IRUN
International Research Universities Network
3rd IRUN Symposium on Nanotechnology
Barcelona October 14-15 2010

BOOK OF ABSTRACTS
INTERNATIONAL RESEARCH UNIVERSITIES NETWORK

The aim of IRUN network is to further improve the quality of research and teaching at the universities involved. Furthermore, the network serves as a platform for joint conferences, symposiums and seminars. Current members of the network are Jagiellonian University in Krakow (Poland), Peter Pazmany Catholic University in Budapest (Hungary), Radboud University Nijmegen (Netherlands), University of Barcelona (Spain), University of Duisburg-Essen (Germany), University of Glasgow (Great Britain), University of Münster (Germany), Université de Poitiers (France), University of Siena (Italy). The 1st IRUN Symposium on Nanotechnology held at the University of Münster in 2008 was the first in a series of annual symposia focusing on various aspects of nanoscience and nanotechnology. This year, the organising committee kindly invites you to participate in the 3rd edition of the symposium, which shall be held in Barcelona in October 14th and 15th.

ORGANIZERS
On behalf of the IRUN Network the 3rd edition of the IRUN Symposium on Nanotechnology is organized by the University of Barcelona.

KEY-NOTE SPEAKERS
- Christian Bobisch, University of Duisburg-Essen, Germany
- Sophie Camélio, Université de Poitiers, France
- Hans Elemans, Radboud University Nijmegen, The Netherlands
- Malcolm Kadodwala, University of Glasgow, Great Britain
- Jerzy Konior, Jagiellonian University, Poland
- Franciszek Krok, Jagiellonian University, Poland

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ADDRESS
c/ Martí i Franquès, nº 1, 3rd Floor, 08028 Barcelona
08:30-09:30 Registration

09:30-09:40 Welcome and opening

09:40-10:15 K1 – Hans Elemans (Radboud University Nijmegen)  
Seeing Single Molecules in a Chemical Reaction

10:15-10:50 K2 – Daniel Navajas (University of Barcelona)  
Nanomechanics of Respiratory Cells: from Bench to Bedside  
Coffee break

10:50-11:20 O1 – Daniel Hagmeyer (University of Duisburg-Essen)  
Self-assembly of Calcium Phosphate Nanoparticles into Hollow Spheres in the Presence of Amino Acids and Peptides

11:20-11:40 O2 – Manuel Neumeier (University of Duisburg-Essen)  
Synthesis of Fluorescent Core-shell Hydroxyapatite Nanoparticles

11:40-12:00 O3 – Paloma Flórez (University of Barcelona)  
Transdermal Permeation Study of a 3% Doxepin Nanoemulsion and a 3% Imipramine Nanoemulsion for Topical Analgesic Purposes

12:00-12:20 O4 – Jan Klesing (University of Duisburg-Essen)  
Nucleic-acid Functionalized Calcium Phosphate Nanorods for Cell-transfection and Genesilencing

12:20-12:40 O5 – Aurora Dols-Pérez (University of Barcelona)  
Dielectric Properties of Supported Lipid Layers at the Nanoscale  
Lunch

13:00-15:00 Lunch

15:00-15:35 K3 – Malcolm Kadodwala (University of Glasgow)  
Ultrasonic Detection of Biomacromolecular Structures using Chiral Nanomaterials

15:35-16:10 K4 – Franciszek Krok (Jagiellonian University)  
High-resolution Kelvin Probe Force Microscopy of Heterogeneous Metal-semiconductor Systems

16:10-16:45 K5 – Xavier Batlle (University of Barcelona)  
Recent Advances in Magnetic Nanoparticles for Bioapplications  
Coffee break

16:45-17:15 O6 – Pietro Tierno (University of Barcelona)  
Giant Transversal Diffusion of Longitudinally-driven Paramagnetic Particles in a Magnetic A-thermal Ratchet Potential

17:15-17:55 O7 – Iranaeus Wlokas (University of Duisburg-Essen)  
Detailed Simulation of Iron nanoparticle Synthesis in Premixed Low-pressure H₂/O₂ Flames

17:55-18:15 O8 – José María Escartín (University of Barcelona)  
Concentric Multiple Quantum Rings

21:00 Conference dinner
FRIDAY, OCTOBER 15
09:30-10:05 K6 – Christian Bobisch (University of Duisburg-Essen)
Transport Phenomena on the Atomic Scale

10:05-10:40 K7 – Blas Garrido (University of Barcelona)
Light Emitting MOS Capacitors and Transistors with Silicon Nanocrystals

10:40-11:10 coffee break

11:10-11:30 O9 – Arkadius Ganczarczyk (University of Duisburg-Essen)
Transverse Ballistic Rectification in Density-Modulated 2D-systems

11:30-11:50 O10 – Gabriel Gomila (University of Barcelona)
Quantifying the Low Frequency Dielectric Constrast at the Nanoscale

11:50-12:10 O11 – Martin King (University of Glasgow)
An Investigation of TaS$_2$ Nanoribbons with Photoelectron Spectroscopy and Electron Microscopy

12:10-12:30 O12 – Vivek Antad (University of Poitiers)
Ag: Si$_3$N$_4$ Nanocomposites Studied for Thermal and Plasma Annealing by Real Time Optical Monitoring and Post-mortem TEM Characterizations

13:00-15:00 lunch

15:00-15:35 K8 – Jerzy Konior (Jagiellonian University)
Experimental and theoretical aspects of friction at atomic scale

15:35-16:10 K9 Sophie Camélio (University of Poitiers)
Optical properties of self-organized silver and gold nanoparticles on rippled dielectric surfaces

16:10-16:30 O13 Gregory Abadias (University of Poitiers)
Intrinsic stress evolution in sputtered thin films using real time multiple-beam optical stress sensor

16:30-16:50 O14 – T. T. H. Pham (University of Poitiers)
AlCrN PVD Thin Films to Harden Engineering Material Structures

16:50-17:20 coffee break

17:20-17:40 O15 – Sonia Estradé (University of Barcelona)
Chemical and Electronic Properties of (001) and (110) SrTiO$_3$/La$_{2/3}$Ca$_{1/3}$MnO$_3$ Interfaces Assessed by EELS

17:40-18:00 O16 – Sonia Conesa-Boj (University of Barcelona)
Defect Formation in Ga-catalized Silicon Nanowires

18:00-18:20 O17 – Elena Xuriguera (University of Barcelona)
Contribution to the Study of Single Core Ni Nanobeads: Synthesis, Characterization and Investigation of Magnetophoresis Behaviour

18:00-18:40 O18 – José Manuel Rebled (University of Barcelona)
Self-assembled BiFeO$_3$ - CoFe$_2$O$_4$ epitaxial nanostructures grown on (001) LaAlO$_3$
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SEEING SINGLE MOLECULES IN A CHEMICAL REACTION

Hans Elemans
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A detailed understanding of chemical reactions is of fundamental importance for the design of new chemical processes. A wealth of conventional spectroscopic techniques is available to study reaction mechanisms at the ensemble level, where their behaviour is averaged, but with the advent of scanning probe microscopy it has become possible to obtain new insight at the level of individual molecules.

I will present the study of chemical reactions in a dedicated Scanning Tunneling Microscope (STM), a device that can image single atoms and molecules while they are reacting at the chemically relevant interface of a solid and a liquid. It will be shown that by studying reactions in the highest detail possible, unique new information about reaction mechanisms can be obtained.

References:
Mechanical properties of cells play a critical role in many essential biological functions including migration, contraction, differentiation and gene expression. Moreover, cells feel and actively respond to adhesive forces and deformations exerted by the adjacent cells and the extracellular matrix. The cell mechanical behavior is increasingly recognized as a key determinant of normal cell function and of its alterations under pathological conditions. However, knowledge of the mechanical behavior of the cell remains largely incomplete.

Recent development of nanotechnologies specially suited for probing biological samples allows the study of respiratory cells at the single cell and molecule level. We developed a novel device to subject cultured cells to dynamic stretch. Combination of this device with nanomanipulation of microbeads attached to the cell surface allowed us to reveal a universal law of strain-induced transient cell fluidization. A novel technique to map traction forces exerted by cultured cells in a stretchable substrate allowed us to show that strain-induced fluidization is associated with a transient disruption of the actin-myosin machinery. We have investigated the physical laws that govern cell dynamics by particle nanotacking, showing that cytoskeleton remodeling is a thermically activated process mediated by ATP.

With atomic force microscopy (AFM) we have shown that the dependence of cell mechanics with temperature is dominated by the contractile activity of molecular motors. AFM is a powerful tool for probing cell nanomechanics. However, contact area between the tip and the cell is not precisely defined in conventional AFM tips. Novel flat ended cylindrical tips allowed us to reveal a differential mechanical response of lung epithelial cells to compressive and tensile local stresses. Neutrophil mechanics was measured with AFM in patients with advanced hypoxemic chronic obstructive pulmonary disease (COPD) before and after bilateral lung transplantation, and compared with measurements taken in healthy nonsmokers. Young’s modulus of neutrophils from patients with COPD was significantly greater than controls. Neutrophil stiffness decreased after lung transplantation showing no significant differences with healthy nonsmokers. Neutrophil stiffening in COPD patients may be related to the abnormal inflammatory response of the lung. Neutrophil improvement after lung transplantation suggests decreased inflammatory pulmonary and systemic responses.

Acknowledgements: Ministerio de Sanidad y Consumo (PI081908).
SELF-ASSEMBLY OF CALCIUM PHOSPHATE NANOPARTICLES INTO HOLLOW SPHERES IN THE PRESENCE OF AMINO ACIDS AND DIPEPTIDES

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Calcium phosphate is the inorganic mineral of bone and teeth. Hollow calcium phosphate microspheres and nanospheres can be prepared by hard-templating synthesis[1, 2] or template-free-synthesis.[3] Here we present a synthesis of hollow spheres of calcium phosphate by spontaneous self-assembly of calcium phosphate nanoparticles in the presence of amino acids and dipeptides. Hollow spheres of calcium phosphate were prepared by precipitation of aqueous solutions of calcium nitrate and diammonium hydrogen phosphate in the presence of the amino acids L-glycine (Gly), L-alanine (Ala), L-tyrosine (Tyr), and L-serine (Ser), or the dipeptides L-alanine-L-tyrosine (Ala-Tyr) and and L-serine-L-tyrosine (Ser-Tyr). The particles had a spherical morphology as shown by scanning electron microscopy (SEM), transmission electron microscopy (TEM), cryo transmission electron microscopy (cryo-TEM) and nanoindentation with atomic force microscopy (AFM). By TEM, we observed a wall thickness of 10-20 nm. The diameters of the hollow spheres were in the range of 100 to 200 nm as shown by AFM, dynamic light scattering (DLS), nanoparticle tracking analysis (NPTA), and SEM.

The hollow spheres were stable against ultrasonication for 30 min and stable at 70 °C for a few minutes. The self-assembly of initially formed calcium phosphate nanoparticles into hollow spheres was completed after 25 seconds as indicated by cryo-TEM.

References:
SYNTHESIS OF FLUORESCENT CORE-SHELL HYDROXYAPATITE NANOPARTICLES

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Inorganic nanophosphors are an interesting class of fluorescing materials. These are usually Ln3+-doped materials, which benefit from the luminescence properties of the lanthanides, which are a large Stokes shift, narrow emission bands and a long fluorescence lifetime [1]. As the lanthanide fluorescence results from parity-law forbidden electronic transitions within the f-subshell, the fluorescence intensity of the aqueous ions is very low [2]. To enhance the fluorescence intensity, the lanthanides can be complexed with energy-transferring ligands or doped into an inorganic lattice [3].

We have synthesized europium-doped hydroxyapatite nanoparticles to achieve a red fluorescence under excitation with UV light. To enhance the fluorescence intensity, the particles were co-doped with yttrium [4]. A subsequent increase of the crystallinity by hydrothermal treatment further enhanced the fluorescence intensity due to a better energy transfer from the lattice. Next, fluorescence quenching on the surface of the particles must be minimized. This was achieved by hydrolysis of silicic acid esters on the surface of the hydroxyapatite nanoparticles, which gave a nanometre-thick silica shell surrounding the nanoparticles.

References:
TRANSDERMAL PERMEATION STUDY OF A 3% DOXEPIN NANOEMULSION AND A 3% IMIPRAMINE NANOEMULSION FOR TOPICAL ANALGESIC PURPOSES

A.C. Calpena\(^{(1,3)}\), R. Lázaro\(^{(1)}\), P. Flórez\(^{(1)}\), A. Flo\(^{(1)}\), F. Fernández\(^{(1)}\) and B. Clares\(^{(2)}\)

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Apart from their antidepressant activity, tricyclic antidepressants such as doxepine and imipramine have a strong local analgesic activity and therefore can lead to long-lasting pain relief which makes them an interesting pharmacological tool for the treatment of chronic pain caused by postherpetic neuralgia or cancer, for instance \([1,2]\). Their analgesic effects may be increased by encapsulation into micro or nanospheres. Nanoemulsions (NE) are also a possible route of drug delivery via topical application \([3]\). The aim of this study was to characterise two NE developed (3% doxepine and 3% imipramine) and determine their drug delivery capability by an ex vivo study (transdermal permeation with human skin) in order to know their feasibility as drug delivery systems for local analgesic purposes. Morphometrical properties of the developed NE were determined. Both formulations showed particle sizes lower than 10 nm and with a polydispersity in the range of 1,33-2,71. Ex vivo transdermal permeation studies with human skin were performed using Franz-type diffusion cells. Stationary state concentrations found were not sufficient to achieve plasmatic therapeutic concentrations with an antidepressant effect; however, these low concentrations may be sufficient to generate the desired topical analgesic activity, being the aim of this study the development of a nanoemulsion formulation.

The results obtained indicate their promising use as topical drug delivery systems for local analgesic purposes, such as the treatment of postherpetic neuralgia.

References:


NUCLEIC-ACID FUNCTIONALIZED CALCIUM PHOSPHATE NANORODS FOR CELL-TRANSFECTION AND GENE-SILENCING

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Calcium phosphate nanorods which are typically used as paste for bone substitution were functionalized by nucleic acids. The structure and morphology of the nanorods were studied by dynamic light scattering (DLS) and scanning electron microscopy (SEM). The colloidal dispersion contained no aggregates. The nanorod length was around 150 nm and the typical width was 25 nm.

We used these nanorods for transfection and gene silencing in vitro. For the transfection with pcDNA3-EGFP (encoding enhanced green fluorescent protein; EGFP) HeLa and T24 cell lines were used. The transfection efficiency of the DNA-functionalized nanorods was around 2% for HeLa cells and 0.6% for T24 cells. This is comparable to the standard calcium phosphate method and also to custom-made single-shell calcium phosphate nanoparticles developed by Welzel et al. [1]. Gene silencing with siRNA against EGFP was performed on HeLa-EGFP cells [2]. The efficiency of gene silencing using siRNA-functionalized nanorods was about 22% and was thereby comparable to the results of Polyfect®. The toxicity of the transfection methods was analyzed using the MTT assay, which showed that the nucleic acid-functionalized calcium phosphate nanorods were not toxic for the cells, unlike Polyfect® which showed some toxicity. The above mentioned efficiency and non-toxicity indicates that an injectable paste of nanoparticles functionalized by nucleic acids may be a promising genetically active biomaterial which can allow the treatment of, e.g. osteoporosis.

References:
The cell membrane is a dynamic system of relevance in different biological areas because of its functions. Membranes are complex systems in which the variations of composition and organization are highly related with the function of the cell type. Recent studies in its organization suggest that membranes are lipid mixtures with ordered domains and disordered areas. For this reason, for the correct characterization of this structure is necessary to use nanoscale techniques able to provide a good lateral resolution without perturbing the intrinsic order and organization. Until now most of the studies have concentrated on determining the spatial structure and composition of membranes with several techniques, but in the study of the membrane properties not only the topography and distribution is relevant, the electrical properties (such as conductivity, charge, polarizability) play also an important role in many cell functions i.e. because its relationship with the protein conformation and signal transduction. In particular, the membrane polarizability of biomembranes, which is quantified through the dielectric constant, is an important parameter of cell bioelectricity as it quantifies the intrinsic dielectric response of the plasma membrane at low-frequencies in processes such as membrane potential formation, action potential propagation or ion membrane transport. Furthermore, it determines the cell response to externally applied electrical fields employed by bioelectrical techniques such as dielectrophoresis, impedance spectroscopy, or electroporation. Existing techniques provide low-frequency dielectric constant values for cell membranes with a spatial resolution limited, in the best of the cases, to a few micrometers. Recently, in our group we have developed a novel nanoscale dielectric characterization methodology based in an Atomic Force microscope (AFM) called Nanoscale Dielectric Microscopy (NDM), which is able to quantify and image the low-frequency dielectric constant of biomembranes with high precision and with nanoscale lateral spatial resolution [1,2]. The demonstration of the technique has been performed with supported purple membrane patches, a natural membrane from the Halobacterium salinarum archea. In the present communication we present results aimed at correlating the dielectric constant of biomembranes with its composition. With this objective in mind we measured the dielectric constant of supported phospholipid layers as model systems of biomembranes by means of dynamic electrostatic force microscopy.

References:
ULTRASENSITIVE DETECTION OF BIOMACROMOLECULAR STRUCTURES USING CHIRAL NANOMATERIALS

Malcolm Kadodwala
University of Glasgow

The spectroscopic analysis of large biomolecules is important in applications such as biomedical diagnostics and pathogen detection, and spectroscopic techniques can detect such molecules at the nanogram level or lower. However, spectroscopic techniques have not been able to probe the structure of large biomolecules with similar levels of sensitivity. Here we show that superchiral electromagnetic fields, generated by the optical excitation of plasmonic planar chiral metamaterials, are highly sensitive probes of chiral supramolecular structure. The differences in the effective refractive indices of chiral samples exposed to left- and right-handed superchiral fields are found to be up to 106 times greater than those observed in optical polarimetry measurements, thus allowing picogram quantities of adsorbed molecules to be characterised. The largest differences are observed for biomolecules that possess chiral planar sheets, such as proteins with high β-sheet content, which suggest that this approach could form the basis for assaying technologies capable of detecting amyloid diseases and certain types of viruses.
HIGH-RESOLUTION KELVIN PROBE FORCE MICROSCOPY

F. Krok, K. Sajewicz, J. Konior, M. Goryl, P. Piatkowski and M. Szymoński
Jagiellonian University

Kelvin probe force microscopy (KPFM), based on dynamic force microscopy (DFM) principles, gives both topography and potential distribution of the sample together with a high spatial resolution. It has already been demonstrated that the KPFM is a powerful tool for a nanometer-scale range work function mapping, evaluation of doping concentration in semiconductors, or determining a local work function distribution in quantum dots. Thus, from many crucial aspects concerning KPFM technique, the limits of potential sensitivity and lateral resolution are particularly important.

In this paper, we present the experimental and theoretical results concerning the limits of lateral resolution of surface potential, measured by means of KPFM, working in frequency modulation mode (FM-KPFM) in ultrahigh vacuum (UHV). To study the limits of potential and lateral resolutions, we have investigated clean surface of compound semiconductor InSb(001) and the same surface with some submonolayer coverages of KBr and Au. It has been found that long- and short-range bias-dependent interactions, acting between the tip and the surface, can be detected and that both interactions contribute to the measured Contact Potential Difference (CPD) signal. First, we have established that when only the long-range electrostatic interactions between the tip and the surface are active, the CPD map provides the distribution of the local surface potential on the imaged sample. For this case, the experimental findings are compared with the predictions of theoretical calculations based on a realistic model for the cantilever-sample geometry. Second, when the short-range and bias-dependent interactions are detected, FM-KPFM provides even the atomic-scale contrast in the CPD signal. In this situation, however, the measured CPD signal is not related to the sample surface potential but rather reflects the properties of the front tip atom-surface atom interactions.
Magnetic nanoparticles (NPs) attract intense research as they provide the critical building blocks for the booming of nanoscience and nanotechnology, and they show enhanced properties over their bulk counterparts, arising from the interplay among quantum, finite-size and surface effects and inter-particle interactions [1]. A key question is how the nanostructure modifies their physical properties and how one can take benefit to improve applications in high-density recording, sensors or biomedicine. Consequently, understanding and controlling the effects of the nanostructure and surface chemistry on the NP properties have become increasingly relevant issues.

As the size is reduced below 100 nm, deviations from the bulk behavior have been widely reported and attributed to changes in the magnetic ordering at the surface layer and finite-size effects, thus giving rise to a significant decrease in the magnetization. However, that particle-like behavior is undesirable in many applications, where the NPs should comply with a variety of requirements. In the case of biomedical applications, those comprise: (i) superparamagnetic behavior at room temperature in order to avoid particle aggregation due to inter-particle interactions; (ii) high saturation magnetization to achieve a high magnetic response under the application of moderate magnetic fields; (iii) limiting size for in vivo applications within 1 and 50 nm, depending on the specific application; and (iv) bio-compatibility and functionality to reach specific targets inside the body. Consequently, biomedical applications require of magnetic NPs of a few nanometers in size showing magnetic properties close to the bulk material. Research in this field is thus mainly focused on new synthesis methods enabling the preparation of NPs with high crystal quality and reduced magnetic disorder. In particular, iron oxide NPs are suitable candidates due to their low toxicity and ease to be functionalized. Magnetite Fe₃O₄ and maghemite γ-Fe₂O₃ are probably among the most widely studied magnetic materials.

Continued on next page
In order to elucidate those phenomena, we compared two sets of samples of 5 nm Fe$_{3-x}$O$_4$ NPs, synthesized either by thermal decomposition of an organic iron precursor in an organic medium or low-temperature co-precipitation in aqueous conditions. In the first case, oleic acid was used as surfactant and was covalently bonded to the NP due to the high synthesis temperature; in the second case, polyvinyl alcohol was used, leading to a protective coating without chemical bond. Magnetic measurements, transmission electron microscopy and X-ray absorption and magnetic circular dichroism showed that covalently bonded NPs displayed very high crystal quality and bulk-like magnetic and electronic properties, while NPs with adsorbed coatings showed poor crystallinity and particle-like properties [2-3], although the values of the surface anisotropy were similar [4]. The key role of the nanostructure is thus suggested since none of the usual particle-like behavior is observed in high quality NPs larger than a few nm in size. These conclusions are supported by Monte Carlo simulations. We also showed that thermal decomposition is capable of producing NPs within 5 and 50 nm in size [5] suitable for liver and brain MRI, and for the determination of the bio-distribution of the NPs in a variety of organs (liver, kidney, spleen...) in mice [6]. A review of all the foregoing will be available soon in Reference 7.

References:

Work in collaboration with:
P. Guardia and Ò. Iglesias (IN2UB); F. Bartolomé, L. M. García and J. Bartolomé (Dep. Física de la Materia Condensada and ICMA, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain); M. P. Morales, A.G. Roca and C. J. Serna (ICMM-CSIC, Cantoblanco, 28049 Madrid, Spain); R. Mejías and D.F. Barber (CNB-CSIC Madrid, Spain).
GIANT TRANSVERSAL DIFFUSION OF LONGITUDINALLY DRIVEN PARAMAGNETIC PARTICLES IN A MAGNETIC A-THERMAL RATCHET POTENTIAL

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Paramagnetic colloidal particles in an aqueous solution are transported on the surface of a uniaxial ferrite garnet film [1,2]. With no field, the colloids confined along the Block Walls (BW) show thermal motion with diffusion $D_0 \sim 10^{-4}$ $\mu$m/s. During motion we measured a transversal diffusion coefficient four orders of magnitude larger and which shows a clear dependency on the driving frequency. We explain this enhancement by invoking the presence of a time-refreshed disordered landscape in the magnetic pattern [3].

References:
DETAILED SIMULATION OF IRON OXIDE NANOPARTICLE SYNTHESIS IN PREMIXED LOW-PRESSURE H₂/O₂ FLAMES

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A low-pressure flame reactor is used for the synthesis of nanosized iron oxide particles from the gas phase. The premixed, burner-stabilized flame is fed by hydrogen, oxygen, and argon, while a mixture of iron pentacarbonyl (Fe(CO)₅) in argon is added to the fresh gases as precursor. Like many metal-organic and metal-carbonyl compounds, Fe(CO)₅ is well known for its strong influence on flame reaction kinetics and it has been used as flame inhibitor and anti-knock agent in fuels [1,2]. A credible simulation requires a detailed understanding of the flame- and precursor chemistry besides the processes of particle dynamics. The present study describes a comprehensive simulation approach for the precursor chemistry, the formation, and the growth of iron oxide nanoparticles.

As a boundary condition for the one-dimensional simulations, the measured temperature distribution within the burner chamber was taken from two- and one-dimensional temperature fields detected by laser-induced fluorescence of NO molecules (multi-line NO-LIF thermometry) [3]. The simulation of the gas-phase reactions of the doped flame was performed based on a reduced Fe(CO)₅ combustion mechanism [4]. The population balance equations were solved for particle volume and particle surface area using a method of moments. The methods applied in one-dimensional simulations were incorporated into multi-dimensional CFD codes for the simulation of the reactive flow.

References:
CONCENTRIC MULTIPLE QUANTUM RINGS

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By means of a full configuration-interaction exact diagonalization (ED) technique that uses local spin-density functional theory (LSDFT) single-electron orbitals to build the basis set of Slater determinants [1], complemented with the more phenomenological LSDFT, we study the electronic internal structure and the far-infrared (FIR) multipole response of nanoscopic concentric double (CDQR) and triple (CTQR) quantum rings [2,3,4] submitted to a perpendicularly applied magnetic field B.

We show that, under these circumstances, few-electron two-dimensional CDQR display radially and azimuthally localized fully-polarized states. A comparison and discussion on the agreement between the results obtained from ED and LSDFT approaches is presented: the ED leads to such crystallized configurations in the two-body density function, while a suitable calculation that makes use of the LSDFT may already display them in the one-body density [5].

We present the ground state energy for CDQR as a function of the total angular momentum of the system, the so-called yrast line, which shows a landscape of isomeric yrast-trapped metastable quasi-degenerate states that display different electron distributions within the two rings. The charge-density response of these isomeric states corresponding to dipole (quadrupole) excitations exhibits very soft modes at energies that roughly correspond to those displayed by a rigidly-rotating N-electron molecule [3]. We also describe the monopole response of the system and the B-dependence of these multipole excitations.

In the CTQR case, we discuss within LSDFT the appearance of the ground state and spin- and charge-density dipole responses for systems hosting several tens of electrons. We pay special attention to the oscillations of the persistent current of the system as a function of the applied B.

References:
TRANSPORT PHENOMENA ON THE ATOMIC SCALE

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The scanning tunneling microscope (STM) is an ideal tool to study surface phenomena on the atomic scale. Beside the analysis of topographic features and the geometric structure of surfaces, it offers the possibility to study their electronic structure as well as it can be used to characterize single organic molecules adsorbed on surfaces.

Firstly, I will present a STM based analysis of two different 2-dimensional electron gas (2DEG) systems. On the one hand the electronic surface structure of epitaxial thin films of bismuth on top of a Si(111)-7x7 substrate was analyzed \([1,2]\). Using scanning tunneling spectroscopy (STS) and imaging the local density of states (dI/dV imaging) the topological surface state of Bi(111) was analyzed in detail.

For the Si(111)-√3 x√3-Ag surface the local variation of the electrochemical potential was studied, if a current is applied across the 2DEG of this surface. A multiprobe STM is used to apply the current across the surface while the topography as well as the electrochemical potential can be measured simultaneously. The data reveal a stepwise decay of the electrochemical potential at surface steps, grain boundaries etc., thus the stepwise decay can be addressed to local resistivities on the atomic level \([3]\).

The last part deals with the organic dye copper-phthalocyanine (CuPc) adsorbed onto a Cu(111) substrate. Low temperature scanning tunneling microscopy allows analyzing a current induced motion of single CuPc molecules. Especially a switching process between transient states of the adsorbed CuPc molecule can be imaged and analyzed with sub molecular precision.

References:


TRANSVERSE BALLISTIC RECTIFICATION IN DENSITY-MODULATED 2D-SYSTEMS

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Ballistic rectifiers are textbook examples for nanoscopic devices, which have a function that is determined by shape, rather than material properties. As an example, in four-probe rectifiers with voltage-tunable geometry, the output polarity can be inverted by introducing a symmetry-breaking shape [1,2]. Here, we study a device, where the rectification occurs in a different geometry in a density-modulated two-dimensional electron gas (2DEG). The measurements supported by transport theory give new insight into ballistic phenomena in 2DEGs.

The 2DEG is patterned into a long narrow channel with source and drain contacts and a voltage probe on each side of the channel. Using gate electrodes we induce two stripes of different charge carrier density running parallel to the channel. Under current bias, the resulting density gradient perpendicular to the channel induces a transverse voltage, which – due to the symmetry of the device – does not change polarity when the current direction is reversed. We observe that the rectified transverse voltage $V_{TR}$ increases with increasing density modulation and is proportional to $1/n_1 - 1/n_2$, where $n_1$ and $n_2$ are the charge carrier densities in the two stripes. Furthermore, $V_{TR}$ depends quadratically on the applied source-drain voltage and increases with increasing mobility. The polarity of $V_{TR}$ corresponds to an induced net current from the high- to the low-density region.

Fundamentally, the observed effect can be linked to the symmetry breaking of the potential between the two regions of different carrier densities and thus to the physics of ratchets [4]. Accordingly, the results can be understood as a rectification in a transversely driven ratchet. The experimental observations are discussed in the framework of a classical, single particle billiard model to obtain a deeper insight into this novel rectification effect. Furthermore, possible thermoelectric effects in the structure are discussed.

**References:**

QUANTIFYING THE LOW FREQUENCY DIELECTRIC CONSTANT AT THE NANOSCALE

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The dielectric constant of insulating materials plays a key role in many electrical, optical, and biological phenomena. With scaling of technological applications toward submicro or even nanoscale lengths, the accurate measurement of this property with high spatial resolution has become increasingly important and difficult. The standard dielectric characterization techniques require large-area test structures and are not capable of addressing the dielectric constant at the nanoscale. For this reason new techniques based on scanning probe microscopy are being investigated.

Very recently, in our group we have developed a methodology, referred to as nanoscale dielectric microscopy (NDM), which allows performing quantitative maps of the low frequency (<1 MHz) dielectric constant at the nanoscale on a broad variety of systems ranging from thin and thick insulating materials to biomembranes and single dielectric nanoparticles. In NDM the quantitative dielectric constant images are reconstructed from local capacitance images (or local capacitance gradient images) obtained with state of the art alternating current (or electrostatic force) atomic force microscopy set ups and with the help of accurate theoretical models (either analytic [1,2] or based on large scale finite element numerical simulations [3]). The dielectric constant values obtained have been found to be independent from the experimental set up (e.g. probe radius, scan height, etc.) and, hence, to represent an intrinsic nanoscale property of the material being investigated.

In the present communication we will present the principles of Nanoscale Dielectric Microscopy and its application to a wide variety of nanoscale systems including solid supported biomembranes (Fig. 1) [1,2], thin dielectric films [2], thick dielectric materials (Fig. 2) [3] and single dielectric nanoparticles.

References:
AN INVESTIGATION OF TaS$_3$ NANORIBBONS WITH PHOTOELECTRON SPECTROSCOPY AND ELECTRON MICROSCOPY

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TaS$_3$ is an interesting material to study because it is a quasi one-dimensional conductor. Nanoribbons of TaS$_3$ were characterised using a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS).

The XPS and UPS data showed that the stability of TaS$_3$ nanoribbons was substrate dependent in ultra high vacuum. When left for prolonged periods of time (e.g. 4 days), on Au, the materials were more TaS$_2$ like in character. This change was reversible through annealing.

The TaS$_3$ sample was annealed sequentially up to 1173 K to decompose the material to TaS$_2$. TaS$_3$ is reported to decompose to TaS$_2$ around 1123 K.[1] Electron diffraction data showed that the transition occurs at a lower temperature (≤ 973 K). XPS data suggested that the material was decomposing, but not entirely, to TaS$_2$.

At 215 K, orthorhombic TaS$_3$ undergoes a Peierls transition.[2] In contrast to previous measurements we do not see any temperature dependence in our data, that is clearly a result from the Peierls transition. For instance, the diffraction data shows little change in superlattice spots. There is also no evidence of a reduction in conductivity in the UPS data, which is indicative of a Peierls transition.

References:
AG: Si$_3$N$_4$ NANOCOMPOSITES STUDIED FOR THERMAL AND PLASMA ANNEALING BY REAL TIME OPTICAL MONITORING AND POST-MORTEM TEM CHARACTERIZATIONS

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In-situ and real time surface differential reflectance spectroscopy (SDRS) [1] is sensitive enough to observe the minute changes in the surface plasmon resonance (SPR), which is a collective oscillation of the electrons around the noble metal nanoparticles (NPs) during their interaction with electromagnetic radiation [2]. This SPR greatly depends upon the morphology (size & shape) and organization (surface density) of NPs. In the present case, a dedicated magnetron sputtering system is used for the fabrication of Ag NPs embedded in Si$_3$N$_4$, on which in-situ SDRS is mounted [3]. Here, we optically monitor the SPR modifications during the deposition of Ag and Si$_3$N$_4$. The optical properties are interpreted from post-mortem TEM analysis, which gives the information on the morphology and the organization of the Ag NPs.

The detail explanation of steps (Fig. A: 1, 2, 4, 5) involved in Fig. A, is given elsewhere [3]. During step (Fig. A: 3), the respective samples are subjected to thermal annealing (Fig. A: red line), plasma annealing (blue line) and, are compared with non-annealed samples (Fig. A: green line). A clear blue shift of about 40 nm in SPR wavelength ($\lambda_{\text{max}}$) can be seen during the thermal and plasma annealing when compared to the non-annealed sample. After annealing, this blue shift is conserved during the recovery of Ag NPs by Si$_3$N$_4$ (Fig. A: steps - 4, 5).

| Table A |
|-----------------|-----------------|
| In-plane TEM analysis | Diameter (nm) |
| Density ($\mu$m$^2$) | Diameter (nm) |
| 6700 | 7.60 |
| 7700 | 6.30 |
| 5800 | 7.20 |

Continued on next page
Even though, the optical signals after thermal and plasma annealing are almost identically blue shifted, the causes are entirely different. Thermal annealing, which accelerates surface diffusion of NPs [4], in turn, decreases the average surface density (Table A). In contrast to thermal annealing, TEM analysis reveals that, the plasma annealing introduces increase in the surface density of Ag NPs with decrease in average diameter. Here, the Ar plasma energy may be used to split the bigger NPs into smaller ones, with a possibility of etching. But, in both annealing, the fact of blue shifted optical signals can be attributed to the presence of more spherical NPs than non-annealed one.

Hence, the real time SDRS sensitively follows the SPR modifications and the responsible morphological, organizational changes for these modifications can be verified by post mortem TEM analysis.

References:
EXPERIMENTAL AND THEORETICAL ASPECTS OF FRICTION AT ATOMIC SCALE

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There has been a growing interest in measuring the friction related phenomena at atomic scale. In this lecture some recent experiments, performed at ionic surfaces with step edges, are presented. The presented measurements allow for imaging the terraces and step edges with a lateral resolution down to the atomic scale. We have also performed theoretical calculations of the friction force that allow for explaining the behavior of the friction force during the surface scanning. The calculations are based on the electrostatic tip-surface interaction and static approximation for the friction force evaluation. The obtained results have the same order of magnitude as the experimental data and they are consistent with the observed asymmetry between the down and up-scanning of the lateral force across the edge.
OPTICAL PROPERTIES OF SELF-ORGANIZED SILVER AND GOLD NANOPARTICLES ON RIPPLED DIELECTRIC SURFACES

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A new route to control the morphology and the spatial organization of metallic nanoparticles, and therefore their physical properties, is to use nanostructured surfaces as templates. We will report on the development of an original approach that integrates the production of nanoripple patterns with long-range order by Xe⁺ ion-etching of amorphous dielectric films (Al₂O₃, BN, Si₃N₄) and the elaboration of organized arrays of aligned Au and Ag nanoparticles by grazing incidence ion beam sputtering. By combining direct imaging methods (TEM, AFM) and grazing incidence small-angle x-ray scattering (GISAXS) experiments associated with quantitative analysis, we will show that valuable information can be obtained on the morphology as well as lateral and vertical correlations of the nanostructures present in the nanocomposite films (i.e., ripples, nanoparticles). In particular, shadowing effects due to the grazing incidence geometry lead to the formation of self-organized nanoparticles with an ellipsoidal shape and a major axis parallel to the ripples. The optical properties of the metallic nanoparticles deposited onto such one-dimensional patterns of nanoripples exhibit a strong dependence on the light polarization, which can interpreted as the consequence of both the in-plane spatial organization of the nanoparticles and their shape anisotropy.
INTRINSIC STRESS EVOLUTION IN SPUTTERED THIN FILMS USING REAL TIME MULTIPLE-BEAM OPTICAL STRESS SENSOR

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Intrinsic stress during polycrystalline growth of metal thin films has been the subject of intense researches in the last years, especially with the implementation of atomic-scale sensitive multiple beam optical stress sensor (MOSS) technique. If the case of Volmer-Weber growth of high mobility metals like Ag or Al has been largely investigated, mainly during thermal evaporation, the case of low-mobility materials like transition metal (Ti, Ta, Zr, Mo or W) remains quite unexplored. In particular, no systematic study has been reported during magnetron sputtering, where the contribution of the more energetic incoming particles may significantly alter the elementary growth processes.

The presentation will be focused on the growth of low-mobility metals (Mo, W, ...) on Si, for which a two-dimensional growth takes place. Films were deposited at room temperature by magnetron sputtering under Ar discharge plasma on ~100 nm thick Si substrates covered with native oxide or with amorphous Si and the stress evolution was recorded in situ and in real time using a MOSS system designed by kSA and implemented in the sputtering chamber. The deposition rate and Ar working pressure were varied in the range 0.11-0.44 Pa and 0.6-3.1 Å/s, respectively, to study the influence of growth kinetics and energetics on the stress generation and relaxation processes. For the Mo/Si system (see fig. 1), importance of interfacial effects and phase transformation on the tensile stress evolution in the early growth stages will be demonstrated [1]. The stress reversal towards compression observed at larger film thickness will be discussed based on existing models reported in the literature.

Force per unit width (stress-thickness product \( \sigma \cdot h \)) measured during growth by magnetron sputtering of Mo/Si multilayers. The stress is tensile in Mo sublayers, while that in Si is compressive. The red arrows indicate the presence of a transient phenomenon during the first stages of Mo growth, which is associated with the crystallisation process.

References:
Materials highly resistant to wear, abrasion, erosion and corrosion are of utmost importance in many different industrial fields, which has led in the past few years to the development of coated tools, parts and components able to endure harsh environments and conditions. The keywords for manufacturers in the search of a higher production and productivity have been the increase in tool life while achieving a reduction in tool costs. Nitride alloys like AlCrN have been employed to produce highly efficient steel based tools. The conditions used for their production change the coating structure and hence the performance of the tool.

We report a study on AlCrN thin films deposited by a system of vacuum deposits Concept™ Alliance by Pulverization Magnetron Gencoat™ 3 " (PUMA) with introduction of Ar and N2 gas, at T = 300 °C, the used targets being 99.99% metallic Al and Cr. The chemical compositions of the films were determined by both Energy Dispersive X-ray Spectrometry (EDXS, for Al and Cr) and Rutherford Backscattering Spectroscopy (RBS, for N), while x-ray diffraction (XRD) measurements were conducted in the Bragg- Brentano configuration (reflection mode) on a four-circle Seifert XRD3000 diffractometer to determine the structure (phases and texture).

The macroscopic residual stresses of films were determined by curvature measurements using DEKTAK IIA, while the “sin²Ψ method” was used to determine the in-grain stresses from XRD measurements. The hardness of the films was extracted by a nanoindenter from CSM (Switzerland).

For the range of compositions Al1-xCrxNy (0.53< x< 0.85) of interest here, a CrN type FCC structure was obtained with a strong (200) fiber texture while hexagonal structure was present for the other compositions. The global stresses were compressive for all FCC films resulting from the high energetic deposition conditions used. Using XRD, plots of ln(ad) as a function of sin²Ψ confirmed the presence of in-grain compressive stresses for the films with thickness < 400 nm. The mechanism responsible for this stress state is attributed to “atomic peening”. In contrast, thicker films (> 400 nm) showed tensile in grain stresses which could be related to a change in microstructure and composition. A grain boundary model based on the presence of a columnar structure is generally invoked. Stress-free lattice parameter a0 strongly decreased from 4.13 to 3.97 Å when the atomic percent of Cr atoms increased from 53 to 85 at. % and this could be correlated to the changes in nitrogen content in the samples. As result, relatively low Hardness values were obtained in a range extending from 18 to 26 GPa, however, hardness to modulus ratio (indicative of tribology performance) could be varied by more than 30%.
5nm- SrTiO$_3$ (STO) capping layers were grown on (001) and (110) La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) thin film electrodes. RSMs data show the (001) LCMO electrode remains fully strained, whilst the (110) is partially relaxed. TC of the bare electrodes is clearly dependent on the substrate orientation, being higher for the (110) one (256 K) than for the (001) electrode (180 K). When depositing 4 nm thick capping layers, the magnetization of the (001) samples is clearly reduced after the capping. On the contrary, no relevant decrease on magnetization is observed for the (110) samples.

In the present work we will show the results of the comparative characterization by (S)TEM – EELS of the STO/LCMO bilayers and corresponding LCMO bare electrodes grown on STO, for both orientations, and we will correlate them with their magnetic properties.

Experiments were carried out in a Jeol J2010F (S)TEM microscope operating at 200 keV, coupled with a GIF spectrometer, and in a Nion UltraSTEM 100 aberration corrected dedicated STEM.
DEFECT FORMATION IN GA-CATALYZED SILICON NANOWIRES

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The synthesis of silicon nanowires by Ga-assisted plasma enhanced chemical vapour deposition (PECVD) has been recently demonstrated. In this contribution, based on Ref. [1], we study in detail the structural characteristics of the synthesized nanowires. High-resolution transmission electron microscopy (HRTEM) analysis reveals the existence of various types of structural defects, which can be classified mainly according to the orientation into axial twins (AT), lateral twins (LT), and transverse twins (TT), (see fig.1). We compare our HRTEM measurements with previous studies of Si nanowires synthesized with other catalyst metals. Understanding both the origin and the effects of the observed defects is important for technological applications. The presence of twinned domains changes locally the structure of the material. As a consequence, one should find a different local density of states and band gap, which should result in a variation of the carrier transport and optical properties of the nanowires.

Fig. 1: Characteristic examples of the three main types of twinning defects which are found in silicon nanowires: (a) Transversal twins in Cu-assisted Si NWs, (b) Axial twins in Ga-assisted Si NWs and (c) Lateral twins in In-assisted Si NWs (indicated by thick yellow arrow).

References:
CONTRIBUTION TO THE STUDY OF SINGLE CORE NI NANOBeadS: SYNTHESIS, CHARACTERIZATION AND INVESTIGATION OF MAGNETOPHORESIS BEHAVIOUR

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Magnetic separation of organic compounds, proteins, nucleic acids and other biomolecules and cells from complex reaction mixtures is becoming the most suitable solution for large production in bioindustrial purification and extraction processes. Commercial magnetic nanobeads have low efficiency due to the low surface/volume ratio of the nanobeads and the unclear magnetic behaviour of the particles. The high cost of the commercial beads is also a considerable limitation for large volume applications. Optimal magnetic properties can be achieved by the use of metals. However, they are extremely sensitive to oxidation and degradation under atmospheric conditions [1,2].

In this work Ni nanoparticles were synthesised by conventional solution reduction process with the addition of a non-ionic surfactant as a surface agent. SQUID, SEM, HRTEM, and Zeta potential techniques were used to characterize the synthesized nanobeads at the different steps of the synthesis route. The shape and size of nickel oxidated NPs were studied by HRTEM. The morphology and structure of oxidation layer were studied by means of Electron Energy Loss Spectroscopy (EELS) [3]. The presence of a discontinuous nickel oxide superficial layer was confirmed.

The Magnetophoresis behaviour at different Magnetic field gradients, and at different steps of synthesis route was monitored. The results demonstrate that in the case of metallic single core nanobeads, the attractive magnetic interactions overcome the electrostatic repulsion allowing a very short reversible aggregation [4].

The authors would like to thank Sonia Estradé, Serveis Cientificotècnics de la Universitat de Barcelona, for help with the HRTEM and EELS analyses.

References:
In recent years, multiferroic materials have attracted a great interest because of their potential for novel multifunctional device applications [1,2]. It has been demonstrated that codeposition of BiFeO₃ (BFO) and CoFe₂O₄ (CFO) can lead to self-assembled heteroepitaxial nanostructures formed by CFO nanopillars embedded in a BFO matrix on (001) SrTiO₃ substrates [3], which, furthermore, show significant magnetoelectric coupling [4]. BFO exhibits rhombohedral R3c phase and ferroelectric character in its bulk form (pseudocubic approximation apc =3.96Å). Recently, highly distorted metastable tetragonal phase of BiFeO₃ (t-BFO) with a large c/a~1.24 ratio could be achieved [5]. The t-BFO is very promising for application purposes since it shows high polarization and large deformation if transformed to its natural rhombohedral BFO phase.

Here, we will report on the simultaneous growth of CFO nanocolumns embedded in a highly distorted tetragonal BFO matrix on a (001) LAO substrate using pulsed laser deposition. Thin foils were prepared by mechanical polishing and ion beam milling and observations were carried out in a JEOL JEM 2010 FEG at 200kV. We will present a detailed characterization of the complex microstructure, with a special focus on the interface formed by the two CFO and BFO film phases and between them and the substrate.

References:
A NANOWIRE CORE/SHELL THERMOELECTRIC/PHOTOVOLTAIC DEVICE CONCEPT

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At the nanoscale the thermoelectric figure of merit increases significantly [1]. In recent studies, the thermoelectric function of nanowires was experimentally verified [2]. The nanowire provides extreme length/diameter ratios at low production cost. In addition, new device concepts may be implemented during the crystal growth of the wires such as energy filtering at atomic layer III/V-heterostructures [3]. In this study, we propose to implement a core-shell pn-junction into the wire. This way an efficient thermoelectric device having both electrodes on the cold side [4] is combined with a photovoltaic element. The basic device concept and the present status of realisation is depicted in Figure 1. The radial pn-junction is implemented in the GaAs material system for carrier separation. The thermal gradient is along the axis of the nanowire while both contacts are on the cold side of the device. The heat of a photovoltaic energy conversion loss generates thermal carrier at the top which may diffuse along the pn-junction. At the cold side electrodes, they can be harvested as thermal excess carriers. Proof of concept measurements will be presented.

Fig. 1: A core-shell nanowire thermoelectric device concept with photovoltaic function.

References:
PHOTOTHERMAL LASER PROCESSING OF THIN SILICON NANOPARTICLE FILMS: PROSPECTS IN PHOTOVOLTAIC APPLICATIONS

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Semiconductor nanoparticles (NP) show great promise as nanoscopic building blocks in a variety of energy applications including thermoelectrics and photovoltaics. They are discussed as a promising material to enhance the properties of current thin film devices as well as an alternative to conventional thin film technology itself. A key step towards functional devices with respect to electrical and thermal conductivity, mechanical and optical properties is the development and optimization of suitable techniques for the fabrication and modification of coatings with nanoparticles. Here, photothermal laser processing of thin silicon NP films on Si substrates is investigated. Ethanolic dispersions of Si nanoparticles (d < 100 nm) from gas phase synthesis are spin-coated on Si substrates yielding films with thicknesses < 0.5 μm. Subsequently, these samples are dipped in aqueous HF-solution in order to remove the native oxide layer of the substrate and the NPs. Laser processing is carried out with a focused beam of an DPSS-laser at λ = 532 nm and 1/e spot diameter of about 1.4 μm in continuous-mode operation. Using a focused laser beam allows one to conveniently investigate the dependence of the initiated processes on the laser parameters on a single sample. For this purpose, the laser power are varied from 50 to 200 mW, respectively. SEM are used for characterization. Generally, laser irradiation results in a local temperature rise that causes sintering and melting of the NPs. Below a laser power of 100 mW, though, the morphology of the nanoparticulate film remains unaffected. Work in progress also considers experiments on other supports and large-area processing with high-power ns-lasers. Prospects of photothermal laser procedures in photovoltaic applications are discussed, e.g. targeting back surface field doping.

References:
ELECTROCHEMICAL PREPARATION OF DIFFERENT CoPt STRUCTURES TO MODULATE THE MAGNETIC PROPERTIES

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There has recently been a significant research effort in the modulation of magnetic properties of different systems for application in microelectromechanical-systems (MEMS), in which both soft and hard-magnetic materials are required. The aim of the present work is to explore the production of different CoPt structures including nanowires, submicron-sized particles, as well as thin-films with different thicknesses, using electrodeposition techniques in order to modulate their magnetic behaviour.

The optimum substrate has been used for each structure. In order to prepare these structures, a solution containing CoCl$_2$, Na$_2$PtCl$_6$, C$_6$H$_8$O$_7$, H$_3$BO$_3$ and NH$_4$Cl was used. Electrodeposition has been carried out using a three-electrode cell under stirring and temperature controlled conditions. A study of the CoPt system was performed to find the optimum range of potentials for working with each substrate.

The electrodeposition method allowed us to prepare nanowires of 100-200 nm of diameter, particles ranging from 150-500 nm and thin films, from 50 to 150 nm-thick. Morphology, composition, structure and magnetic properties of deposits were studied. The electrodeposition conditions were adjusted to attain an hcp cobalt phase distorted by the presence of high platinum percentages (65-70 wt.%). For similar compositions, modulation of the magnetic properties of the CoPt system was obtained by electrodepositing different structures.
The thermoelectric properties of conventional materials can be significantly improved by nanostructuring [1]. Materials exhibiting intrinsic nanostructures possibly provide not only good properties for thermoelectric applications, but also an easy synthesis. For the well known superconductor Yttrium Barium Cuprate (YBa2Cu3O7-δ, YBCO) a relatively high figure of merit $ZT$ of 0.6 at room temperature has been demonstrated [2].

A solid state reaction of well mixed corresponding oxide or nitrate powders is performed with different time-temperature profiles in order to tailor the nanostructure of the complex oxide. Twin distance and homogeneity of these nanofeatures is investigated using transmission electron microscopy (TEM, see Fig. 1). The thermoelectric properties of YBCO can additionally be tuned by varying the oxygen content $7-\delta$ ($0 \leq \delta \leq 1$). Results concerning the mean distance of the twin boundaries, the oxygen content, and the thermoelectric characteristics (Seebeck coefficient, electrical conductivity, and thermal conductivity) are presented. By adjusting the nanostructure and the oxygen content these transport properties can be tuned over a wide range.

References:
POTENTIAL USE OF NANOSTRUCTURED LIPID CARRIERS FOR OCULAR DELIVERY OF FLURBIPROFEN

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Flurbiprofen (FB), a water insoluble NSAID drug, is currently used as a first line ophthalmic medication for the inhibition of miosis induced during the course of cataract surgery, by inhibiting the cyclooxygenase [1]. In order to improve its therapeutic efficiency, the development of novel delivery systems for ocular instillation is a demand. Nanostructured lipid carriers (NLC) is a new generation of solid lipid carriers which overcome several limitations of others, due to their biocompatibility of lipid materials, modified release, avoidance of organic solvents during the production process and easy large scale production.

The aim of the present study was to investigate the potential use of NLC composed of stearic acid (SA) or Compritol®888 ATO (C888) as solid lipids, and a mixture Miglyol®812 and castor oil as liquid lipids, for ocular administration of FB. Two different optimized NLC formulations (FB-SANLC based on SA vs. FB-C888NLC based on C888), with respect to the morphometrical properties (particle size < 228.3 nm and polydispersity index < 0.2) and the entrapment efficiency (~90%), were used in this study. FB from these NLC showed an in vitro sustained-release. The ex vivo permeation studies were carried out to assess the transcorneal absorption and bioavailability of FB from these lipid carriers. The NLC dispersions possessed sustained drug permeation over a period of 6 h. As the results showed, the percentage corneal hydration of formulations after the studies was not increased over 3%, which indicates that any damage to the epithelium or endothelium was caused during the studies [2]. Topical application of formulations to rabbit eyes showed no sign of toxicity or irritation to the external ocular tissues after the Draize test [3].

References:
PHOTOTHERMALLY INDUCED MICROCHEMICAL FUNCTIONALIZATION OF ORGANIC MONOLAYERS

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Photopatterning of organic coatings represents a key step in many technological applications ranging from microchip fabrication to the design of bioarrays and microfluidic devices. A simple routine for subwavelength patterning of organic monolayers relies on photothermal processes. In photothermal processing a focused laser beam is used to locally heat the substrate and initiate chemical reactions. Commonly photothermal processing of organic monolayers results in local decomposition of the coating. Here we report on a photothermal procedure for local functionalization of alkylsiloxane monolayers on surface-oxidized silicon substrates in a gaseous bromine ambient. At low laser powers, monolayer bromination in micron-sized areas is observed. Additionally, at high laser powers, decomposition of the monolayer takes place at the center of the brominated areas. Functional groups were identified using labeling techniques and spectroscopic measurements. In order to investigate the underlying mechanism experiments at different wavelengths have been carried out (λ1 = 514 nm, 570 nm, 650 nm). Further work also considers two-color-experiments (514 & 650 nm) which allows to trigger distinct processes in the gas phase and at the substrate surface. Prospects and limitations of this procedure in fabrication of multifunctional templates are discussed.

References:
SYNTHESIS AND CHARACTERIZATION OF METALLIC NANOSTRUCTURES FORMED AT RUTILE TiO$_2$(110)-(1×1) SURFACE

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The fabrication methods of the existing semiconductor industry will soon reach their physical limits. The concept of the molecular electronics seems to be a good alternative for future computing technology. Nowadays, constructing the conductive interconnects, providing electric contact with basic elements of the molecular circuits, is a crucial task [1]. Therefore, the growth and self-assembling of metallic nanostructures on semiconductor and dielectric surfaces are one of the most important research trends [2,3].

In this presentation the scanning tunneling microscope studies, concerning the epitaxial metallic nanostructures formed as a result of submonolayer deposition of platinum and palladium on rutile TiO$_2$(110)-(1×1) surface kept in elevated temperatures, are presented.

In case of Pd evaporated on substrate with temperature about 900 K two distinct types of structures with height smaller than 5 nm have been observed: flat-topped pseudohexagonal nanoislands and nanowires up to 200 nm long. Nanowires, parallel to the [001] surface crystallographic direction, represent however less than 30% of all Pd island. For Pt evaporated on TiO$_2$(110)-(1×1) kept in 950 K about 1 nm high, metallic clusters with diameters up to 6 nm are formed.

References:
GROWTH PARAMETERS INFLUENCE ON THE EMISSION BANDS OF ZNO NANOWIRES

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ZnO nanowires (NWs) are increasingly attracting much attention for its size-dependent optical properties. NWs offer new fabrication and sensing possibilities due to their high surface-to-volume ratio, and present new physical properties tightly related to their length and diameter. On the other hand, ZnO is a direct wide bandgap semiconductor material ($E_g=3.37\text{eV}$) with a large exciton binding energy (60 meV), which gives a large UV light emission once excited. Also an impurity-related broad band in the visible range is observed. Due to these emission bands, ZnO NWs can become the basis to develop self-powered UV lasers as well as a new generation of white LEDs. The aim of this work is the study of the variation of these emission bands as a function of the growth parameters for ZnO NWs.
SIZE DEPENDENCE OF THE NONLINEAR OPTICAL RESPONSE IN SI-NANOCRYSTALS

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Silicon nanocrystals (Si-nc) embedded in oxide matrices have shown upstanding properties for nonlinear photonic applications, as their nonlinear optical properties were found to be larger than the ones in silica or Si. Observations of a strong size dependence of their nonlinear optical properties has been reported in the literature, nevertheless the results display a large scatter in their data.[1,2] Consequently, an accurate knowledge of their nonlinear optical properties as a function of the Si-nc size is crucial for the conception and design of highly efficient photonic structures.

Here we present a z-scan study of SiO/SiO$_2$ multilayers exciting in the ns-regime with pulses of $\lambda = 1064$ nm. Films were deposited on silica substrates by evaporation and annealed up to 1100 °C in a conventional furnace for 10 minutes. Si-nc with sizes ranging from 2 nm to 5 nm were obtained. The nonlinear absorption and nonlinear refractive index have been measured by z-scan experiments using a ns-pulsed Nd:AG laser working at $\lambda = 1064$ nm. We found an increase of the nonlinear absorption coefficient and the nonlinear refractive as the Si-nc size increases.

The nonlinear optical response has been analyzed using a nonlinear model that includes the contribution of the excited free carriers during the z-scan measurements. The results will be commented and discussed in terms of the Si-nc size, their volume and surface to volume ratio.

References:
In recent years nonlinear laser processing with continuous-wave lasers has been demonstrated as a facile means for rapid nanopatterning of silane-based organic monolayers down to the sub-100-nm range.[1] Here we report on laser patterning of thiol-based organic monolayers with sub-wavelength resolution. Gold-coated silicon substrates are functionalized with thiol-based monolayers, such as 1-Hexadecanethiol, 16-Mercaptohexadecanoic acid, 11-Mercaptoundecanol or Perfluorodecanethiol. Irradiation with a focused beam of an argon ion laser operated at a wavelength of 514 nm allows local removal of the monolayer. Subsequently, the patterns can be transferred into the gold film via selective etching in a ferri/ferrocyanide solution or used as chemical templates for the directed self-assembly of nanoscopic components, such as thermoresponsive polymers. Despite a 1/e2 spot diameter of about 2.7 μm, structures with lateral dimensions down to 250 nm are fabricated. The underlying nonlinear dependence of the patterning process on the laser intensity is traced back to the interplay between the laser-induced transient local temperature rise and the thermally activated desorption of the thiol molecules. A simple thermokinetic analysis of the data allows the determination of effective kinetic parameters of the patterning process[2].

References:
PHOTOTHERMALLY INDUCED BROMINATION OF ORGANIC MONOLAYERS ON OXIDE-FREE SILICON SUBSTRATES

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Surface properties of technologically important materials, such as silicion oxide, silicon and gold, can be engineered via self-assembled organic monolayers (SAMs). In conjunction with patterning techniques and other chemical transformations, SAMs represent an efficient route to build up more complex surface structures. A simple routine for nanopatterning of organic monolayers down to 100 nm and below relies on photothermal processes [1, 2]. In photothermal processing a focused laser beam is used to locally heat the substrate and initiate thermal decomposition of the monolayer. Here we use a simple photothermal procedure for direct functionalization of organic monolayers. Hydrogen-terminated silicon samples are coated with 1-alkynes monolayers [3]. Through irradiation with a focused beam of an argon ion laser (\( \lambda = 514 \) nm) in gaseous bromine local bromination of the monolayer takes place. Mechanistic aspects and prospects of photothermal routines in micro- and nanofabrication of multifunctional organic monolayers are discussed.

References:
AMPHIPHILE-BASED GOLD NANOPARTICLES FOR DRUG DELIVERY

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Nanomedicine is an emerging field where various disciplines are brought together to apply nanotechnological “know-how” to therapy and diagnosis. Among the materials used, gold is widely used, for its physical and chemical characteristics[1], both in the production of nanoparticles for targeted therapy and biodiagnostic tools.

In this work, we present a novel bis-imidazolium amphiphile that has the ability to interact with anions[2] and gold[3], producing nanoparticles. This molecule works as a synthesis promoter, a stabilizer of the gold nanoparticles and also, as an anion receptor, which allows these nanoparticles to be used as vehicles for delivery of negatively charged drugs.

The results shown were obtained using ibuprofen as a model drug. The produced nanoparticles were characterised, and the release profile for both nanoparticles loaded with ibuprofen and the amphiphile-ibuprofen complex were assessed, as well as the permeation of the nanoparticles across skin from a healthy human donor.

References:
PHOTOTHERMAL LASER MICRO- AND NANOPROCESSING OF MESOPOROUS GOLD

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In recent years, mesoporous gold has gained significant attention as a novel material in actuation, sensing and catalysis. The particular properties of this material result from its spongelike open-cell morphology with small pore sizes of about 25 nm. Techniques which allow one to engineer mesoporous gold on a micro- and nanoscale, of course, are of high interest in view of applications in fundamental studies and technology. Common annealing procedures, for example, provide a means to adjust the pore size in the range of 50 - 600 nm and investigate size dependent properties, such as the enhancement effect in surface enhanced Raman spectroscopy \cite{1}. Here we report on a photothermal laser technique for micro- and nanoprocessing of mesoporous gold, cf. ref. 2. A focused beam of a continuous-wave laser operating at $\lambda = 532$ nm with a 1/e\textsuperscript{2} spot size of 2 $\mu$m is used to locally anneal the substrate and fine tune the pore structure. In addition, thiol-based self-assembled monolayers are shown to offer unique opportunities as ultrathin resists in order to transfer patterns into the bulk of the porous material.

References:


\cite{2} D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, Nano Lett. 6 (2006) 2358.
LOCAL ATTACHMENT OF THIN POLYMER FILMS TO AZIDE TERMINATED ALKYLSILOXANE MONOLAYERS VIA LASER-INDUCED THERMAL ACTIVATION

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Covalent attachment of polymer films can be versatilely employed to tailor chemical and physical surface properties. Alternative to the approach of growing a polymer on a surface, which requires particular functional groups at both reactive sides, the polymer and the surface [1], here we report on a simple and flexible photothermal procedure for local attachment of thin polymer films to solid surfaces. In photothermal processing a focused laser beam is used to locally heat the substrate and initiate thermal reactions on the surface [1,2]. Surface-oxidized silicon samples are coated with alkylsiloxane monolayers. After wet-chemical treatment in order to form azide-terminated monolayers a thin polymer film is spin-coated on top of the monolayer. Local irradiation with a focused beam of a diode-pumped solid-state laser (λ = 532 nm) thermally activates the azide groups and leads to local covalent attachment of the polymer. Subsequently, polymer material, which is not coupled to the surface, is removed via sonication. The influence of incident laser power and irradiation time is investigated. At a 1/e² focal spot diameter of about 3 μm dots with diameters close to 1 μm can be fabricated. This procedure allows for patterned attachment of a wide spectrum of polymers, can be carried out over macroscopic lengths scales and at short processing times.

References:

THERMOELECTRIC PROPERTIES OF SPARK-PLASMA SINTERED NANOCRYSTALLINE SILICON/GERMANIUM COMPOSITES

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Silicon/germanium alloys are known for their good thermoelectric performance at elevated temperatures [1]. The alloy structure hinders the short wavelength phonon transport in the material which leads to an appreciable figure of merit. By introducing a nanostructure to the material, it is expected to generate a barrier for the mid to long wavelength phonons as well and therewith cause an increase of thermoelectric efficiency [2].

Therefore, silicon and germanium nanoparticles are synthesized in a gas phase process based on a microwave plasma reactor. By variation of the microwave power, chamber pressure and concentration of the precursor gases silane (SiH₄) and germane (GeH₄) respectively as well as the plasma gases Ar and H₂, crystalline particles with a mean diameter from 5 to 100 nanometer can be obtained. N-type doping or p-type doping can be realized by adding phosphine (PH₃) or diborane (B₂H₆) to the precursor gases.

In a second process step the nanoparticles are compacted in a spark-plasma sintering process. Several grams of the nanoparticles are pre-compacted and subsequently sintered to dense pellets. Thereby the sintering temperature and the hold time can be varied.

Structural information of raw powder and sintered pellets is gained by transmission electron microscopy and x-ray diffraction combined with Rietveld-analysis. The Seebeck-coefficient α and the electrical conductivity σ are measured using a direct measurement setup, while the thermal conductivity κ is obtained by a laser flash method.

First results of a nanocrystalline Si/Ge alloy will be shown.

References:
The clinically used anti-inflammatory drugs suffer from the disadvantage of side effects and high cost of treatment. Alternative to these drugs there are traditional medicines and natural products which offer a great hope in the identification of bioactive lead compounds and their development into drugs for treating inflammatory diseases. Since ancient times, traditional medicines and phytopharmaceuticals have been used for the treatment of inflammatory and other disorders. [1] In this way, the Eysenhartia platycarpa [2] has been used to reduce symptoms of inflammation and, from it, there been isolated and characterized new prenylated flavanones, which have anti-inflammatory capacity as demonstrated in a model in vivo. [3]

We have prepared a new formulation based in a noestructured anhydra emulsion (Z-Average 90.52 d.nm / PdI: 0.381) containing the flavanone which was also used for a biopharmaceutical delivery study. As the experimental data obtained from various flavanones tests indicate that they present less activity orally than topically [4], we have decided to choose the topical route as the administration via for this new anti-inflammatory agent.

The results from these assays indicate that this compound follows a kinetics of release of first order with constant K: 0, 0186 min -1. According to which, the release of this flavanone contained in a nanostructured emulsion will not be a limiting factor in subsequent permeation studies.

References:
TRANSDERMAL PERMEATION OF IBUPROFEN LOADED PLGA AND PCL NANOSPHERES IN HUMAN SKIN

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The use of colloidal drug delivery systems, such as poly(D,L-lactide-co-glycolide) (PLGA) and poly-ε-caprolactone (PCL) nanospheres (NS), is considered nowadays a strategy to enhance the bioavailability of topically administered drugs [1]. The encapsulation of NSAID drugs such as Ibuprofen (IBU) in particulate drug delivery systems represents an innovative alternative to minimize side effects [2], while preserving their efficacy. This can be obtained by the capacity of these systems to provide controlled release or to improve the drug penetration into the skin.

Based on these considerations, the aim of the present work was to evaluate the feasibility of PLGA and PCL NS to improve the skin permeation of IBU. Morphometrical properties of the NS developed were determined. All formulations showed particle sizes lower than 300 nm and negative zeta potential values (around -20 mV). Drug entrapment efficiency obtained was > 90% for both PCL and PLGA NS.

In vitro permeation studies were performed using Franz-type diffusion cells. NS showed higher penetration behaviour of IBU into the receptor compartment than the reference solution. PCL NS produced a 3-fold increase of FB permeation flux when compared with PLGA NS.

In vivo skin irritation was studied by the Draize test [3]. Topical application of formulations to rabbit skin showed no sign of toxicity or irritation. From the results obtained, it can be concluded that polymeric NS are promising delivery system for topical administration of FB. This has important implications for the treatment of diseases like arthritis.

References:
INFLUENCE OF HUMIDITY ON ATOMIC-SCALE FRICTION ON STEPPED SURFACES OF NaCl AND MoS₂

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High-resolution friction force microscopy (FFM) measurements on stepped NaCl(001) and MoS₂ surfaces under controlled atmosphere conditions and in UHV were performed. The dependence of frictional forces on the load and on the relative humidity was measured on the flat terraces as well as step edges. The measurements reveal the increased frictional forces at step edges tranversed upwards and downwards as compare to the friction on flat terraces. The friction for the upward direction exhibits a linear increase with load force and if compare with the work by Hölscher et al. [1] is always higher than the load-independent friction for the down-step direction. Significant dependence of the friction on the relative humidity was observed but only for the upward steps for which decrease of the relative humidity from about 30% to about 0% leads to the increase of the frictional force by a factor of 3. Long-lasting NaCl surface exposure to atmospheric conditions leads to considerable increase of friction both on step edges and on flat terraces. The experimental findings point out the important role of adsorbed water layers in the total tip-surface lateral interaction.

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