the effective-mass approximation (EMA). The dependence of the binding energy and excitonic oscillator strength of the ionized donor bound exciton complex on all possible combinations of the involved parameters, as doping position, quantum well width, Al concentration at the well center and the strength of the applied electric field, has been obtained.

References


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Light emitting diodes with InAs/GaAsSb self-assembled quantum dot layer embedded in GaAs

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Structures with embedded InAs/GaAs quantum dots (QDs) are attracting considerable interest due to their potential applications in novel light emitting sources for optical fiber telecommunication bands of 1.3 and 1.55 μm [1]. In this paper, we report about optical properties of light emitting diodes (LEDs) suitable for these bands with active layer formed by InAs QDs covered by different GaAs\(_{1-y}\)Sb\(_y\) strain reducing layers (SRLs). LEDs were prepared by metalorganic vapor phase epitaxy (MOVPE) in AIXTRON 200 reactor on Si doped GaAs substrate using Stranski–Krastanow growth mode. TMGa, TEGa, TMIn, AsH\(_3\), TBA and TESb were used as precursors. The first GaAs buffer layer was grown at 650°C then the temperature was decreased to 510°C for the growth of the second GaAs buffer, InAs QD layer (growth interruption 15s), undoped thin GaAs\(_{1-y}\)Sb\(_y\) SRL and the GaAs cap. The rest of the structure (undoped GaAs, p-type and p\(^+\)-type C doped GaAs top anode layer) was grown at 650°C. Structures were characterized by atomic force microscopy (AFM) and X-ray diffraction. Optical properties of QD LEDs were measured between 10 – 320 K by photo-, electroluminescence (EL) and photocurrent spectroscopy. Results show that MOVPE grown LEDs with QDs (AFM shows 4-6 nm high InAs lenses) covered by GaAs\(_{1-y}\)Sb\(_y\) SRL exhibit strong EL which is red shifted from 1.2 to 1.4 μm with increasing Sb content. In all cases, the strong ground state emission is given by recombination of electrons and holes confined in the QDs while the emission from excited states, which dominates at lower temperatures, origins from states located in the SRL and the wetting layer. Fast thermal quenching of EL from excited states is then given by the escape electrons from the wetting layer and holes from SRL.

Structural transformation of MOVPE InGaN QDs during capping with GaN at high temperature

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Self-organized In$_{0.26}$Ga$_{0.74}$N QDs were grown in MOVPE at 650-675 °C by Stranky-Krastanov-growth mode. From AFM images at different thickness we estimated a wetting layer thickness of 4 nm [1]. Capping of such QDs with GaN was performed without growth interruption at 650°C, and by ramping temperature up to 920°C. After overgrowth at 650°C the QD height reduced from 3-4 nm to 2 nm on a 4 nm thick wetting layer. Overgrowth at higher temperatures did not dissolve the QD into a homogenous QW, contrary to many reports (for example [2] ). In our case 4-6 nm thick layers were formed with strong 15 to 160 nm long lateral fluctuations of indium concentration. Z-contrast imaging, generated by high angle annular dark field scanning transmission electron microscopy, energy dispersive X-ray spectroscopy and electron energy loss spectroscopy (EELS) clearly identify that these region as partially relaxed wurtzite phase containing up to 80at% of In. Metallic indium platelets similar to ones reported in [3] were found. Metallic indium was recognized by the characteristic plasmon peak in EELS and by analysis of Cs-corrected HRTEM images. We assume the formation of such structures is driven by strain which occurs between higher indium content in QDs and the wetting layer containing 20-30at% of indium.

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High-density uniform quantum dots in narrow-gap InSb/InAs(Sb,P) system


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We report on study of structural, transport and optical properties of narrow-gap type II heterostructures with InSb QDs inserted into the InAs-based matrix. The self-assembled InSb QDs were obtained on the (100)-orientated surface under Stranski-Krastanow growth mode. The high density (2*10^{10} cm^{-2}) uniform QDs with dimensions of 3 nm in height and 14 nm in diameter were found to be dislocation-free without any extended defects. Structural parameters of the InSb QDs such as size, shape and internal strain will be demonstrated and discussed. Use of the multicomponent Ga-In-As-Sb and In-As-Sb-P solid solutions lattice-matched with InAs substrate as matrix layers leads to a considerable change of the surface chemistry of a matrix material and allows controlling size distribution and sheet density of the InSb QDs deposed. High-resolution TEM cross-section images of the free-standing InSb QDs and ones buried into the InAs(Sb,P) matrix were obtained for the first time.

Local I-V characteristics of the single InSb QD situated on the InAs-rich surface were studied by scanning probe microscopy at room temperature to investigate tunnelling carrier transport through the confined states. Intense positive and negative electroluminescence (EL) for the mesa-diode heterostructures with the InSb QDs was found in the spectral range 3-4 μm at temperatures 77-300 K. Evolution of the EL spectra in dependence on applied external bias was observed. The energy band diagram of the InSb/InAs(Sb,P) heterostructure with a type II quantum dot at the heterointerface will be proposed.

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Photoluminescence and Raman studies of InN-GaN nano-heterostructures selectively grown in small holes of an oxide mask using Metal-Organic Vapor Phase Epitaxy

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InN-GaN pyramids were prepared by selective area Metalorganic Vapor Phase Epitaxy (SA-MOVPE) in small holes of an SiO₂ layer. The oxide layer was obtained after annealing an HSQ layer (hydrogen-silsesquioxane-H₈Si₈O₁₂) which coated a 2 µm thick GaN on sapphire template. E-beam lithography was used to produce hexagonal arrays of holes with a diameter of 50-200nm and with a hole to hole distance of 3 µm. The SA-MOVPE of ordered GaN pyramid arrays and their optical properties has been reported previously [1]. Using the same technique, InN dots were deposited on SA-grown GaN pyramids as well as directly as pyramids in mask holes on the template. The spectral photoluminescence (PL) of our wellordered InN dots investigated as a function of temperature and laser power intensity exhibits a similar behavior as those of InN nanowires obtained by MBE growth [2]. The energetic position of the PL peak is about 750 meV and slightly dependent on the growth parameters. The efficiency is linearly dependent on the laser excitation power and almost constant up to 100 K. The PL intensity decreases at higher temperatures with a deactivation energy of about 20 meV. Further structural and morphological studies of the nanostructures using AFM, SEM and µ-Raman spectroscopy will also be presented. The obtained InN-GaN dots in nano-heterostructures selectively grown in regular arrays with precise localization are very promising for nano-optoelectronic applications. Up to now, nanopyramid InGaN light emitting diode structures, synthesized in a less-controlled fashion by SA-MOVPE using self-organized porous anodic alumina have been reported [3].

Micro-Raman phonon scattering by InAs/AlAs quantum dot superlattices

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Semiconductor nanostructures such as superlattices and quantum dots (QDs) offer unique opportunity of engineering their electron and phonon spectra with the most appropriate properties for nanodevices. Among other optical techniques Raman spectroscopy is considered as the most informative method for determining phonon spectra of semiconductor nanostructures [1].

We present the results of micro-Raman scattering study of acoustic and optical phonons of InAs/AlAs QD superlattices.

Samples composed of 20 periods of InAs QD layers with a nominal thickness of 2.8 monolayers separated by 8 nm of AlAs were grown by molecular beam epitaxy in the Stranski-Krastanow growth mode.

Raman scattering from the planar surface and the cleaved (110)-oriented edge of the nanostructures was investigated. A microscope was employed to focus the light to a 1 μm spot. Doublets of folded longitudinal acoustic (FLA) phonons up to 4th order were observed in the Raman spectra measured in the z(x,x)-z scattering geometry whose energy positions are well described by the elastic continuum model of Rytov [2]. The in-plane Raman scattering spectra measured in the y’(x’,x’)-y’ geometry reveal the changing energy positions and intensities of the FLA doublet components which are consistent with the changing effective wave vector in the nanostructures induced by the momentum transfer of the light. The Raman selection rules for the FLA phonons with different symmetries are discussed.

Beside the acoustic phonons the spectra display features related to confined transverse and longitudinal optical as well as interface phonons in QDs and spacer layers whose frequency positions are discussed in terms of phonon confinement, elastic stress and atomic intermixing.


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Nanostructured Oxide Surfaces for Advanced Applications: from Individual Building Blocks to Functional Films

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The synthesis of oxide layers with tailored structural and functional properties is of paramount importance for a number of applications ranging from sensing and biotechnologies to photovoltaics and catalysis/photocatalysis. Pulsed Laser Deposition (PLD) in a background atmosphere is here shown to be a versatile technique for the synthesis of nanostructured surfaces and thin films with a fine control of structure and morphology at the nm/μm scale, even at room temperature, since it allows cluster nucleation and tuning of their deposition kinetic energy and oxidation [1].

We first discuss how the use of in-situ Scanning Tunneling Microscopy (STM) characterization permits to investigate and control the size, kinetic energy regime and aggregation/growth mechanisms of the individual building blocks in the PLD process (with particular reference to the case of W and Pd nanoislands on different surfaces [2]).

We then present examples of functional oxide films developed in view of different applications, e.g. self-assembled hierarchical tree-like TiO₂ surfaces as novel photoanodes for dye-sensitized solar cells (DSCC) or hybrid oxide-polymer solar cells, with a potential also for photocatalysis and proteomics [3]; room temperature synthesis of Al:ZnO nanostructured transparent conductive oxides (TCO) with controlled structure, doping and mesoscale morphology for improved light management in organic/hybrid photovoltaics [4]; WO₃ nanorods/nanoparticles for chemical gas sensing [5].

References:
Multifunctional arrays of dendronized iron oxide nanoparticles

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Self-assembly of nanoparticles (NPs) into tailored structures is a promising strategy for the production and design of materials with new functions. Furthermore, modulation of the particle interactions has a pivotal influence on the structure and the quality of the NP assemblies. The interparticle interactions in these arrays may be tuned by controlling the interparticle distances (ID). Few studies are devoted to the modulation of the ID in 2D arrays, since the modification of NP surfaces may affect the deposition conditions and also the NP properties. In this work, the ID in 2D arrays have been modulated by grafting dendrons at the surface of NPs. Dendrons display an arborescent structure which allows one to bring together a variety of functionalities and control ID by the generation number of the dendron. Iron oxide NPs of 10 nm diameter have been functionalized with linear and branched dendrons displaying fluorescent properties. Then their organization into uniform 2D arrays has been achieved over large areas with a high density using the Langmuir-Blodgett technique: the anchoring agent and Janus structured of NPs have been shown to be key parameters driving the deposition. Finally the influence of the anchoring agent and the ID on the collective magnetic properties has been clearly demonstrated by DC and AC SQUID measurements. The dipolar interactions as predicted by theoretical simulations vary strongly with ID and don’t affect the dendron’s fluorescent properties.
Energy Level Alignment and Electronic properties at the dye/ZnO interface: a Ultra-High Vacuum investigation on nitrocatechol adsorption on ZnO(10-10) surface

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Catechol chromophore adsorbed on single-crystal ZnO non-polar surfaces has recently attracted wide interest as model system to study the electronic and structural properties of dye-sensitized oxide interfaces, in view of possible application in photovoltaic devices[1-3]. It has been recently proposed that tuning of the interface electronic properties can be achieved by tailoring the dye moieties, for instance by adding suitable lateral functional groups [3].

In this work, Ultra-High-Vacuum deposition of nitro-catechol on the single-crystal ZnO(10-10) surface has been experimentally investigated by means of Ultraviolet and X-ray Photoemission spectroscopies (UPS and XPS) and High-Resolution Electron Energy Loss Spectroscopy (HREELS). In particular, energy level alignment of molecular filled states, adsorption induced work function variation and band bending at the interface has been investigated. A work function increase of more than 1 eV has been observed, which can be ascribed to the molecular intrinsic dipole moment. Furthermore, UPS valence band measurements clearly show that the molecular HOMO lies inside the ZnO gap, thus confirming the type –II character of this interface. Comparison with DFT theoretical calculation are also presented and discussed.

Clathodoluminescence characterization of ZnO Tetrapod structures

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ZnO micro- and nanostructures are excellent candidates for use in ultraviolet (UV) and white light emitters devices, owing to their direct and wide band gap and large exciton binding energy. Furthermore, an ability of ZnO to easily crystallize in differently shaped low dimensional structures with good crystalline quality is beneficial for deliberate tailoring of material properties towards desired applications. In order to fully realize the potential of ZnO nanostructures for device applications, their material-related properties need to be fully understood and optimized. Such understanding, however, is currently not complete. For example, though higher defect densities in the nanostructures have often been concluded, spatial location of the defects and causes for their formation remain controversial. Also not known are effects of surface morphology on properties of ZnO micro-cavities.

The purpose of the present study is to clarify these issues by performing cathodoluminescence (CL) characterization of individual ZnO tetrapods grown by thermal evaporation. Their high optical quality is concluded based on the observation of intense free excitonic (FE) emission at room temperature and a low intensity of the so-called green emission (GE). CL mapping has revealed that the defects responsible for the GE are mainly located in core regions close to legs junctions. Variations of the spectral positions of the FE emission with the diameter of the tetrapod legs were also observed and attributed to formation of whispering gallery mode polaritons within the tapered microcavity. These findings are of importance for further optimization of micro- and nonstructured ZnO for future opto-electronic applications.
Protein coated silica magnetic nanoparticles for environmental and medical applications

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This talk will present two applications of protein coated silica magnetic nanoparticles. In first part, an enzyme-silica magnetic nanoparticle conjugate is prepared via conjugation of Ni$^{2+}$ ions onto the surface of silica magnetic nanoparticles to interact with a six histidine-tagged enzyme. The catalytic properties and enzyme rigidification of the conjugates are more stable at high concentration of aromatic hydrocarbons. In second part, multimeric protein Gs coated silica magnetic nanoparticles were prepared for the effective and self-oriented immobilization of antibodies. Amino-functionalized silica-coated magnetic nanoparticles (SiO$_2$-MNPs, Fe$_3$O$_4$@SiO$_2$) were prepared and coupled to the protein G multimers, giving the final magnetic immunosensor. Cysteine-tagged recombinant dimers and trimers of protein G were produced in Escherichia coli BL21 by repeated linking of protein G monomers with a flexible (GGGGS)$_3$ linker. The use of multimeric protein Gs had the higher antibody immobilization when compared to monomeric protein G. Finally, sensitivity of the HBsAg immunoassay is enhanced 10-fold when the trimeric protein Gs was used in place of the monomeric protein G to immobilize antibody.

Microscopic studies of polymer-wrapped nanotubes for solar cells

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Conventional solar cells based on Si are still expensive; their production requires high temperature and a large amount of energy, causing environmental concerns for their extensive application to solve the global energy crisis. The discovery of fullerenes [1] and conducting polymers at the end of last century[2], opened a new avenue, offering the possibility to create solar cells by using simple and environmentally friendly chemical processes. Solar cells based on polymer-fullerene mixtures (bulk-heterojunction) recently achieved 8% efficiency[3], sparking enthusiasm all over the world, but several hurdles still limit a widespread application of this technology. Our group recently obtained very high resolution images [4-6] of polymers wrapped on carbon nanotubes (Fig. 1) and local spectroscopic measurements on covered and uncovered section of the nanotube opening the way to a better understanding of the charge transfer in these nanostructures. Recent reports based on photoluminescence measurements suggest that charge separation can be obtained by using single wall semiconducting nanotubes [7], while other researchers found that efficient charge separation is also possible with metallic nanotubes [8].

In this talk, recent Scanning Tunnelling Microscopy and Spectroscopy investigations on mixtures including selected semiconducting or metallic nanotubes will be presented, unveiling interesting physical phenomena occurring in these nanostructures.

References
Development and characterization of polymer nanocomposites using carbon nanotube – silica hybrids as reinforcing fillers

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In recent years, carbon nanotubes (CNTs) have been the focus of considerable research because of their unique properties and tremendous potential applications. For their exceptional mechanical properties and low density, CNTs are used as novel fillers to reinforce many kinds of materials including metal, polymer and ceramic. Furthermore, CNTs possess fascinating electrical properties. These excellent electrical properties combining with exceptional mechanical properties make CNTs candidate for fabricating composites polymers conductors with good mechanical properties.

On the other hand, silica particles (SiO$_2$) have attracted a keen scientific interest due to their fundamental and practical importance in materials science. Nanostructure based on silica nanoparticles has found extensively applications in areas like optoelectronic devices, photonic crystal, and chemical/biological sensor.

In this context, we envisage to develop new polymer nanocomposites using CNTs/SiO$_2$ hybrids as reinforcing fillers. Indeed, the physicochemical properties of the nanotubes are uniquely combined with those of the silica constituent, thereby leading to remarkable functionalities that do not exist in the individual components.

A simple method to graft carbon nanotube on silica microparticles surfaces was developed. This method is based on the covalent bonding interaction between carboxylic acid-functionalized carbon nanotube (CNT-COOH) and amino-functionalized silica microparticles (SiO$_2$-NH$_2$). Indeed, amino-functionalized silica microparticles were prepared by a silanization with 3-aminopropyltriethoxysilane (APTES), while carboxylic acid-functionalized carbon nanotubes were prepared by acid treatments (a mixture sulfuric acid/nitric acid) [1].

In this study, we describe the preparation of carbon nanotube – silica – PVA composites films. The dispersion and morphology of nanoparticles were investigated by Scanning Electron Microscopy (SEM) and Transmission Electron Micrographs (TEM). The mechanical properties were performed by tensile tests.

The experiments show that the mechanical properties of the composites are highly dependent on the dispersion and the microscopic orientation of fillers in the polymer matrix and their interfacial interactions with the polymer. Furthermore, we observed an improvement of mechanical property and electrical conductivity at the same time. The thermal stability of PVA composite was promoted greatly by adding nanofillers.

Reference:

Super-strained epitaxial growth of metal islands on multiwalled carbon nanotubes

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The engineering of composite carbon-based materials through the decoration with metal nanoparticles has proved to be key for the improvement of the intrinsic physico-chemical properties of graphene and carbon nanotubes (CNTs). Although the role of the metal-carbon interface in the catalysis of carbon nanotubes is already being studied, a clear picture of the fundamental processes involved in nucleation and growth of metals on graphene lattice has until now been unavailable. Differently from the simpler case in which nanoparticles adhere to the tubes via short-range potentials, when nanoparticles grow epitaxially, the strain energy due to the lattice misfit has to be considered. Here we show the first direct experimental evidence of the local microscopic imprint left by Au, Ag and Cu island nucleation on the carbon nanotube walls (Fig. 1). The weak interaction between noble metals and graphene substrate leads to the formation of disconnected particles with \{111\} crystal orientation [1], following the Volmer-Weber mechanism. The key role played by the strain energy relaxation in determining the morphological reshaping of metal decorated carbon nanotubes is investigated. The island footprint is a result of the strain energy relief and it proves the pseudomorphical character of the system, even in the case of high lattice misfit (~15% for Au and Ag). Finite-element simulations within continuum elasticity theory indicate that the super-strained epitaxial growth is made possible by relaxing the elastic strain energy of the system through the observed local deformation of the tube walls. A very good match between the data provided by transmission electron microscopy and the simulated strain induced deformation is found.

Reference

Fig 1. Au nanoparticle imprint on CNT. High-resolution TEM image of an Au island grown on a MWCNT. In the inset, the Fast Fourier Transform performed on the image shows two main contributions: one coming from the graphene planes, as pointed out by white arrows (0.34 nm), and one from the Au (111) crystal planes (red arrows, 0.235 nm).
Kondo impurities in nanotubes

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The Kondo effect of a transition metal impurity atom on a metallic carbon nanotube will influence electron transport, leading to zero bias anomalies in the conductance. Applying the density functional plus numerical renormalization group approach of Lucignano et al. [1], we explore this problem from first principles, specializing to Co (S=1\(\frac{1}{2}\)) and Fe (S=1) impurities adsorbed outside or inside (4,4) and (8,8) single wall nanotubes [2,3]. The predicted Kondo temperatures and zero bias anomalies, small outside the nanotube, turn large and strongly radius dependent inside, due to a change of symmetry of the magnetic orbital. These results foreshadow an interesting field and temperature dependence conductance, to be addressed in future experiments.

FePt(L10)@MWCNTs/Ru(NPs):
A smart nanocomposite for catalysis applications

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Heterogenic catalysis is frequently carrying out with heavy metals, which are generally expensive and pollutants. The problems increase if the catalysts are used at nanometric scale because it is easier to lost material during the working cycle. This problem has doubled if we also consider the environmental pollution cost due to the nature of the metals and the nanoparticles (NPs) pollution (see asbestos problems). Usually, nanometric metal catalyst is supported on inert material like alumina or silica. In the last ten years carbon nanotubes (CNTs) have been also used as support in catalysis research. CNTs are one or more graphene rolled sheets. This structure allows having an empty internal cavity and an external wall. Often, CNTs support metal NPs on the external side and the empty nanocavities could be used to add other property to get a very smart new nanocomposite with more peculiar properties. Therefore, CNTs could be decorating with metals NPs outside and magnetic NPs inside. The magnetic character could be exploited: i) to move the nanometric catalyst by applying a magnetic field gradient, ii) to locally increase the temperature by applying a AC magnetic field, saving energy to heating the whole reactor.

In this work the authors describe a new synthesis method to produce a three blocks nanocomposite formed of FePt NPs (L10 phase) inside, and Ru NPs outside MWCNTs and indicate as: FePt(L10)@CNTs/Ru(NPs), with out mix the different nanoparticles. In this nanocomposite the catalytic and magnetic property are together available. The products are characterized by TEM, HRTEM, SEM, XRD and magnetic measurements. To the best of our knowledge this is the first case of this kind of three block nanocomposite based on CNTs, and because to fill the cavity the author used a general wet method, and a lot of decoration methods are proposed in the literature and can be used here, our method can be considered a general wet method to get this three block nanocomposites. The property of separate nanoparticles and CNTs can be combined in many ways as: catalytic-magnetic, catalytic-optics, optics-magnetic or other and could be useful in many applications like medicine, electronics or energy.

References

SILVER NANOCOMPOSITES THIN FILMS GROWN BY PULSED LASER DEPOSITION


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Nanocomposites thin films based on silver nanoparticles (NPs) supported and/or embedded on/in various matrices have been widely investigated for their appealing chemical and physical properties. The possible applications domains include biochemistry, environment, medicine, catalysis, electronics and optics. The mutual interactions between silver nanoparticles and their surroundings result in peculiar features not displayed by the metal alone. Pulsed laser deposition (PLD) has been successfully been used to produce such embedded noble metals NPs.

We report the deposition of Ag embedded in different matrices thin films by laser ablation (PLD). Three type micro- and mesoporous host materials have been used : i) Mg-Al based layered doubles hydroxides LDHs ii) mesoporous SBA-15 and/or MCM-41 iii) zeolite A and zeolite ZSM-5. LDHs are synthetic anionic clays with brucite [Mg(OH)2]-like layers in which some of divalent cations have been replaced by trivalent ions. The layers are bound together by the interlayer counter anions and by water molecules. The host materials MCM-41 and SBA-15 are 2D ordered mesoporous silica materials with pores sizes ranging from 2 to 30 nm. Zeolites are microporous crystalline silica materials with pores sizes ranging from 2 to 10 Å sized channels. Cations balance the negative charge of the zeolite lattice and water molecules are present in the channels.

X-Ray Diffraction, Atomic Force Microscopy, Scanning Electron Microscopy combined with energy dispersive X-ray analysis and Secondary Ions Mass Spectrometry were the techniques used for the investigation of structure and the surface morphology of the deposited films. Optical absorption properties of the Ag nanocomposite thin films were also investigated.
Lasing performance of organic heteroepitaxial nanofibers realized by periodic deposition of \textit{para}-sexiphenyl and sexithiophene on muscovite

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Vacuum deposition of \textit{para}-sexiphenyl (p-6P) on muscovite is known to yield linear aggregates of co-oriented nanocrystals, usually referred to as \textit{nano}fibers [1,2], which have precise epitaxial relationships to the muscovite substrate [3]. These epitaxial nanofibers exhibit important optical properties, such as highly polarized blue luminescence [1] and laser action [4,5], which could be exploited for applications in photonic and sensing technologies [6]. Recent advances in the field include (i) the achievement of highly polarized, red-green-blue (RGB) emission from epitaxially aligned bilayer nanofibers obtained upon deposition of sexithiophene (6T) on p-6P/muscovite templates [7], and (ii) the development of a roll-printing technique for high-yield and massive transfer of nanofibers from the native substrate to a receiving substrate for device applications [8].

We report successful tuning of laser wavelength from \(\sim\)420nm to \(\sim\)600nm in epitaxially aligned nanofibers grown by \textit{periodic} deposition of p-6P and 6T on p-6P/muscovite templates. The nanofibers are photoexcited by subpicosecond pulses tuned to the lowest p-6P absorption band, and the emission of 6T, whose coverage is kept in the submonolayer regime, is efficiently sensitized through resonance energy transfer [9]. 6T lasing is achieved at room temperature with threshold fluences as low as \(10 \, \mu\text{J/cm}^2\) per pulse. Transient photoluminescence measurements with picosecond resolution show that at these pump fluences the decay dynamics of 6T emission is independent of the excitation density, thereby demonstrating the attainment of room-temperature \textit{monomolecular lasing} from epitaxially oriented 6T submonolayer aggregates. Main lasing properties remain unaltered upon direct photoexcitation of 6T below the p-6P absorption edge [10].

\textbf{References}
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Modeling morphology and electronic properties of organic oligomers on ZnO

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Hybrid systems made of conjugated organic molecules and inorganic semiconductors are attracting great interest in recent years since they combine the favorable features of both components in a single new material [1]. Driven mainly by photovoltaic applications, much attention has been paid to the linkage between organic dyes and polymers with zinc oxide surfaces [2]. Accurate characterization of these interfaces remains an open issue due to the difficulty in measuring properties across a single junction at the nanometric and sub-nanometric scale. This challenge makes atomistic simulations an important tool for understanding and predicting the interfacial morphology and electronic properties. Here, we perform a combined model potential molecular dynamics plus density functional theory study on hybrid systems composed by oligothiophene derivatives adsorbed on ZnO. We investigate the energetics of adhesion and the morphological features at the interface as well as the electronic and optical properties of the hybrids considered [3].

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References
Theoretical design of self-assembled interlayers for efficient photoconversion at polymer/metaloxide interfaces

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Polymer metaloxide hybrids have emerged as promising systems for future solid-state photovoltaics. The actual microstructure of the polymer/metaloxide interface critically controls the photoconversion efficiency that is still too low[1]. Here we adopt molecular dynamics to generate models of polymer/metaloxide interfaces (e.g. P3HT/ZnO[1,2]) and we study the effect of molecules that can self-organize at the interface. We consider both the cases of optically active metal-organic macrocyclic complexes (e.g. zinc phthalocyanines ZnPc’s[3]) and small organic heterocyclic compounds. As for the first case, we provide evidence that ZnPc’s lie parallel to the ZnO surface and self-assemble into elongated stripes[2] that are able to red-shift the optical absorption and are beneficial for charges injection. As for the second case, we consider ordered interlayers formed by heterocyclic molecules covalently bonded to the metaloxide. By suitable choices of the molecules, the corresponding interlayer is able to improve the polymer organization at the interface, and eventually the photoconversion efficiency[4]. This work is funded by the Italian Institute of Technology (IIT) Seed Project “POLYPHEMO” and Regione Autonoma della Sardegna.

References
Atomistic investigations of the P3HT/ZnO interface by including solvent effects

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Hybrid nanosystems are extensively studied for low cost photovoltaics. Systems formed by poly(3-hexylthiophene) (P3HT) and ZnO allow to combine the excellent transport properties of ZnO with the tunable optical properties of the polymer [1].

We studied the P3HT/ZnO interface by means of classical molecular dynamics methods and we provide evidence that the polymer is likely disordered close to the ZnO surface, even in ideal conditions. To prove this result, we analyzed how the molecules stack within realistic models of interface by quantifying the unavoidable disorder induced by the surface. To study the effect of the interface microstructure on charge transport, we calculate the corresponding hole mobility by developing an effective model based on first principle calculations of the intermolecular transfer integral [2].

Furthermore we focus on the issues related to the possible presence of residual solvent at the interface. By studying the interaction between ZnO and the THF solvent we found that the latter binds to the surface, resulting in a molecular layer of THF spontaneously formed at the interface that affects the morphology of the system.

Finally the assembling of the polymer on the ZnO surface in presence of solvent is studied [3].

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Synthesis of two-dimensional polymers on surfaces

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The controlled growth of covalent organic frameworks at surfaces (two-dimensional polymers) is a crucial point for the development of robust molecular nanostructures that could have applications in ambient conditions. Recently we have obtained a fully conjugated organometallic sheet using a metal-directed approach\(^{(1)}\). Iron atoms and 1,2,4,5-tetracyanobenzene (TCB) molecules were evaporated onto various substrates in ultra-high vacuum, leading to the direct synthesis of either phthalocyanine molecules, or two-dimensional phthalocyanine polymers.

By adjusting metal and molecule fluxes one could form FePc(CN)\(_8\), with the ratio Fe/TCB = \(\frac{1}{4}\), or a 2D Fe-Pc polymer with the ratio Fe/TCB = \(\frac{1}{2}\). When FePc(CN)\(_8\) molecules are obtained they can self-assemble by the way of hydrogen bonds leading to the formation of a supramolecular network similar to networks obtained from M-PcX\(_8\) molecules directly evaporated on surfaces (X = F, Cl).

The Fe-Pc polymer has been grown in patches of limited lateral extension on various oriented metal surfaces: Ag(100), Ag(111), Au(111). Remarkably the polymer was also readily grown onto thin insulating NaCl films deposited on Ag(100)). The latter situation is very favourable for the growth a defect free Pc polymer, which can be spread over large areas. The Fe-Pc 2D polymer appears generic of a new class of two-dimensional materials, whose properties could be tuned either by changing the central cation or the ligands.

\(^{(1)}\) Single layer of polymeric Fe-phthalocyanine: an organometallic sheet on metal and thin insulating film

M. Abel, S. Clair, O. Ourdjini, M. Mossoyan, L. Porte
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Thermoelastic force-extension behavior of polymers with elastic bonds

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Stretching experiments on arbitrarily long single molecules opened the way for studying the statistical mechanics of small systems with relevant applications to structured materials of biological interest. The results of stretching performed on the double-stranded DNA has been found to be in very good agreement with some analytical treatments of the worm-like chain (WLC) model [1,2] while being only in partial agreement with the freely jointed chain (FJC) model; the latter model typically provides, however, a better fit for single-stranded DNA and RNA [3]. This results and successive experimental evidences suggested that the mechanical properties of DNA, and in particular its flexibility (described by the persistence length) [4], have a relevant role in many biological process [5]. The importance of understanding the force-extension relationship for macromolecules has therefore attracted the attention of theoretical physicists and mathematicians, who produced several models and relationships to explain the experimental results. This contribution deals with the thermoelastic response of a single chain under stretching with two specific features: the extensibility of the bonds between the monomers and the possibility to be far from the thermodynamic limit (arbitrary number of monomers). These points are very important for understanding the structure and the assembly features of several biological molecules and tissues. In many cases in which the thermodynamic limit is not satisfied (relatively short polymer chains), different macroscopic boundary conditions yield different macroscopic force-displacement curves, or constitutive equations [6,7]. We formulate analytical expressions to quantitatively evaluate the difference between the behavior of the Helmholtz (imposed end to end distance and measured force) and the Gibbs (imposed force and measured distance) ensembles for a wide range of polymer models of biological relevance, including generalizations of the freely jointed chain model and of the worm like chain model with extensible bonds. In both cases we draw some comparisons between the analytical treatment and the Monte Carlo simulations. In particular we evaluate the critical exponents describing the convergence of the system (with an increasing number of monomers) towards the thermodynamic equilibrium (where the Helmholtz and the Gibbs ensemble lead to the same behavior).

References
Nanofibers and Characterizations of Polypyrrole /Poly(Acrylonitrile-co-Methylacrylate) Composites

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Conductive polymers and their composites are being interested frequently in recent years due to their usability for sensors, batteries, smart windows, electronic devices, etc [1]. Polypyrrole is one of the most preferable conductive polymer due to its easy polymerization, high conductivity and good thermal stability. However, it’s mechanically weak properties such as brittleness and hard processibility necessitates to copolymerize it with insulating polymers to improve their mechanical properties without loss of conductivity [2]. In this study, acrylonitrile and methylacrylate were copolymerized by emulsion polymerization with the presence of ammonium persulfate and surfactive dopant sodium dodecylbenzenesulfonate. Acrylonitrile was chosen since it is one of the most popular monomers of chemical and textile industry due to its excellent properties to be used in various applications [3]. Hydrophobic interfacial properties of methylacrylate provide to obtain core-shell composite structures [4]. Then pyrrole was added into polymer emulsion. Resulting polymers were characterized in terms of conductivity, morphology, particle size and chemical structure. Nanofibers were obtained by the electrospinning method. The effect of the PPy content on the resulting nanofiber composites was characterized by spectroscopic, morphological, mechanical and conductivity measurements.

Fig. 1: Schematic Copolymerization Mechanism of Core-Shell Conductive Nanoparticles

References
Confinement effects of a nanoporous network on the Copper surface

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The perylene derivative DPDI (4,9-diaminoperylene-quinone-3,10-diimine) forms a very stable nanoporous network on Cu(111) crystals upon thermal dehydrogenation.[1] This remarkable stable hexagonal network has been intensively investigated and has proven to serve as an ideal structure for the studying of host-guest assemblies.[2] The pores of the dehydro-DPDI network act as quantum wells confining surface states of copper electrons and thereby producing 2D arrays of quantum dots.[3] The DPDI network was predicted to consists of dehydrogenated DPDI forming hydrogen bonds but the recently obtained data[4,5] hints at the possibility that DPDI is bound through a complex coordination network which includes copper adatoms after thermal activation/dehydrogenation. A new model has now been developed, where the DPDI is expected to undergo three dehydrogenation steps in total as well as an additional cyclization step (see Figure 1.). The hereby obtained “dehydro-DPDI” is then postulated to form the coordination network. Theoretical studies as well as recent experimental results obtained by Normal Incidence X-ray Standing Wave (NIXSW) technique strongly support this new model.
Figure 1(a) postulated reaction pathway involving three dehydrogenation steps as well as a cyclization step yielding the “tridehydro-DPDI”; (b) postulated coordination network of tridehydro-DPDI; (c) honeycomb network of tridehydro-DPDI simulated by first principle calculations.

References


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Nanoscale effects on polymer-ZnO hybrids for photovoltaics

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Hybrid devices formed by low-dimensional nanostructures (e.g. ZnO nanoneedles and nanodots) and conductive polymers (e.g. thiophene derivatives) are promising systems for third generation low cost photovoltaics. Nevertheless their efficiency is still too low to be competitive with Si-based solar cells [1] and a deeper understanding of nanoscale phenomena in such systems is required. For example, it has been observed that polymer chains can helically wrap nanostructures, with sizable effects on optical and transport properties. Here, we study hybrids consisting of thiophene derivatives and ZnO nanostructures (nanoneedles and nanodots) by a combined model potential and density functional theory approach, providing evidence that helical configurations occur on nanoneedles [2]. The local curvature of ZnO nanodots induces a specific electronic coupling between the inorganic and the organic component that affects the energy-level alignment at the interface. The effects on the charge separation efficiency are discussed [3]. This work is funded by the Italian Institute of Technology (IIT) under Seed Project “POLYPHEMO” and Regione Autonoma della Sardegna under L.R.7/2007.

References
Nanocomposites properties variation under UV-exposure

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Novel materials composed of nanoparticles (NPs) embedded in various matrices attracted a lot of interest during past decades. Wide possibilities to combine size-dependent properties of NPs with advantages of various matrices facilitate creation of nanocomposites with the properties required for diverse applications ranging from electronics to medical studies. Colloidal semiconductor NPs in polymers are among the most intensely studied materials. Polymers are convenient media for NPs, however, they are known to degrade under ionizing radiation, which can change the properties of nanocomposite as a whole. We report the study of the influence of ultraviolet (UV) light on light-emitting properties of the composite nano-CdS/polyvinyl alcohol (PVA). It is shown that UV-irradiation induces strong non-monotonous changes of the luminescence intensity and monotonous shift of its maximum wavelength. The kinetics of intensity changes is qualitatively similar in composite and in unloaded PVA but the processes in composites demonstrate lower rates. This behavior is attributed to the interplay between formation of new light-emitting species both within PVA and at NP/PVA interface, on the one hand, and emerging and healing of non-radiative recombination channels, on the other hand.
The Voltage Effect on Impedance of Polythiophene Obtained from Boron Trifluoride Diethyl Etherate Solution

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Conducting polymers have attracted more attention due to their high conductivity, facile switching properties, and controllable optical properties [1]. Being an important member of conducting polymers, thiophene (Th) and their derivatives are especially interested by scientists because of their relatively low band gap. During the past decade, boron trifluoride diethyl etherate (BFEE) was used as a solvent and supporting electrolyte for electropolymerization of monomers having high oxidation potential [2]. In our study we present that Th can be polymerized in BFEE electrolyte solution on ITO-PET at 100 mVs⁻¹ scan rate at potential range of 0-1.5V. The monomer was oxidized at 0.9V under these conditions. The electrochemical impedance data of poly (Th) coated electrode were investigated at different applied DC voltages (-0.6V/to +0.6V). The characterizations of the polymer were performed by using Fourier Transform Infrared (FTIR-ATR) spectra for structural analysis, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) for morphological analysis, Cyclic Voltammetry (CV) and Electrochemical Impedance spectroscopy (EIS) for electrochemical analysis. [3] EIS and Equivalent Circuit modeling (ECM) were employed to investigate the electrochemical behavior of the polymer obtained on ITO-PET/Poly (Th)/electrolyte system. Double layer capacitance (Cdl) value is changed from 4.522 mF to 0.629 mF at range of (-0.6V)-(+0.6V), as well phase angle changed from 80 to 70°. The FTIR-ATR results indicate that the dopant anion included in the structure of resulting polymer. R(C(R(QR)))CR equivalent circuit model was found in simulation of the impedance data of the film.

Key word: Thiophene, BFEE, Electrolys, Electrochemical Impedance Spectroscopy, Atomic Force Microscopy.

![Fig.1. Bode Magnitude and Phase plot of poly(Th) coated ITO-PET electrode.](image)

References:
Layering transition in thin films of partially fluorinated bolaamphiphiles at the air-water interface

Jan Paczesny* (1), Krzysztof Sozański (1), Patrycja Nitoń (1), Andrzej Żywociński (1), Marcin Fiałkowski (1), Robert Holyst (1), Benjamin Glettner (2), Robert Kieffer (2), Carsten Tschierske (2), Damian Pociecha (3) and Ewa Górecka (3)

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Partially fluorinated bolaamphiphiles of different shapes studied in this work exhibit a layering transition from monolayer to multilayer films when spread on the air-water interface and compressed using Langmuir technique. The monolayers do not collapse during compression and ordered lamellar structures are formed instead. The balance between rigidity and flexibility of the molecules, adjusted by partial fluorination and the shape of the molecules, seems to be the key factor to avoid irreversible aggregation of the molecules and to create ordered multilayer structures. Several peaks and plateaus corresponding to layering transitions were observed in the Langmuir isotherms of the investigated compounds. The first plateau always corresponds to the formation of a trilayer. Further compression gives different results depending on the shape and degree of fluorination of the molecules. Only partially fluorinated compounds give well defined multilayers created in reversible process. Anchor-shaped bolaamphiphiles form a trilayer and, subsequently, a 9-layer film due to a double roll-over mechanism. In contrast, when the trilayer films of X-shaped bolaamphiphiles are compressed, 5-layer and 7-layer films are created according to another mechanism. X-ray reflectometry (XRR) was used to measure the thickness of the layers. Perfect fits of the XRR data to theoretical equations allowed for conclusion that the multilayers are really well-ordered lamellar structures. These investigations lead to general understanding of trilayer and multilayer formation and indicate that in exceptional cases it is due to a roll-over process. Films with a thickness of up to nine layers, obtained by compression of Langmuir films, can be transferred from water surface to solid substrates in a single step procedure without any distortion in the structure of the layers.

**JUNE 29 FRIDAY**

**NAUTILUS ROOM**

**9:00 - 10:00  MOLECULAR SELF ASSEMBLY**

9:00 - 9:15  **Bournel, LCPMP, Université Pierre et Marie Curie, Paris, France and Synchrotron SOLEIL, Gif-sur-Yvette, France**  
Auto-organized adsorption of triethylamine on Si(001)–2x1 at room temperature: a scanning tunneling microscopy and a X-ray photoemission study

9:15 - 9:30  **Swartz, Physics of Interfaces and Nanomaterials, MESA and Institute for Nanotechnology, University of Twente, The Netherlands**  
Nucleation in action: BDA on Cu(001) studied by LEEM

9:30 - 9:45  **Gallet, LCPMR, Université Pierre et Marie Curie, Paris and Synchrotron SOLEIL, Gif-sur-Yvette, France**  
Reactivity of TetraEthylOrthoSilicate (TEOS) on clean Si(001)–2×1 surfaces

9:45 - 10:00  **Patrone, CNRS, IM2NP, Université Aix-Marseille Université, Toulon, France**  
N and P type sigma-pi-sigma self-assembled monolayers studied by STM

10:00 - 10:30  Coffee break

**10:30 - 12:30  POLYMERS, COLLOIDES AND QUANTUM DOTS**

10:30 - 10:45  **Miszta, Istituto Italiano di Tecnologia, ITT, Genova, Italy**  
Cation Exchange Reactions in Colloidal Nanocrystals - A route toward new materials

10:45 - 11:00  **Salaun, CNRS/UJF-Grenoble /CEA LTM, Grenoble, France**  
PS-b-PDMS block copolymer directed self-assembly by topographical and chemical substrate engineering

11:00 - 11:15

11:15 - 11:30  **Miszta, Istituto Italiano di Tecnologia, Genova, Italy**  
Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures

11:30 - 11:45  **Georgieski, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic**  
Polydopamine-modified Nanocrystalline Diamond Thin Films as a Platform for Future Bio-sensing Applications

11:45 - 12:00  **Cozzarini, Dipartimento di Ingegneria Industriale e dell’Informazione, Università degli Studi di Trieste, Trieste, Italy**  
Synthesis of CdSe/CdS nanostructured, multiphase material via heat treatment of colloidal quantum dot assemblies
12:00 - 12:15

12:15 - 12:30 Vanetsev, Kurnakov Institute of General and Inorganic Chemistry RAS and Lomonosov Moscow State University, Moscow, Russia
Microwave-hydrothermal synthesis of monodisperse luminescent nanoparticles of Rare Earth compounds

ASTREA ROOM

8:30 - 10:00 NANOMATERIALS

8:30 - 8:45 Deokar, Institute of Nanosciences de Paris, Université Pierre et Marie Curie, CNRS, Paris, France
Study of the influence of 10 degree off-Si substrate on growth of 3C-SiC nanocrystals

8:45 - 9:00

9:00 - 9:15 Kanzari, Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs, Ecole Nationale d’Ingénieurs de Tunis, Tunis, Tunisie
Study of structural, morphological and optical properties of Sb2S3 thin films deposited by obliquely angle deposition

9:15 - 9:30 De Calheiros Velozo, Dep. de Física, Instituto Superior Técnico (UTL), Lisboa, Portugal
Thermal Dehydrogenation of Amorphous Silicon: Effect of the Substrate Temperature During Deposition

9:30 - 9:45 Ferid, Laboratoire de Photovoltaïque et Matériaux Semi-conducteurs, Ecole Nationale d’Ingénieurs de Tunis, Tunis, Tunisie
Structural, morphological and optical evaluation for nanosculptured CuInS2, CuIn3S5 and CuIn5S8 thin films by Glancing Angle Deposition

9:45 - 10:00 Lepore, Laboratory of Bio-Inspired Nanomechanics “Giuseppe Maria Pugno” and Politecnico di Torino, Torino, Italy
Biomimetic water repellent hierarchical coatings by co-assembled nanospheres

10:00 - 10:30 Coffee break

10:30 - 12:30 THIN FILMS

10:30 - 10:45 Lancok J, Institute of Physics AS CR, Prague, Czech Republic
Investigation of ultrathin noble metal films and nanoparticles by advanced NanoESCA instruments

10:45 - 11:00 Meneghini, Università di Roma Tre, Dipartimento di Fisica E. Amaldi, Roma, Italy
The corrosion process: the case of Cu3Au thin films studied using x-ray standing wave techniques
11:00 - 11:15  **Sliwinsk**, *Photophysics Dept., The Szewalski Institute of F-FM, Polish Academy of Sciences, Gdansk, Poland*
Nanopatterning of the Au thin films by pulsed UV laser irradiation

11:15 - 11:30  **Dole**, *Advanced Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India*
Structural, electrical, magnetic and morphological characterization of Pr substituted (Eu, Gd) – 123 high Tc nanosized superconductors

11:30 - 11:45  **Gorisse**, *CEA-Grenoble/INAC/SiNaPS-MINATEC, Grenoble, France*
Self-Assembly Porous Anodic Alumina by NanoImprinting Lithography

11:45 - 12:00  **Rau**, *Istituto di Struttura della Materia, CNR, Rome, Italy*
Bioactive glass-ceramic coatings for regenerative nanomedicine

12:00 - 12:15  **Carles**, *CEMES, CNRS-Univ. Toulouse, Toulouse, France*
Three dimensional design of silver nanocrystals assemblies embedded in dielectrics for spectroscopy enhancement and dark-field imaging

12:15 - 12:30  **Colantoni**, *Università di Roma “Tor Vergata”, Dipartimento di Fisica, Roma, Italy*
Study of the crystalline phases in paste coating deposition of CIGS

**CYPRE'A ROOM**

8:30 - 10:00  **NANOPARTICLES**

8:30 - 8:45

8:45 - 9:00  **Sashuk**, *Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*
Creating ultra thin films via self-assembly of charged nanoparticles at fluid interfaces

9:00 - 9:15  **Benedetti**, *Dipartimento di Fisica, Università di Modena e Reggio Emilia & Centro S3, CNR, Modena, Italy*
Substrate-driven self-assembling of metal nanocluster ordered arrays

9:15 - 9:30  **Benkovicova**, *Institute of Physics SAS, Bratislava, Slovak Republic*
Preparation of gold nanoparticles for plasmonic applications

9:30 - 9:45  **Chibotaru**, *Division of Quantum and Physical Chemistry, K.U. Leuven, Heverlee, Belgium*
Theoretical modeling of the confinement of surface state electrons in self-organized Co and Au islands on Au(111)

9:45 - 10:00  **Coursault**, *CNRS, Institut des Nano-Sciences de Paris & Univ Paris 6, Institut des Nano-Sciences de Paris, Paris, France*
Linear self-assembly of nanoparticles within smectic liquid crystal defect pattern

10:00 - 10:30  Coffee Break
10:30 - 12:30 NANO PARTICLES

10:30 - 11:00 **Invited**

**Bulir**, Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Preparation of nanostructured silver layer: the process control and monitoring

11:00 - 11:15

**Lacava**, Leibniz Institute for New Materials, Saarbrücken, Germany

Self-Assembly of nanoparticles into Lennard-Jones-like clusters

11:15 - 11:30

**Megiel**, Faculty of Chemistry, University of Warsaw, Warsaw, Poland

Gold Nanoparticles covered by nitroxide radicals – synthesis, electrochemical characteristic and catalytic ability

11:30 - 11:45

**Batocchio**, Department of Physics, INSTM and CISDiC, University Roma Tre, Rome, Italy

Silver nanoparticles capped by Pt-containing organometallic dithiols: interaction at the metal/ligand interface and surface structure studied by SR-XPS and XAS

11:45 - 12:00

**Anastossopoulos**, Department of Electrical and Computer Engineering, National Technical University of Athens, Athens, Greece

A three-dimensional WKB calculation of the charging and retention times of metal nanoparticles embedded in a dielectric matrix

12:00 - 12:15

**Courty**, Laboratoire des Matériaux Mésoscopiques et Nanométriques, CNRS, Université Pierre et Marie Curie, Paris, France

3D Supracrystals of Ag Nanocrystals: Control of Order and Periodicity
Auto-organized adsorption of triethylamine on Si(001)–2×1 at room temperature: a scanning tunneling microscopy and a X-ray photoemission study

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The fabrication of hybrid organic/inorganic semiconductor structures is the subject of a worldwide research effort due to possible applications in the field of organic electronics. In particular, the (001) oriented silicon, reconstructed 2×1, can be used as a template to graft ordered organic arrays via the reaction of molecular functionalities (π bonds, amines etc.) with the surface silicon dangling bonds in ultra high vacuum (UHV) conditions [1, 2]. However, the most interesting molecular objects (dyes, molecular wires, actuators etc.) directly grafted on a semiconductor surface are multifunctional, which often leads to competitive reactions and subsequently to multiple adsorption geometries.

We present here a scanning tunneling microscopy and a X-ray photoemission study of the adsorption of triethylamine (TEA, (C₂H₅)₃N) on Si(001)–2×1 at room temperature. The N1s photoemission line reveals that TEA chemisorbs on the surface through its electron lone pair with a silicon dangling bond inducing a local static buckling. This surface modification drives the localization of a subsequent molecule adsorption. This leads to self-organized domains of TEA on the surface. At very high coverage, this patterned is lost due to a molecular dissociation.

References
Nucleation in action: BDA on Cu(001) studied by LEEM

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The growth and structure of 4,4’-biphenyldicarboxylic-acid (BDA) on Cu(001) at temperatures between 300 K and 400 K was studied by LEEM and μ-LEED. BDA is a linear molecule consisting of two phenyl rings with a carboxylic-acid group at opposite ends. During growth on Cu(001) the adsorbed BDA molecules form first a disordered 2D gas phase. Once this phase reaches a sufficiently large density, a crystalline phase nucleates, in which the molecules form a hydrogen-bonded 2D supramolecular network.

By a careful analysis of the bright-field image intensity we can measure the density of the 2D gas phase, which is up to 40% of that in the crystalline phase. From the equilibrium densities at different temperatures we can construct the 2D phase diagram and extract the cohesive energy (0.42 eV).

During the distinct nucleation period we can observe a fascinating phenomenon: sub-critical nuclei form, grow up to 4000 nm² in size and decay with lifetimes of several seconds. These sizes are considerably larger than what is usually seen in epitaxial growth and we explain this observation with the relatively weak intermolecular interactions.
Reactivity of TetraEthylOrthoSilicate (TEOS) on clean Si(001)-2×1 surfaces

J.-J. Gallet* (1,2), H. Tissot (1,2), F. Bournel (1,2), A. Naitabdi (1,3), F. Rochet (1,2), F. Finocchi (4), and A. Pietzsch (5)

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Organosilanes have been used for many years as precursors to improve adhesion of polymers to oxidize substrate and are considered for possible applications in molecular electronic [1, 2]. In particular alkoxyisilane can be used to form self-assembled monolayers (SAMs) on hydroxylated silica surfaces, in the presence of an adsorbed water layer [3]. We present a recent study of the reactivity of TetraethylOrthoSilicate (TEOS, Si(OC2H5)4) on a clean Si(100)-2×1 surface. Using X-Ray Photoemission Spectroscopy induce by synchrotron radiation in high surface sensitivity and for high coverages, we shown that TEOS reacts with the surface via the cleavage of the four ethoxy groups (via, Si–O bond breaking) which graft on the surface. Complementary microscopy studies (Scanning Tunneling Microscope) at low coverage shown that the ethoxy bind on two silicon dimers of the same row, releasing the silicon atom on the adjacent row (first direct observation of an ad-atom on the Si(100) surface). The isolated silicon ad-atom then diffuses to form an ad-dimer by reaction with another ad-atom. At high coverage, STM images show a patterned surface where the ad-dimer occupies alternate rows.

References
N and P type $\sigma$-$\pi$-$\sigma$ self-assembled monolayers studied by STM

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Downscaling of silicon-based electronics leads to a revival of efforts to build molecular-scale devices [1]. In this field, self-assembled monolayer (SAM) [2] is one of the most promising issues of bottom-up building approach, and molecular-based memory cells, such as resonant tunneling diodes (RTD) [3], attract a lot of interest for hybrid molecular electronics [4]. A proposed architecture of such molecular RTD devices consists in a monolayer of $\sigma$-$\pi$-$\sigma$ organic molecules sandwiched between two electrodes, composed of alkyl-chains ($\sigma$ parts) acting as tunnel barriers while a $\pi$-moiety acts as a potential well [5]. In this work, we focused on new $\sigma$-$\pi$-$\sigma$ compounds specifically synthesized based on either P-type terthiophene (3T) or N-type naphthalene tetracarboxydiimide (NaPh) cores, with various alkyl chain lengths, and bearing adequate grafting function. For thiolate SAMs grafted on gold, scanning tunneling microscopy (STM) revealed domains with a typical hexagonal arrangement [2] for 3T SAMs, the alkyl chain giving the molecules the necessary flexibility for their ordering. Nevertheless molecular organization is not observed for NaPh SAMs, the larger conjugated part of the molecule hindering a close-packed arrangement. Current-voltage (I-V) characteristics of the SAM performed locally under STM tip are shown to correlate well with macroscopic ones using eutectic InGa contacts, related in both cases with the intrinsic electrical properties of molecules. For a pure dodecyl SAM, I(V) curve is rather symmetric with a low current level. Conversely, N or P type of $\sigma$-$\pi$-$\sigma$ SAMs is revealed by an opposite rectifying behavior, in agreement for 3T with asymmetric electrical conduction properties measured by STM on terthiophene molecules [6].

References

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Cation Exchange Reactions in Colloidal Nanocrystals – A Route Toward New Materials

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The recent development in the synthesis of new types of nanomaterials is the exploitation of cation ex-change reactions. Recently, at the nanoscale, different types of cation substitutions have been investigated, and they were shown to be promising and versatile way to obtain a variety of interesting materials. During a cation exchange reaction, the sublattice of anions remains in place, while the cation framework is replaced by cations of another chemical species. These reactions extend therefore the range of nanocrystals that can be synthesized with controlled shapes and compositions, as one can start from nanocrystals of a material (or combination of materials) for which the synthesis is well established and then convert them into other nanomaterials with desired/new composition while preventing the shape.1-3

During the presentation several recently obtained and published examples of this synthetic approach will be presented. 4,5 For instance, due to the capability of Cu2-xSe to undergo a fast and quantitative cation exchange reaction in the presence of excessive Cd2+ ions, big 10nm sphalerite CdSe seeds can be synthesized. The sphalerite CdSe seeds with these dimensions were not synthesized till now. Additionally they hold great potential for the further elaboration. The obtained seeds can be further used to produce branched CdSe/CdE nanocrystals. Which consist of a sphalerite CdSe core and wurtzite CdE arms. Depending on the used chalcogenide E (Te,Se, or S) for the reaction different structures are obtained. In the case of the S precursors Octapod-shaped colloidal nanocrystals composed of a central “core” region of cubic sphalerite CdSe and pods of hexagonal wurtzite CdS can be produced.

Another example of the cation exchange reaction is the progressive cation replacement from Cd-based octapods to their Cu based analogs. The reaction starts from the tip regions of the CdS pods and proceeds toward the center of the nanocrystals while the shape of the particles stay the same. During the exchange, the hexagonal wurtzite CdS pods are converted gradually into pods of hexagonal Cu2S chalcocite. Therefore, the partial cation exchange reactions lead to the formation of a ternary nanostructure, consisting of an octapod in which the central core is still CdSe, while the pods have a segmented CdS/Cu2S composition. When the cation exchange reaches the core, the cubic sphalerite CdSe core is converted into a core of cubic Cu2-xSe berzelianite phase. Therefore fully exchanged octapods are composed of a core of Cu2-xSe and eight pods of Cu2S. All these structures are stable, and the epitaxial interfaces between the various domains are characterized by low lattice mismatch. The Cu2-xSe(core)/Cu2S(pods) octapod represents another example of a nanostructure in which branching is achieved by proper organization of cubic and hexagonal domains in a single nanocrystal.


PS-b-PDMS block copolymer directed self-assembly by topographical and chemical substrate engineering

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Block CoPolymer (BCP) self-assembly creates periodical pattern with feature size below 10 nm. However, on plain substrates, ordering is only obtained in grains not larger than a few micrometers. Segalman et al. [1] demonstrated that BCP self assembly in trenches of a pattern could create long-range order between the polymer micro-phases. Lately, researchers show increased attention to PolyStyrene-block-PolyDiMethoxySilane (PS-b-PDMS) due to its natural tendency to create highly ordered patterns and due to the high plasma etching resistance of the PDMS block compared to the PS one. Nevertheless, due to the difficulty to fabricate neutral surfaces for PS-b-PDMS, only very few results on PDMS vertical features (lamellas or cylinders perpendicular to the substrate) have been reported up to now.

Figure 1: SEM images of directed self-assembled Poly(styrene-block-dimethoxysilane) features in a SSQ resist template (230 nm wide SSQ lines, 270 nm large trenches between the SSQ lines). Orientations perpendicular (a) or parallel (b) to the substrates plane are observed depending on the nature of the SSQ.

In this work, we present results on directed self-assembly of PS-b-PDMS performed on pre-patterned SilSesQoxane (SSQ) based substrates. These templates are made by soft UV-imprinting of different kinds of liquid SSQ-based resists using a hard-PDMS stamp. Surface properties of synthesized SSQ resists are tuned by grafting different kind of ligands to a same T8 SSQ cage (fluorinated, phenyl, acrylate, methacrylate, glycidyl and or epoxy ligands are used). The residual resist layer after the nanoimprint process is eventually removed by plasma etching at the bottom of the trenches, providing different surface chemistry geometries (SSQ walls with Si or SSQ bottom layer). Either vertical or horizontal orientations of the PDMS cylinders could be obtained in these templates by solvent annealing with a remarkable long-range order and registration (Figure 1). Investigations are now undergoing to understand more precisely the dependence of the self-organization process to experimental conditions.

References:
Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures

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Self-assembly of molecular units into complex and functional superstructures is ubiquitous in biology. The number of superstructures realized by self-assembly of man-made nanoscale units is also growing. However, assemblies of colloidal inorganic nanocrystals are still at an elementary level, not only because of the simplicity of the shape of the nanocrystal building blocks and their interactions, but also because of the poor control over these parameters in the fabrication of more elaborate nanocrystals. Here, we show how monodisperse colloidal octapod-shaped nanocrystals self-assemble, in a suitable solution environment, on two sequential levels. First, linear chains of interlocked octapods are formed, and subsequently the chains spontaneously self-assemble into three dimensional superstructures. Remarkably, all the instructions for the hierarchical self-assembly are encoded in the octapod shape. Our group has recently developed a synthesis scheme to create octapod-shaped nanocrystals in which eight CdS ‘pods’ are grown from a central region made of CdSe. Further refinements of the synthesis have allowed us to prepare octapods with unprecedented shape homogeneity and monodispersity. These nanocrystals are coated with hydrophobic surfactant molecules and therefore they favourably interact with hydrophobic solvents, that is, non-polar or moderately polar solvents and this provides base for ordering process. Overall, the sequential steps described here, namely synthesis of complex building blocks and their hierarchical assembly; represent an innovative route towards the realization of ordered mesostructures by a pure bottom-up approach.

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Polydopamine-modified Nanocrystalline Diamond Thin Films as a Platform for Future Bio-sensing Applications

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Diamond exhibits good biocompatibility and a large electrochemical potential window, which make it particularly suitable for bio-functionalization and bio-sensing [1, 2]. Modification of the diamond surface, while keeping its intrinsic properties can be achieved through mussel-inspired surface chemistry based on polydopamine [3].

We present a comparative study on the polymerization/deposition of polydopamine from an aqueous solution of dopamine on hydrogen- (H) and oxygen- (O) terminated nanocrystalline diamond films (NCD). The dopamine polymerization/deposition was carried under mild conditions which resulted in confluent polydopamine layer. A detailed investigation of polydopamine growth kinetics on H- and O- terminated NCD films were performed using spectroscopic ellipsometry (SE). X-ray photoelectron spectroscopy (XPS) was used to evaluate the chemical composition of the diamond surfaces before and after the surface modifications. The success of the modifications was further evidenced by water contact angle measurements. The changes in surface topography of the bare and polydopamine modified NCD films were investigated by atomic force microscopy (AFM).

Based on the findings, the polydopamine layer can be successfully used as a platform for future bio-functionalization and/or optical bio-sensing applications [4].

References
Synthesis of CdSe/CdS nanostructured, multiphase material via heat treatment of colloidal quantum dot assemblies

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Nanostructured thin films consisting of an array of CdSe quantum dots (QD) embedded in a continuous CdS matrix have been obtained by heat treatments of CdSe/CdS core-shell nanocrystals, assembled on glass substrates from colloidal solutions. The treatments were conducted at 300-500°C for 1 to 120 min. The nanostructure evolution during the heat treatment was monitored by photoluminescence spectroscopy. Initially, the QD first exciton PL peak shifts towards lower energy, indicating a delocalization of the exciton due to the merging of CdS shells by sintering, thus forming a continuous CdS matrix. Further treatment leads to a hypsochromic shift of the PL peak, indicating that the CdSe dots and the newly formed CdS matrix are interdiffusing. The kinetics of these two distinct phases of the PL evolution were characterized ($G_{ACT}$: 70 and 120 kJ/mol, respectively). By observing that sintering has to be faster than interdiffusion for obtaining the nanostructure described above by thermal treatment of colloidal films, general guidelines are identified for the choice of materials and process parameters in such approach.
Microwave-hydrothermal synthesis of monodisperse luminescent nanoparticles of Rare Earth compounds

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New methods of synthesis of monodisperse nanoparticles is one of the crucial steps on the way to production of various commercial materials. One of the most important applications of such nanoparticles is biomedicine and luminescent coatings. The most promising luminescent materials for such applications, namely Rare Earth compounds, at the same time require the largest amounts of energy during synthesis. Therefore, development of energy-saving methods of synthesis of luminescent nanoparticles, including self-assemble processes, is very vital task. Microwave treatment possesses many advantages, including higher velocity of heating, homogeneity of heat distribution and lower power inputs.

In present work new facile method for synthesis of nanosized phosphors of Rare Earth compounds, including vanadates and phosphates, using microwave-hydrothermal treatment was developed. It was shown that proposed technique allows to obtain weakly aggregated monodisperse powders with particle sizes varying from 10 to 100 nm, depending on the synthesis conditions. Mechanism of synthesis and influence of synthetic conditions on luminescent properties has been studied.

The work was supported by RFBR (grants # 12-03-01055-a and 11-02-91152-GFEN_a), grant of President of Russian Federation for support of young Russian scientists (MK-2607.2011.3) and Complex Program for Scientific Research of Presidium of RAS.
SiC nanocrystals (NCs) below 10nm size are known to show luminescence due to quantum confinement effect. Orderly growth of the luminescent SiC NCs could be used to fabricate light emitting displays and field emitters.

Here, we show heteroepitaxial, β-SiC NCs growth on Si (001) substrate. For that a simple method was used: the NCs were grown by heating silica layer on Si samples in few hundreds of mbar of CO₂ at 1100 °C for 1 to 12 hours. High resolution scanning electron micrographs have evidenced formation of isolated, plus shaped NCs on both 10° off-Si and Si without miscut. Nucleation density (ND) estimation showed over one order of magnitude enhancement in the ND of the NCs for 10° off-Si as compared to the ND for on-Si. The NCs size and the ND estimation for various treatment times and pressures, showed that NCs size and the ND can be controlled by these two parameters. For the 10° off-Si cross-section TEM showed that the NCs nucleation occurred at the steps edges. These NCs were preferential aligned along step edges (in the (1-1 0) direction). Thus the surface atomic steps are playing vital role in enhancement of nucleation and alignment. Further work to obtain optimized parameters for fabrication of one or two dimensional ordered arrays of SiC NCs is in progress. This investigation illustrates the possibility of fabrication of self organized SiC NCs.

Study of structural, morphological and optical properties of Sb$_2$S$_3$ thin films deposited by obliquely angle deposition

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Sb$_2$S$_3$ thin films were deposited by thermal evaporation method with evaporated obliquely incidence angle technique. During the deposition, the substrate temperature was maintained at $T_s=180^\circ$C and the deposition angle was fixed at $\theta=0^\circ$, $20^\circ$, $40^\circ$, $60^\circ$, $70^\circ$ and $85^\circ$. X-Ray Diffraction, Atomic Force Microscopy and UV- Vis- NIR spectra were used to characterize the structural, surface morphology and optical properties of the deposited Sb$_2$S$_3$ thin films. Due to the shadowing effect, the structure of the resulting film consists of nanocolumns that are progressively inclined towards the evaporation source. Optical transmission spectra in the spectral range 300-1800 nm have been used to study the optical properties of these films. We show that the refractive index and thickness decreased with increasing of the incident angle. It was found that the refractive index decreased from 2.86 at $\theta=0^\circ$ to 2.4 at $\theta=85^\circ$. The relationship between the flux incident angle $\theta$ and the column angle $\beta$ was also explored in detail.
Thermal Dehydrogenation of Amorphous Silicon: Effect of the Substrate Temperature During Deposition

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Doped hydrogenated amorphous silicon (a-Si:H) can be deposited by PECVD on crystalline silicon as a pre-deposition layer for a subsequent diffusion, in order to form pn junctions. However, when a-Si:H is heated beyond 300ºC, thermal dehydrogenation occurs liberating molecular hydrogen. If the dehydrogenation rate is too high, mechanical stress appears in the films that can lead to pin holes or even to a complete peel-off. The initial hydrogen concentration of the as-deposited films is, then, of major importance as well as the dehydrogenation process time and temperature, for a smooth hydrogen exodiffusion.

In this work, samples of doped and undoped a-Si:H were deposited at temperatures ranging from 100ºC to 350ºC and then submitted to different dehydrogenation temperatures (from 350ºC to 450ºC) and times (from 1h to 10h). Initial and final film parameters were measured in order to determine the a-Si:H characteristics, namely hydrogen content, optical gap, refractive index, growth and etch rates, conductivity and thermal activation energy of conductivity.
Structural, morphological and optical evaluation for nanosculptured CuInS$_2$, CuIn$_3$S$_5$ and CuIn$_5$S$_8$ thin films by Glancing Angle Deposition.

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Nanosculptured CuInS$_2$, CuIn$_3$S$_5$ and CuIn$_5$S$_8$ thin films were deposited by thermal evaporation method using Glancing Angle Deposition. In this paper, we study the evaluation of incident angle in the fabrication of nano-columns. During the deposition, the incident angle was set at $\theta=0^\circ$ and $80^\circ$ and the substrate temperature was maintained at $T_s=180^\circ$C. X-Ray Diffraction, Atomic Force Microscopy and UV-Vis-NIR spectra were used to characterize the structural, surface morphology and optical properties of the deposited thin films.

The optical description leads to an incidence angle dependence of thickness and density, allowing for the porosity in samples with different morphologies and thickness calibrations. In addition, variation of the incidence angle creates a nonhomogenous variation of the film thickness and porosity with the substrate tilt. Optical transmission spectra in the spectral range 300-1800 nm have been used to study the optical properties of these films. We show that the refractive index and thickness decreased with increasing of the incident angle. The X-Ray Diffraction shows that the GLAD thin films become amorphous when the incident angle increase. The relationship between the flux incident angle $\theta$ and the column angle $\beta$ was also explored in detail.
Biomimetic water repellent hierarchical coatings by co-assembled nanospheres

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Water-repellent (or super-hydrophobic) and dirt-free natural surfaces were observed for the first time more than 2000 years ago; however, only in the 20th century scientists studied these two related phenomena on some natural leaves [1-2], e.g. the famous lotus *Nelumbo nucifera*, on which “raindrops take a clear, spherical shape without spreading, which probably has to be ascribed to some kind of evaporated essence”, as Goethe described in 1817, see [3].

We considered the surface morphology of the most famous superhydrophobic and self-cleaning lotus leaf and we realized an artificial biomimetic superhydrophobic polystyrene (PS) surface by co-assembling PS nanospheres of different diameters[4]. In particular, we used PS nanospheres with a diameter of 0.1 and 3 µm and mixed them in five different solutions as follows: 10% (and 90%), 30% (and 70%), 50% (and 50%), 70% (and 30%) and 90% (and 10%) of 0.1 µm-diameter (and 3 µm-diameter) nanospheres over the volume or area of the final solution. Finally, the solutions were directly cast on a PS hydrophilic substrate. In this way, we obtained an artificial surface with two different hierarchical levels as is on the lotus leaf, where we find convex micro-structures of ~10 µm covered with a superimposed layer of hydrophobic 3D wax nanotubules of ~200 nm in diameter. We characterized the water sliding behaviour by measuring the contact angle (CA) and we increased the value of CA from ~85° (for a PS flat control surface) to ~131°, so obtaining a hydrophobic and water repellent surface starting from an intrinsically hydrophilic material. The effect of oxygen plasma treatment of such a surface as a function of contact angles has also been studied.

References
Investigation of ultrathin noble metal films and nanoparticles by advanced NanoESCA instruments

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Metal nanostructures are known to have unique properties such as enhanced absorption associated to their surface plasmon resonance (SPR), reactivity or catalytic activity. To enhance the chemical reaction or catalytic capabilities, metals such as Pt or Pd by using nanoparticles are very attractive. Production of bimetallic nanostructures, which exhibit characteristics that are not just the addition of the properties of the two constituent metals, could produced a new properties with big application potential. In this work, we study the structural features, electronic and chemical properties of ultrathin Ag, Pd and Ag:Pd multilayers with total thickness <10 nm. They are fabricated by means of magnetron sputtering. The films were subsequently thermally annealed (up to 600 ºC) under UHV conditions to form metals nanoparticles on the Si substrate.

To study structural and morphology properties we used advanced NanoESCA instrument [1], AFM and SEM facilities. It enables to show the properties on nanoparticles depending on the chemical composition and state, e.i. to found the relation between the workfunction changes (PEEM) and chemical composition (XPS-mapping).

Chemical state and possible alloying of Ag:Pd layers we investigated with NanoESCA together with element mapping, work function and morphology features on the scale of >20 nm. The annealing produced nanoparticles of maximum 30 nm diameter and their work function strongly depend on the size and chemical composition.

The corrosion process: the case of Cu₃Au thin films studied using x-ray standing wave techniques

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Metals and their alloys are highly susceptible to corrosion in wet environment. Dealloying is a particular type of corrosion, attacking practically all metals in industrial use, as they are usually alloys composed of metals of different “nobility”. In fact when a metallic alloy is in contact with an electrolyte, the less noble metal tend to go into solution, typically causing crack formation and subsequent material failure upon stress. Efficient strategies against corrosion. Understanding the corrosion processes is relevant to provide efficient strategies against it. Potential controlled corrosion of ordered Cu₃Au single crystal in sulfuric acid had been earlier investigated in situ [1] showing that, far below the critical potential E_c, at which Cu and Au are massively dissolved, Cu goes into solution, leaving a ≈ 1 nm thick film of small, Au-rich clusters. Just below E_c, the surface is eventually covered with about 10-20 nm large gold islands with a thickness of 2-3 nm. The Au-rich surface protects the bulk of the alloy against further corrosion (unless E_c is exceeded).

In order to push the knowledge onto effectively used materials we exploited state of the art synchrotron radiation probes to investigate the action of corrosion process on thin Cu₃Au films simulating a real coating layer. Complementary details are obtained combining x-ray standing wave (XSW), x-ray photoelectron spectroscopy (XPS) and x-ray absorption fine structure (XAFS) spectroscopy. Ultra-thin Cu₃Au films (2.5 nm) were deposited on a Ru/B₄C multilayer to provide a stable XSW field. The XSW study provide detailed information about the concentration profile of Cu and Au upon dealloying to determine precisely the amount of Cu and/or Au going into solution as a function of applied potential. XPS provide electronic details such as oxidation states of Au and Cu ions. Finally XAFS technique allows describing the local atomic structure around Cu and Au.

The pristine Cu₃Au film appear partially oxidized containing CuO and Cu₂O. Corrosion provokes the partial Cu dissolution leading to the formation of Au-rich film having CuAu₃-like composition. It is observed that dealloying below E_c (~500 mV vs. Ag/AgCl) not only removes Cu but also some Au from the thin film alloy.

Nanopatterning of the Au thin films by pulsed UV laser irradiation

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In this work the properties of the Au nanostructures are discussed and observed via indirect spectroscopy of the material and geometry dependent resonance profiles and damping rates of surface plasmons (SPR) which provide complete description of the plasmonic properties of particles. Moreover, components of the plasmonic decay $1/ T_2$ reflect the role of different dephasing mechanisms. Recently, it was reported that the experimentally observed bandwidth of the SPR is found to follow the theoretical predictions for a wide range of nanoparticle geometries. In particular, for particles of diameters larger than 20 nm the position of the resonant energy peak compared to that of smaller particles (2-4 nm in dia) is red-shifted due to retardation effects as well as to increasing contributions from multipolar terms. For dimension larger than 50 nm, radiative damping of the electronic excitations broadens the linewidth [1-4]. It is also known, that intensive pulsed laser irradiation enables to stimulate nano-fragmentation at fluencies near and above the melting point of the metal. Here, the ultrafast dephasing of the (SPR) of structures consisting of relatively large gold nanoparticles (mean diameter > 20 nm) embedded in SiO$_2$ glass substrate was investigated. The dephasing time was obtained from absorbance spectra of structures produced from thin Au films (10 nm) sputtered on glass substrate and annealed by pulsed (6 ns) laser radiation at 266 nm and at fluencies between 60-120 mJ/cm$^2$. It was found, that values of $T_2$ in the range from 2.2 to 4.5 fs correspond to particle diameters of 20-60 nm and are in pretty good agreement with literature data.

References
Structural, electrical, magnetic and morphological characterization of Pr substituted (Eu, Gd) – 123 high Tc nanosized superconductors

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Samples of RE$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ where (RE = Eu & Gd) with compositions $x = 0.0, 0.1, 0.2, 0.3, 0.4$ & 0.5 were prepared by solid state reaction route. The XRD studies of the samples show orthorhombic pervoskite structure. It is found that the oxygen deficiency increases with increasing Pr concentration and plays very important role in the structural properties of REPr-123 superconductors. The resistivity measurement was carried out at 300 K to 4 K of all samples using physical property measurement system (PPMS). It is observed that the samples $x = 0.0, 0.1, 0.2$ & 0.3 are superconductors while $x = 0.4$ and 0.5 are not superconductors. The increment in resistivity with enhancing Pr concentration may be due to decrease in the amount of charge carriers & hole localization. It is found that the transition temperature suppresses in GdPr-123 faster than the EuPr-123 system. The suppression in the transition temperature $T_c$ shows that Pr enters in the (Eu, Gd) - 123 lattices when it is in $3+$ valence state. SQUID technique was used for the determination of Curie constant, Curie temperature and effective Bohr magneton number. It is found that the effective Bohr magneton number reduces in GdPr-123 system as well as increases in EuPr-123 system with increasing Pr content. It means the magnetic moment plays very important role in these systems. Our experimental results strongly confirm that magnetic pair breaking mechanism is responsible for the destruction of superconductivity in Pr substituted Gd-123 samples. The morphological analysis was carried out using SEM. It shows that the grain size of samples increases with increasing Pr concentration. One may say that the suppression in transition temperature is highly sensitive to the grain size as well as oxygen content and magnetic moment ($\mu_B$) in the samples.
Self-Assembly Porous Anodic Alumina by NanoImprinting Lithography

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Alumina nanopore arrays [1] are promising nanostructured templates for numerous applications such as information storage and solar energy harvesting [2]. It is produced by an electrochemical oxidation of aluminum in acid solutions. By varying experimental parameters as the acid electrolyte or the applied voltage, geometrical characteristics of the porous membrane can be modified (diameter and depth of pores, distance between nearest neighbor) [3]. In conventional methods, simple or double anodization, the hexagonal order is uneven over a large distance.

We present an innovative route including Thermal Nano Imprint Lithography (TNIL) prior to aluminum anodization, to prepare flawless hexagonal arrays on surfaces as large as 4 cm². Figure 1.a shows an image of the arrays characterized by Scanning Electron Microscopy (SEM). Interpore lengths vary between 100 and 250 nm and pore sizes from 30 to 150 nm.

![SEM images of alumina after direct anodizatoin (aluminum was TNIL patterned); a. anodization at 40V, interpore distance 100nm; b. anodization at 100V, generation of guided pores between three imprinted pores; c. cross section of guided pores in oxalic acid; d. cross section of guided pores in phosphoric acid.]

In addition, original structures with generation of guided pores have been developed. Indeed, we can force the growth of a pore between three imprinted pores by adapting the anodization voltage, as seen on Figure 1.b. Shapes of the pores can be modified varying the electrolyte, Figure 1.c and 1.d illustrate the differences.

These alumina nanopore arrays are used as templates for the self organized epitaxial silicon nanowires growth in a chemical vapor deposition reactor. Hexagonal nanowire arrays grown perpendicularly to <100> silicon substrates have been successfully produced.


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Bioactive glass-ceramic coatings for regenerative nanomedicine

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The scope of the present research is to realize bioactive glass-ceramic coatings doped with various ions for application in regenerative nanomedicine as bioreabsorbable and bioactive third generation biomaterials. Porous glass-ceramic matrix structures, containing various homogeneously dispersed micro- and nano-phases, can be prepared. For this scope the sol-gel synthesis technique can be used. The choice of doping ions will be governed, first of all, by their presence in the human body, exploiting, along with the various literature sources, also the long-lasting experience in thermal mud-bath treatments. Following this way, biomaterial can be recognized by biological system mimicking its composition. The actions of the appropriate ions and their controlled release should induce the cells of different specialization and their genes to adhere to the artificial biomimetic composites.

The coatings of titanium implants utilizing various glass-ceramic targets will be prepared by means of Pulsed Laser Deposition technique, with priority goal - preservation in the coatings of stoichiometry of the initial target materials. The properties of films will be investigated by microscopical, spectroscopical and diffractometric techniques, namely: scanning electron microscopy (SEM-EDS), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), angular and energy dispersive X-ray diffraction (ADX and EDXD). Vickers microhardness measurements will be performed. Finally, well characterized coating-substrate systems will be tested in vitro and in vivo.
Three dimensional design of silver nanocrystals assemblies embedded in dielectrics for spectroscopy enhancement and dark-field imaging

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A strategy to fabricate hybrid metallic-dielectric substrates for optical spectroscopy and imaging is proposed. Different patterns of metallic nanocrystals embedded in dielectric layers are conceived to simultaneously exploit near field effects, optical interference phenomenon in stratified media and localized surface plasmon resonance on metal nanostructures. These structures are based on a simultaneous control of opto-electronic properties at 3 scales (3S) (~ 2 / 20 / 200 nm) and along 3 directions (3D). By ultra-low energy ion implantation through a stencil fabricated by focused ion beam technique we control the size, density, and location of silver nanocrystals embedded in silica/silicon thin films [1,2].

Elastic (Rayleigh) and inelastic (Raman) scattering imaging assisted by simulations were used to analyze the optical response of these “3S-3D” patterned layers. The reflectance contrast is strongly enhanced when resonance conditions between the stationary electromagnetic field in the dielectric matrix and the localized plasmon resonance in the silver nanocrystals are realized [2].

These novel kinds of plasmonic-photonic systems are reproducible and stable; they preserve flatness and chemically uniformity over large surfaces, offering efficient and reusable substrates for optical spectroscopy enhancement and high contrast imaging. Recent results on deposited graphene layers will be presented.

Study of the crystalline phases in paste coating deposition of CIGS

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One or two microns of CIGS can absorb most of the incident solar radiation because CuIn$_{1-x}$Ga$_x$Se$_2$ have a direct band gap with a high absorption coefficient. The theoretical predictions explain that the optimum photovoltaic performance should be provided by a high gallium concentration, but experimentally is observed that above 30% of Ga the efficiency is reduced. This contradictory behavior is not completely understood. Using paste coating technique for CIGS deposition, we have recently shown a strong correlation among Ga concentration, structural properties and compound stoichiometry. The desired stoichiometric compound will be obtained varying the concentration of the basic elements in the paste. Our diffraction data show that the maximum of the crystalline phase is reached when CIGS have a Ga concentration higher. Furthermore the SEM EDX quantitative analysis performed on the same samples have shown the presence of different phases. Such a phases separation find a theoretical explanation as ODC (Ordered Defect Compound) in Cu-poor system. X-ray absorption spectroscopy reveals the structure around a specific atomic species and allow us to understand the type of phases in chalcopyrite structure.
CONTROLLING THE GEOMETRY OF SILVER NANOSTRUCTURES FOR BIOLOGICAL APPLICATIONS

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Nobel metal nanostructures particularly silver have attracted much attention in the fields of electronics, chemistry, physics, biology and medicine due to their unique properties which are strongly dependent on the size and shape of metal nanomaterials [1-3]. This study discusses on silver nanostructures with various geometries including sphere, wire, cube and triangle prepared using solution-phase method. In this regard, silver nanostructures with four different morphologies were synthesized and applied for antibacterial activities. X-ray diffraction (XRD), Ultra Violet Visible (UV-Vis) spectroscopy and microscopic studies of different types of silver nanostructures revealed distinct optical and structural properties of an individual silver nanostructure. XRD analysis exhibited formation of metallic silver with no impurity and oxide phase. Optical absorption spectroscopy revealed different plasmon resonances according to the symmetry and shape of the nanostructures which makes these structures a good candidate for biology, medicine and specially cancer therapy. SEM and TEM analyzes (illustrated below) confirmed formation of cubic, wiry, triangular and spherical silver nanostructures. Antimicrobial properties of silver nanostructures with various shapes against three types of different bacteria demonstrated shape and bacterial dependency of this property.

References
Creating ultra thin films via self-assembly of charged nanoparticles at fluid interfaces

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Self-assembly of nanoparticles (NPs) at fluid interfaces has recently emerged as a powerful tool for constructing multifunctional, highly ordered 2- and 3-D nanostructured materials.\textsuperscript{[1]}

Herein we want to report a facile route to the fabrication of hexagonally close-packed charged NP monolayer films based on the self-assembly phenomenon.\textsuperscript{[2]} In our approach we employ noble metal NPs covered with a mixture of polar (charged) and nonpolar ligands. Such NPs, dispersed in a bulk phase, spontaneously absorb at fluid interfaces affording monolayers. We found that the NPs self-assembled at fluid interfaces exhibit Janus-type amphiphilic structure and possess well defined and constant charge. At oil-water interface the NPs autonomously form hexagonally packed lattices as a result of a fine balance between repulsive electrostatic and attractive hydrophobic forces.\textsuperscript{[2a]} In turn, at air-water interface, the NPs arrange into sparse monolayers which then can be readily compressed to give dense films by using Langmuir-Blodgett technique.\textsuperscript{[2b]} The NP monolayers squeezed into such films can be used for coating of various materials.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Self-assembly process of charged nanoparticles at fluid interfaces.}
\end{figure}

\begin{thebibliography}{9}
\bibitem{2} a) V. Sashuk et al, Chem. Eur. J. \textbf{18}, (2012), accepted; b) V. Sashuk et al, submitted
\end{thebibliography}
Substrate-driven self-assembling of metal nanocluster ordered arrays

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Ordered arrays of metal nanoclusters are of great interest for their applications in nanomagnetism, optics and catalysis. Amongst possible fabrication methods, the exploitation of a thin film as a support is appealing, where the nanopatterning induced by a misfit dislocation network can guide the nanocluster self-assembly into an ordered array [1]. This method has been successfully proved on semiconductor supports, while on oxides long-range order has been observed only by diffraction techniques [2]. In this work we prepared a MgO film on Mo(001), where the presence of an interfacial dislocation network induces a surface periodic deformation connected with a modification in the workfunction [3,4]. The deposition of Fe atoms leads to the spontaneous formation of nanoclusters disposed in a square array, with about 6 nm average distance, corresponding to the dislocation periodicity. Increasing MgO film thickness, the order of metal nanoparticles fades away and completely disappears for 40 ML MgO. Cluster size increases by increasing Fe coverage, while the mesh of the cluster array does not change. In spite of the presence of grain boundaries and edges that breaks the oxide film, both dislocations and Fe cluster ordering show a clear continuity on a larger scale.

Preparation of gold nanoparticles for plasmonic applications

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We present a simple hot injection method for the preparation of colloidal solutions of hydrophobic spherical gold nanoparticles with the diameter around 20 nm and size dispersion below 20%. The preparation is based on thermal decomposition and reduction of chloroauric acid (HAuCl₄·3H₂O) in the presence of a stabilizing capping agent (surfactant). A mixture of metal precursor with small amounts of organic solvent and stabilizing agent was very slowly injected into a hot solvent where the stabilizer was dissolved. Various surfactants with different lengths of hydrocarbon chains were used such as oleylamine, 1-octadecanethiol, polyvinylpyrrolidion, AgNO₃ in 1,5-pentanediol. The long chain capping allows synthesis of relatively stable and well-ordered nanoparticles while the short chain capping results in the nanoparticle aggregation. The choice of the stabilizing agents provides control over the particle size and shape. The hydrodynamic nanoparticle size and size dispersion were determined by the dynamic light scattering (DLS) while the small-angle X-ray scattering (SAXS) from the colloidal solution provided information on the size of the metallic nanoparticle core (without surfactant). Plasmon enhanced resonant absorption peak at 560 nm was detected by the UV-VIS-NIR spectrophotometer. The ability of plasmonic nanoparticles to self-assemble into ordered structure was tested by the colloidal solution drop casting on a silicon substrate followed by spontaneous solvent evaporation. The dried samples were inspected by high-resolution SEM and grazing-incidence SAXS (GISAXS) techniques. The presence of side maxima in the GISAXS pattern gives evidence of the nanoparticle ordering while very close values of the interparticle distance derived from GISAXS and the nanoparticle size derived from DLS indicate a close-packed order. These results demonstrate viability of the method developed to fabricate gold nanoparticles for application in thin film solar cells with enhanced power conversion efficiency.
Theoretical modeling of the confinement of surface state electrons in self-organized Co and Au islands on Au(111)

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We devise a new theoretical approach for the treatment of surface electrons confined by metal/semiconductor islands of arbitrary shape. Instead of conventional grid method for the solution of electronic Schrödinger equation, we apply a radial rescaling approach which maps efficiently the eigensolutions of a particle in arbitrarily shaped box onto known solutions for a particle in a circular disk [1]. The method is particularly efficient for nanoislands of polygonal type, giving accurate analytical solutions for regular polygons.

The developed methodology was applied for the simulation of local density of states (LDOS) patterns derived from low temperature scanning tunneling spectroscopy measurements performed on two-dimensional Co and Au islands self-organized on clean Au(III) films [2,3]. In both materials the nanoislands had various shapes and very small sizes, of the order of several nm$^2$. The experimental LDOS patterns were found to fit accurately to the calculated wavefunctions and the variation of these patterns with the energy (sample voltage) was also nicely reproduced. Our results support the general validity of the particle-in-a-box model.

References


Linear self-assembly of nanoparticles within smectic liquid crystal defect pattern

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Technical progress offers now various methods to build hybrid and nanostructured materials with new properties (ie different from bulk properties). In particular nanoparticles assemblies of controlled geometry can be formed, combining the properties of nano-objects with the one of their host matrix. In case of gold nanoparticles (GNPs), the creation of straight chains of single nanoparticles is of great interest due to the induced anisotropic optical properties associated with localized surface plasmon resonance (LSPR). However it still remains difficult to create them on a large scale. To the best of our knowledge, “isolated” straight chains of nanoparticles in close contact do not exist. We show that self-assembly within liquid crystals is particularly promising for such a goal.

Mixing GNPs with liquid crystals (LC) will present the added value of the LC optical anisotropy, thus providing new means of tuning LSPR, e.g. with an electric field or with light polarization. However, a well-defined orientation on one hand of the LC around the NPs, on the other hand of the NPs themselves is needed, though being difficult to realize. Here, we demonstrate that patterns of linearly self organized LC defects in smectic phase [1] can force self-assembly of NPs. We evidenced straight and parallel chains of gold nano-spheres and quantum dots. [2] The chains have a width comparable to the size of a single particle, 5 nm, and can be as long as hundreds of µm. Separation between nano-particles in a given chain varies from a few µm to 1.5 nm as the concentration increases by 4 orders of magnitude, and chains transform into ribbons when the concentration is further increased. Such hybrid system, combining GNPs and liquid crystal, is optically active, showing a polarization-dependent plasmon resonance that can be tuned as a function of particle concentration.

Preparation of nanostructured silver layer: the process control and monitoring

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Silver exhibits a great potential for a fabrication of metal-dielectric and plasmonic optical devices due to its unique optical constants and excellent electrical properties. In this work, we show preparation of nano-structured ultra-thin silver layer possessing a plasmon resonant behavior. The silver layers were deposited by RF magnetron sputtering in pure argon or its mixture with nitrogen. Typically, the growth of Ag layer is governed by Volmer-Weber mechanism, which is characterized by the isolated islands formation at the initial stage of the silver nucleation on a substrate. Nevertheless, we show that the growth mode of the silver can be controlled by the deposition condition. We demonstrate that the nucleation process is significantly influenced by presence of the reactive gas and the plasma parameters. Thus an ultra-thin, continuous and smooth silver layer can be prepared using this method. The prepared ultra-thin continuous layers were thermally annealed exploiting the effect of Rayleigh instability for transformation of continuous layer to semi-spherical silver nanoparticles. Both, the deposition process and the thermal annealing was monitored by means of the spectral ellipsometry. The nano-granular character of the nano-structured layer is revealed by resonant features in the extinction coefficient spectra. The surface morphology of the completed layer was analyzed by scanning electron microscopy (SEM), and atomic force microscopy (AFM).
Self-Assembly of nanoparticles into Lennard-Jones-like clusters

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Nanoparticles self-assemble into regular superstructures when carefully destabilized from dispersion, during evaporation at the gas-liquid interface or when spread on a Langmuir–Blodgett trough. In these processes, however, the number of particles in the superstructure is undefined. Here, we present a process where the particle number is defined and small. We assemble particles inside microemulsions droplets and study the process by observing the emulsion. Our strategy is derived from Pine’s assembly of microparticles inside oil droplets [1]. In contrast to his results with microparticles, we find that nanoparticles yield clusters with geometries that strongly remind of atomic Lennard-Jones clusters (Fig.1, left panels). In this contribution, we discuss why and how such clusters form.

To assemble clusters, monodispersed gold nanocrystals (6 nm core diameter) were introduced into the disperse phase of an emulsion. The dispersed solvent was evaporated until the nanoparticles agglomerated inside the droplets. In emulsion, particles often segregate to the oil-water interface and form Pickering emulsions. Here, we used surfactants to tune the surface energy so that the particles remain inside the bulk of the droplets. In-situ observation of the assembly process via surface plasmon spectroscopy and small-angle x-ray scattering suggests that assembly occurs rapidly, shortly before the dispersed phase is entirely evaporated (Fig. 1, right panels). We believe that the resulting Lennard-Jones geometries represent minimum-energy arrangements of particles, in analogy to the atomic packing of metal and noble gas clusters.

Figure 1: Left panels: A comparison of TEM micrographs showing supraparticles of 6-nm-diameter gold nanoparticles and simulated projections of the corresponding Lennard-Jones clusters (numbers indicate the number of particles). Right panel: Plasmon resonance shift of gold nanoparticles as a function of droplet diameter (from dynamic light scattering) during the evaporation process. The largest part of the shift occurs towards the end of the evaporative process, which indicates agglomeration.

Reference:
Gold Nanoparticles covered by nitroxide radicals – synthesis, electrochemical characteristic and catalytic ability.

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Functionalized gold nanoparticles (AuNPs) are very promising precursors for designing new materials. [1] They can find application as biosensors [2], in therapy and diagnosis of cancer [3], in the catalysis [4], and optoelectronics [5]. Progress in modern materials is also associated with spin decorated AuNPs that can be used, for example, in cancer diagnostics/therapy [6], designing spintronic devices, as nanospin probes in biochemistry and medicine [7].

We report the one-phase synthesis of gold nanoparticles covered by nitroxide radicals with spherical shape, small range in diameter, narrow size distribution (1.90 nm ± 0.54). The presented method of synthesis consists in direct grafting of nanoparticles with bisnitroxide disulfide without coating them first with any ligands. The average number of ligands per core has been derived from X-ray photoelectron spectroscopy (XPS), thermogravimetric and elemental analyses. TEM and AFM observation and Small angle X-ray scattering (SAXS) analysis allowed to determine nanoparticles size and distribution. FTIR, EPR spectra confirmed nitroxide functionalization of the synthesized nanoparticles. Cyclic voltammetric behavior of gold electrode modified with obtained nanoparticles was examined and kinetic parameters for nitroxide/nitrosonium cation redox system were determined. The catalytic ability of the obtained nanoparticles in alcohol oxidation reactions was evaluated on modified gold electrode by cyclic voltammetry.

Silver nanoparticles capped by Pt-containing organometallic dithiols: interaction at the metal/ligand interface and surface structure studied by SR-XPS and XAS

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Noble metal nanoparticles (MNPs) functionalized with molecular ligands are potential materials for applications in different areas as for example electronics, optics, catalysis, sensors and biotechnology. As a consequence, considerable effort is devoted to the synthesis and characterization of such materials. One of the most emerging topic is the preparation of 2D and 3D MNPs networks and the first step for the achievement of complex networks can be envisaged with the formation of dyads and linkages between MNPs. Bifunctional organometallic ligands such as terminal dithiols have been proposed as efficient stabilizing agents. While many studies have tackled the synthesis and characterization of gold dimers and networks, which have peculiar plasmon resonance behavior, AgNPs assembly into networks and superstructures is more unusual.

In this work, synchrotron radiation (SR) induced X-ray Photoelectron spectroscopy (SR-XPS) and X-ray Absorption Spectroscopy (XAS) were used to investigate AgNPs functionalized by organometallic dithiols. In particular, combining SR-XPS and SR-XAS allow probing in detail the surface nature (structure, chemical composition, electronic state) of the NPs sowing, in particular, the existence of two states for S: a fraction stays at the NP surface bridging the thiols molecules, a fraction sinks into the NP producing a thin AgS shell around the metallic core.
A three-dimensional WKB calculation of the charging and retention times of metal nanoparticles embedded in a dielectric matrix

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When an assembly of metal nanoparticles (mNPs) is found in a dielectric matrix over a Si substrate, with an applied bias the mNPs are filled with electrons (or holes depending on the polarity of the bias). It is customary to calculate the times for either charging or discharging when the bias is removed (retention) by either (i) simple capacitor models or (ii) solving the three-dimensional (3D) Poisson equation and using a simplified 1D-WKB model for the tunneling current despite the 3D nature of the potential profile. In this paper we use a fully 3D self-consistent method in which both potential and current are calculated by a 3D Poisson and a 3D-WKB [1] method respectively. The methodology is applied with considerable success to Non-Volatile-Memory structures with Au NPs in a SiO2/HfO2 matrix fabricated by our group and reported previously [2].

3D Supracrystals of Ag Nanocrystals: Control of Order and Periodicity.

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Self-assembled metal nanocrystals passivated with organic molecules have attracted the attention of several research groups. We get evidence of the ordering effect in 2D or 3D assemblies by observing changes in the vibrational [1] and crystalline growth properties [2] between ordered and disordered assemblies. Under these conditions, the crystalline structure of the self-assemblies may affect significantly their physical properties, which motivates the need for understanding nanocrystal organization. 5 nm silver nanocrystals are synthesized in mixed functionalized reverse micelles and coated by either decanethiol (C_{10}) or dodecanethiol (C_{12}) [3]. They are then dispersed in decane and deposited on highly oriented pyrolitic graphite (HOPG) substrate. We show, by small-angle-X-Ray diffraction, that the same silver nanocrystals (same size, shape and crystallinity) passivated by C_{10} chains can adopt either hexagonal close packed (hcp) or face centered cubic (fcc) structures at a given pressure depending on the deposition temperature. However, when passivated by C_{12} chains (i.e., with two more carbon atoms) the phase diagram includes the dense fcc and the loose bcc lattices as well as disordered regions of random-close-packing (rcp). The effect of the solvent on the supra-crystal formation has been also studied [4]. The formation of the bcc structure is shown to be solvent independent. In contrast the hcp and fcc structure depend on the nature of the solvent. These observations are strongly supported by a new theoretical model [4]. It is shown that the bcc structure is mainly governed by van der Walls attractions whereas the hcp and fcc structures are due to kinetic processes.
