

## POSTER A1

### Fabrication of functionalized Polypyrrole-based micro and nano-structures

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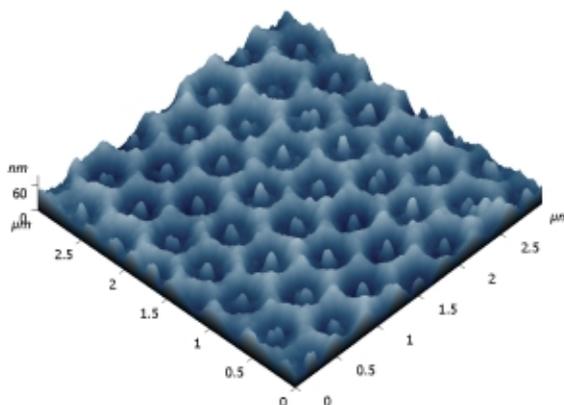
Conductive polymers, although already used in the field of enzyme based biosensors [1-3], have properties which make them uniquely suited to an increasing number of new biological, biomedical and analytical applications. PPy has good environmental stability, excellent biocompatibility and higher conductivity than many other conductive polymers and so is a preferential material in use for this type of applications [4]. Furthermore, studies specifically aimed to determine the biocompatibility of PPy have shown the material to be inert and to exhibit no serious biocompatibility problems in either cell culture or in-vivo applications [5]. Unfortunately, this polymer has no specific chemical functionality which can be used for covalent immobilisation of biomolecules. To overcome this limitation it is desirable to develop methods to controllably introduce suitable reactive groups onto the polymer. One method of achieving this is to graft reactive groups onto the surface using UV induced radical activation of functionalised alkenes. The aromatic bonds of the PPy and the alkenes carbon double bond are sensitive to UV light and when exposed, radicals may be formed and used to induce grafting.

In this work PPy film was deposited on porous silicon by electrochemical oxidation and then modified by UV light induced grafting of Allylamine or AAc to introduce respectively amine and carboxylic functionality onto the polymer surface. The ability of this technique to controllably produce micro-patterned functionality surfaces through the use of optical masks was also examined. The effectiveness of the grafting was quantified by combining functional group derivatisation techniques and XPS.

Results show this to be an efficient and controllable method of introducing surface functionality to the normally inert PPy polymer. Moreover, in order to provide high sensitivity of detection in biosensors and analytical devices, the design of nano-structured poly pyrrole-based surfaces covers a fundamental role [6]. In this work we describe a novel technique to produce Polypyrrole based nano-structured surfaces. The fabrication process relies on the creation of patterned nano-templates i.e. nano-metric gold spots surrounded by an electrically insulating material (SiOx). From these templates, Polypyrrole nanopillars are grown by classical electrochemical methods. Atomic Force Microscopy demonstrates that Polypyrrole grows selectively inside the gold nano-templates (Figure 1).

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**Figure 1.** AFM picture of Polypyrrole nano-pillars grown on the pre-patterned nano template.



## POSTER A2

### Hybrid bio-organic functional systems and electronics devices

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We are investigating the behaviour of Field Effect Transistors based on ultra-thin films (one-two monolayers) of conjugated molecules in the presence of biomolecules adsorbed on the organic semiconductor surface. The interaction between the charge carriers in the accumulation layer with the biomolecules close to the organic semiconductor is transduced in the FET response. Our aim is to develop a new ultra-sensitive transducer for the adsorption of biomolecules and their dynamics. Here, we present our first results on these hybrid bio-organic devices.

We deposit double stranded linear DNA molecules in a buffer solution on two monolayer-thick sexithiophene or pentacene transistors by either drop casting or a microfluidics. DNA coverage is controlled down to submonolayer by its concentration in the starting solution and the choice of microfluidics conditions [1]. AFM in air and liquid shows that DNA chains adsorb in an elongated form on the organic semiconductor. This suggests that the organic semiconductor does not strongly perturb the DNA chains.

The characteristics of the transistors in controlled relative humidity conditions are acquired using a home-built chamber for electrical measurements in high-vacuum and inert gases. Control experiments on the response of the pristine transistor, prior and after exposure to the buffer solution, is made. It is observed that:

- i) the transistors with DNA exhibits modest changes in the charge mobility of the gate-generated carriers with respect to the pristine ones;
- ii) the transfer characteristics of the DNA exhibit marked changes in the power law dependence vs gate voltage and the threshold voltage.

Variable Range Hopping model [2] is used to assess the effect of the DNA adsorption on the energy distribution of charge carriers in the organic semiconductor.

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## POSTER A3

### **Towards a new generation of DNA chips: nanografted DNA nano-arrays**

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It has been shown by Stellacci and coworkers [1] that, using a technique that can be best described by the label “micro contact copying”, it is possible to reproduce rapidly and cheaply a “master copy” DNA chip in a single hybridization-contact copy-dehybridization cycle. This cycle can be repeated, in principle, a very large number of times producing, from the same master, a very large number of copies. The method involves making first the master copy by a suitable micro-lithographic method. This master needs to be fabricated on a very flat substrate and ultimately consists of an array of micro islands of DNA samples pinned to a flat gold substrate, typically by a sulfur-gold bond. Each island of the array has an “address” on the surface and contains a DNA sample different from all other samples placed at a different address on the chip. A useful chip may contain from hundreds to ten thousand different addresses.

We will suggest here that combining the copying technique described above with the recently developed AFM-assisted lithographic technique called nanografting one obtains a new method of DNA chip fabrication that has an ultimate high density of addresses ( ~ 500 addresses per square micrometer should be achievable ) and it is easier to implement.

Nanografted single-stranded DNA arrays in a matrix of alkanethiols self-assembled on gold films will be shown, and details about hybridization and copying of the array will be discussed.

[1] A. Amy Yu, F. Stellacci *et al.*, Nano Letters **5**(6), 1061 (2005)

## POSTER A4

### Laser tweezers for 3D control of ultrasound contrast agent microbubbles during high-speed optical observations

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#### Abstract

Micron-sized gas bubbles are used in medical ultrasound imaging for enhancing the blood pool visibility. In this work we present a setup for manipulation and control over bubbles position, which enables high-speed optical observation of bubble dynamics with controlled, repeatable boundary conditions.

Phospholipid-coated microbubbles (BR14, Bracco) are trapped with a laser tweezer, a versatile tool for non-contact, non-destructive manipulation, capable of applying forces in the pN range. As gas bubbles exhibit a lower refractive index than the surrounding liquid, a standard gradient trap based on a focused Gaussian beam will repel such particles. Here, a donut-shaped Laguerre-Gaussian trap is generated, where a low-index particle can be trapped in its dark core. A Laguerre-Gaussian beam is obtained by converting a Gaussian beam through diffractive optical elements, implemented on a spatial light modulator; dynamic laser beam shaping enables to trap not only individual, but also multiple bubbles in suitable configurations, for studying bubble-to-bubble interactions.

The Brandaris 128 ultra high-speed imaging system, capable of recording 128 frames at 25 million frames per second, is used to record the nanoseconds dynamics of the manipulated bubbles oscillating upon insonification with ultrasound of a frequency of 2.25 MHz.

## **POSTER A5**

### **Combining advanced force and optical microscopy techniques for biophysics research**

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The range of biophysical applications for atomic force microscopy (AFM) continues to grow, as the advantages of high resolution imaging in physiological environments are combined with measuring and manipulating the structures under investigation. A key factor is the ability to combine AFM with advanced optical techniques, such as phase contrast, DIC and epifluorescent, TIRF or confocal imaging. This enables correlation of the high resolution structural information with specific labelling of active molecules. The BioCell allows full environmental control of samples on coverslips in liquid, for maximal optical resolution, single molecule imaging and spectroscopy, and cell studies. The CellHesion development kit has been specially designed to extend the capabilities of AFM in cell binding and recognition assays, giving reproducible and quantitative analysis of cell-cell and cell-substrate binding forces. Single cells within a culture can be selected, attached to a flexible cantilever and subsequently allowed to adhere to a second, specific cell or region of substrate. Simultaneous information from advanced optical techniques gives insight into many additional cellular processes that occur on binding, such as changes to actin structure, calcium flushes, distribution of labelled proteins, or morphological changes.

## POSTER A6

### Microfluidic devices for investigating and manipulating fluid dynamics

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Miniaturized microfluidic devices allow the manipulation of minute volumes of fluids -in the nl to pl range- in microfabricated channels and offer many advantages in terms of reduction in reagent, sample and waste volumes, more homogeneous reaction conditions and shorter times for diffusion-driven reactions, automation, massive parallel processing. By analogy with electronic integrated circuit, microfluidic elements, such as fluid injectors, filters, pumps, valves, mixers, separation elements, detectors, can be used as building blocks for lab-on-chip devices specifically designed for genomics and proteomics [1-3]. Microfluidic devices offer a high degree of integration, presenting potential applications in biomolecular separations, enzymatic assays, polymerase chain reaction, and immunohybridization reactions. During the past years, many biotechnology and pharmaceutical researchers have employed microfluidics chips, especially in the area of high-throughput drug screening, DNA sequencing, gene-expression profiling, protein analysis, and cell-based assays [4-6].

In this work, microfluidic techniques are employed for the basic understanding of fluid dynamics, of diffusion and non-Newtonian phenomena within capillary circuits driven by natural capillarity or applied forces, and of the investigation of the dependence of performance on the viscosity, interfacial free energies, flow rates, and geometries. We developed well optimized multilevel photolithographic approaches for realizing microfluidic circuits with dimensions in the range of 10-100  $\mu\text{m}$ . The availability of microfluidic elements with different height onto the same substrate allows us to obtain a simple and efficient integration of external elements, such as pump syringe and valves, in order to have a better control of the liquid injection in the fluidic network.

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## POSTER A7

### Cubic Phases from Nucleolipids

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Lipidic cubic phases and their nanoparticles are considered interesting candidates for drug delivery. The reason is that their unique structure lends itself well to controlled release applications in medical and pharmaceutical fields. In this context, we have started to study a new smart amphiphile, 1,2-di-Palmitoyl-*sn*-Glycero-3-Phospho-Uridine (DPPU), which is able to arrange in cubic phases when hydrated. This molecule belongs to a new class of compounds, called phosphatidynucleosides (PLNs), which are composed of a phospholipid backbone and a nucleotide polar head and reproduce the chemistry and the charge of DNA monomers. Therefore these molecules represent interesting structures to design surfaces able to display biological functionalities, acting, for instance, as biocompatible vectors of complementary DNA, RNA or PNA.

DPPU combines these features with the existence, in a well defined region of its binary phase diagram, of a cubic order and is therefore a remarkable candidate for many biological and medical applications.

The phase behavior and structural properties of DPPU mesophases were studied by SAXS-WAXS measurements, DSC analysis and FTIR experiments. The combination of the former methodologies has permitted to detect cubic phase (Pn3m) at low water content (< 50% w/w) and at room temperature. This investigation has also verified a transition between cubic and lamellar liquid-crystalline phase at relatively low temperature (T=40°C).

In the last part of this work the possibility to obtain nanoparticles with cubic symmetry was also explored.

## POSTER A8

### A Study on interaction between water and 1-Palmitoyl-2-oleoyl-*sn*-Glycero-3-Phospho-Uridine lamellar phase

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#### Abstract

The interest toward lipid bilayers/DNA interactions has recently grown amongst scientists with the final purpose to design molecular arrays for non-viral plasmid delivery. From our point of view, we are interested in the characterization of lipidic systems modified by functional nucleic bases (liponucleosides) that form several types of aggregates in aqueous systems [1-3]. The structure of the liquid-crystalline lamellar phase of an innovative synthetic phospholipid (1-Palmitoyl-2-oleoyl-*sn*-Glycero-3-Phospho-Uridine, POPU) has been investigated by X-ray scattering experiments (SAXS-WAXS), calorimetry (DSC) and Fourier Transform Near Infrared (FT-NIR) measurements as a function of hydration. This investigation was especially focused in determining water/lipid interactions at a molecular level and to detect different extents of binding.

The former complementary experimental approaches have permitted to determine the kind and number of different types of water molecules imbibed onto POPU liponucleoside membranes. Three types of water were inferred: free, medium bonded and strongly bonded to the bilayers.

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## POSTER A9

### Charge transport in disordered films of non-redox proteins

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Proteins are well suited to the implementation of electronic devices, due to their size, self-assembling capabilities, and intrinsic functional properties [1-4], even though the mechanism underlying electrical conduction in proteins is still matter of controversy. Here, we demonstrate electrical conduction in solid-state disordered multilayers of non-redox proteins. We also show that conduction can be modulated by means of a gate field. These results may lead to the implementation of protein-based transistors, and open new perspectives for a wide range of bioelectronic/biosensing applications.

The devices for our transport experiments consisted of a pair of planar metal nanotips with a typical gap of ~100 nm, which were fabricated on a Si/SiO<sub>2</sub> wafer by Electron Beam Lithography. A silver back electrode served as a gate. Proteins films were made primarily from two redox-inactive variants of the blue copper protein azurin, i.e. the apo- and the zinc forms, which, apart from the metal site, show nearly identical fold patterns to the wild-type protein. The two variants gave essentially identical results. Protein films were formed by cast deposition of a drop of protein solution onto the inter-electrode gap. After incubation, the solution was removed, the samples dried, and maintained and measured at ambient conditions (20 °C, atmospheric pressure, ~50% of humidity). Protein films had an average thickness of around 30 nm (approximately corresponding to 7-8 protein layers), as probed by Atomic Force Microscopy (AFM). AFM images of the same sample taken up to 2-3 weeks after preparation revealed no significant change, indicating stability at ambient conditions, consistent with previous findings [5].

Two-terminal transport experiments revealed a quasi-ohmic behavior over the investigated bias range, with the current reaching about 1 nA at 1 V. These results were similar to those obtained with wild-type, redox-active azurin. An ohmic behavior, albeit with slightly different current values, was also observed with two different polypeptides, Bovine Serum Albumin (BSA) and a synthetic peptide (poly(ValGlyGlyLeuGly)). Hence the transport mechanism is completely independent of a redox function. Conduction decreases only by 20-30% after two weeks at ambient conditions. Moreover, azurin and its derivatives apparently maintain their native fold even when subjected to electric fields comparable to those reached inside the nanogap (~10<sup>7</sup> V/m) [6].

It is very unlikely that the observed conduction is due to residual salts from the buffers. Current values were essentially identical in devices made from protein solutions in different buffers, or, in the case of the synthetic peptide, in high-purity water. However, we have observed that the temperature and humidity have a significant effect, suggesting a key role of water molecules in the transport mechanism.

STM experiments confirmed that the protein multilayers can sustain electrical conduction. STM images suggest an isotropic mechanism of charge transport, regardless of the orientation of the single proteins. STM scans confirmed that the transport mechanism is marginally affected by ageing. Moreover, STS experiments performed at various points of the protein layer showed an ohmic behavior, consistent with the characteristics obtained with the two-terminal nanodevices. We conclude that: i) solid state disordered protein films are capable of sustaining a current flow at ambient conditions, and ii) the transport mechanism responsible for this conduction is independent of redox activity.

Additional three-terminal measurements were performed in order to investigate the effect of a gate field on conduction. We found that, while positive values of the gate field do not induce significant variations, the application of negative gate voltages results in a remarkable enhancement of the current intensity (up to a ~27-fold increase at  $V_G = -4$  V).

The complexity of our protein films makes it difficult to propose a reliable transport model. Qualitatively, it has been proposed that charges can travel through a protein molecule, via intra-molecular charge-transfer (CT) pathways, and then jump to an adjacent molecule likely due to the presence of hydration shells [7]. The formation of continuous molecular chains in the solid-state assembly would allow for long-range charge transfer. According to this model, the efficiency of the transport mechanism is, therefore, directly related to: i) intra-molecular CT and, hence, protein conformation in the film environment, which governs possible intra-protein CT pathways; ii) inter-

molecular CT, which likely depends on the retention of protein hydration shells in the solid state. The effects of temperature and humidity that we have observed on conductance may occur on either/both mechanisms.

Independently of the transport mechanisms, our solid-state protein films may find practical application as transistors. Estimates of three key parameters (the transconductance ( $g_m \sim 12 \text{ nA/V}$ ), the voltage gain ( $A_V \sim 3.7$ ), and the charge mobility ( $\sim 100 \text{ cm}^2/\text{Vs}$ )) compare favorably with other molecular devices, especially in terms of  $A_V$  [8-10]. This makes them potentially attractive to the electronics industry. Our findings have several additional practical implications:

- 1) Conduction is observed with a wide class of polypeptides, regardless of their redox activity, hence devices can be realized by means of easily available materials.
- 2) Conduction does not entail either ordered layers or particular molecular structures. Moreover, layer assembly is achieved by physisorption and does not require chemical functionalization and/or patterning.
- 3) The films are stable even at ambient conditions.

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## POSTER A10

### Twin Cantilevers Devices For Single Molecule Detection

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The detection of bio molecules up to single molecules precision is, at present, definitely one of the most researched areas. Successful detection would lead us towards the single molecule manipulation which will open the new horizons. The detection of single molecule has many facets of application, for example, in the development of agriculture, bio-engineering and most prominently in medicine.

In the present work we propose an approach/technique which consists of the fabrication of pair of identical micron-sized silicon cantilevers, separated by a narrow gap (of the order of few nm), by using photolithography. We have used SOI as a starting material while 100 nm of oxide layer was deposited as a top most layer through a PECVD process, which will act like a mask for KOH etching of silicon. We used SOI because there are some specific limitations which are associated with the usage of deposited polysilicon films for MEMS manufacturing. These limitations include polysilicon's low thermal conductivity and roughness, film thickness (MEMS applications typically require thicker structures), and inherent stresses and stress gradients in polysilicon films that are detrimental to cantilevered structures with high aspect ratios, which are often used in MEMS applications. There are two possible approaches to replace the polysilicon with single-crystalline silicon. The first is bulk micro machining, in which deep etching separates regions of the bulk wafer from the substrate; this technique is suitable for structures with vertical dimensions up to and even less than 100 $\mu$ m. Precise control of the etch depth is challenging in this case and etching in the lateral direction under the MEMS structures is even more difficult. The second approach is to use SOI, which provides a well-defined film thickness that assures an accurate frequency of oscillation for the moving parts plus all the advantages of single-crystalline silicon. The latter, in particular is important because it allows us to produce on the edge of the cantilevers a surface that is flat at the atomic level, by cleaving them along a crystallographic plane with the help of an AFM tip.

In the measurement of the resonant devices we used a piezoelectric actuation method. The oscillation of the cantilever is monitored by the deflection of a laser beam on a four quadrant photodiode, in a fashion similar to the standard AFM detection system. The resonant frequency was measured in vacuum, with different environmental conditions like in humid conditions and after annealing. The best Q factor we observed was as high as 15000.

The molecular detection idea is based on the following mechanism. Before depositing the molecules under study, each pair of twin cantilevers oscillate at the same frequency, in a non degenerate mode. When molecules are introduced across the gap, they perturb the fundamental oscillation mode causing the degeneracy to break, and the twin cantilevers to vibrate with a different frequency. The observation of shift in the resonance frequency can be then ascribed to the presence of one or more molecules across the gap, being the size of the shift proportional to the number and to the physical properties of the molecules.

Details on the fabrication procedure, the device characterization and the modelling of the system will be presented.

## POSTER A11

### Interactions of Boron-containing Nucleosides with Stealth and Functionalized Liposomes

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Liposomes have gained considerable interest as drug delivery tool for therapy of cancer and infectious diseases. They have therapeutic advantages, such as the ability to deliver large amounts of drugs to specific sites, spare healthy tissue from toxic effects, and increase the systemic circulation time of the drug. For this last purpose, the liposomes are sterically stabilized, commonly by incorporating an appropriate amount of lipid with a covalently anchored homo-polymer, usually a poly(ethylene glycol) (PEG) chain.[1] In this study we have investigated the effect of hydrophobic carboranyl-derivatives inserted in liposome bilayer composed of EPC/DSPE-PEG2000 and DSPC/DSPE-PEG2000 (96:4 mol/mol). Cryo-transmission electron microscopy (cryo-TEM) was used to visualize changes in aggregate structure whereas the lipid packing order and motional features of liposomal membrane were monitored by electron paramagnetic resonance (EPR) spectroscopy of doxyl stearic acids (n-DSA).

The boronated compounds used are b-5-o-carboranyl-2'-deoxyuridine (CDU, scheme a) and two nucleoside-metallo-carborane conjugates: 6N-diethylenoxy-COSAN-2'-deoxyadenosine (scheme b) and 4O-diethylenoxy-COSAN-2'-deoxythymidine (scheme c). They are candidate drugs for Boron Neutron Capture Therapy (BNCT) of brain tumors, which have been extensively studied for their cytotoxicity, anticancer, antiviral activity and cellular uptake.[2-3] The results have showed that the presence of CDU affect the integrity of the phospholipid membrane and may have a dramatic effect on the overall aggregate structure in the dispersions. The cryo-TEM investigations have revealed the time-dependent formation of thread-like micelles and membrane pores when the liposomes are formed of EPC:DSPE-PEG2000. In the case of PEG-stabilized DSPC membranes, the boronated compound promoted the formation of discs, as well as small angular bilayered structures with sharp angles and edges. Incorporation of the boronated compound leads to severe packing disturbances and to the formation of highly unfavourable voids in the inner hydrophobic part of the membrane, as indicated by ESR results.

Although liposomes based on PC are the most commonly used for applications involving systemic administration, several other interesting alternatives have been suggested and evaluated. In particular, we have used a functionalized synthetic phospholipid amphiphiles bearing a nucleoside moiety on the polar head group.[4] Palmitoyl-oleoyl-phosphatidyl-adenosine (POPA) self-assembled in water and formed stable unilamellar liposomes. Studies with cryo-TEM and EPR were performed in order to investigate if some selective interaction occur between the boronated nucleosides and phosphatidyladenosine.

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## POSTER A12

### Controlled processing of giant functional macromolecules in crystalline architectures by soft landing mass spectrometry

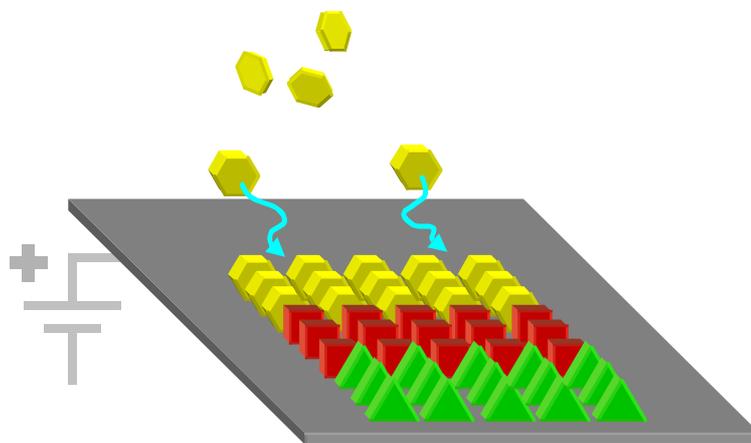
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The processing of giant macromolecules into ultrapure and highly ordered structures at surfaces is of fundamental importance to study chemical, physical and biological phenomena, as well as for their use as active units in the fabrication of hybrid devices. The possibility of handling larger and larger molecules grants access to increasingly complex functions. Unfortunately, larger molecules usually imply lower processability due to either their low solubility in liquid media or the occurrence of thermal cracking during vacuum sublimation. The search for new strategies to process and characterize giant molecules is thus a key goal in materials science. Here we report a new general route to process at surfaces extraordinarily large molecules, i.e. synthetic nanographenes, into ultrapure crystalline architectures.<sup>[1]</sup> Our method relies on the soft-landing of ions generated by solvent-free matrix assisted laser desorption/ionization. The nanographenes are transferred to the gas phase, purified and adsorbed at surfaces. Scanning tunnelling microscopy revealed the formation of ordered nanoscale semiconducting supramolecular architectures. The unique flexibility of this method allows growth of ultrapure crystalline films of various systems, as organic, inorganic and biological molecules, hence it can be of interest for applications in electronics, (bio)catalysis and nanomedicine.



<sup>[1]</sup> H.J. Räder, A. Rouhanipour, A.M.Talarico, V. Palermo, P. Samorì, K. Müllen, *Nature Materials* **2006** in press. (doi:10.1038/nmat1597)

## POSTER A13

### Peptides with regular enantiomeric sequences as self-assembling nanotubes for nanotechnology

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The wide interest in the nanoscience and nanotechnology of carbon and inorganic nanotubes raised a renewed attention to organic tubular assemblies. In fact, organic trans-annular assemblies constitute an expanding class of structures with promising applications in supramolecular chemistry and realistic perspectives for the design of nanotechnological devices for molecular electronics and membrane separation technology. Among the strategies developed for the design and engineering of organic nanotubes, those characterized by regular alternating enantiomeric amino acid sequences have been proven particularly useful. The basic principles that regulate the conformational stability of enantiomeric sequences were formulated by us about thirty years ago [1]. Amino acid sequences with alternating configurations have the propensity to form self-assembling trans-annular nanotubes (or helical channels) stabilized by multiple hydrogen bonds with different inner radius and quantized lengths. These can be further stabilized by suitably designed amino acid sequences, which provide cross-links between the adjacent cyclic DL-peptides (or helical spires).

On the basis of the theoretical predictions, more than twenty years ago, long time before nanotubes were conceived, we synthesized and investigated the properties of poly(DL-proline) as an ion channel and found regular current fluctuation events due to a single channel molecule in bilayer membranes, doped with the polypeptide [2-5]. We are at present investigating the possibility to obtain self-assembling nanotubes using different amino acids and adopting suitable strategy of stabilization. In particular, DL-cysteine and DL-lysine seem to be promising. In fact, DL-cysteine could be stabilized by vulcanization of adjacent annular peptides (Figure 1) while DL-lysine nanotubes could be obtained by formation of metal complexes between their salicylaldehyde derivatives (Figure 2) [7-8].

In all cases, it is possible to separate nanotubes with differently sized lengths. Such nanotubes are characterized by high rigidity and modularity and provide the possibility to build ion single molecule conductors, nanomemory for electronics obtained by the quantized states of a suitable cation confined in a nanotube. Self-assembled nanotubes with peptide architecture can be used for casting metal nanowires, for example to be used as tips for Atomic Force Microscopy and improve the resolution power. The peptide nanotubes coated with suitable metal complexes of lysine derivatives are easily oriented under magnetic field on suitable surfaces and could be used as rigid linear building blocks for spintronic devices.

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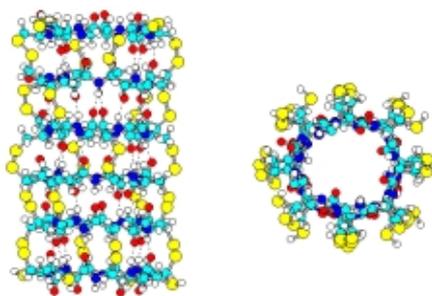


Figure 1

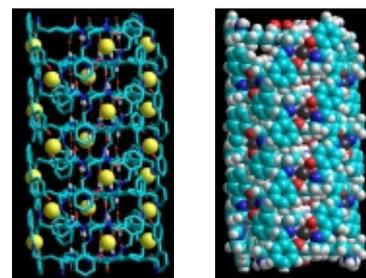


Figure 2

**POSTER A14**  
**SNOM in Nanomedicine: observation of nanostructures in renal glomerula membrane**

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In the last years Scanning Probe Microscopy has gathering the interest in biology and medicine.

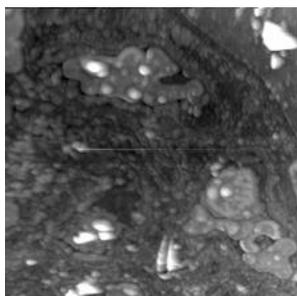
In this study we want to compare a traditional, more known technique like TEM, with the Scanning Near-field Optical Microscopy (SNOM). SNOM microscope gives submicrometric 3D reconstruction of the surface, like Atomic Force Microscope, but also an optical imaging, acquiring transmitted and reflected light like optical microscopy. Moreover its optical resolution overtakes the diffraction limit (up to  $1/20$ ).

The aim of the work is the ultrastructural observation of the membrane of renal glomerula. In particular we want to study the permeability of glomerular capillary membrane involved in many kidney diseases, like in Focal Segmental Glomerulosclerosis (FSGS). FSGS is a renal syndrome characterized by proteinuria (excessive protein excretion in the urine) and glomerulosclerosis (scarring in the filtering part of the kidney). The control mechanism of renal permeability to proteins (Permeability Factor Protein) is correlated with the transmembrane contacts among the foot processes of the renal podocytes. In this work we just studied the podocytes and the glomerular filtration barrier in isolated rat glomerula by SNOM and TEM.

We isolated renal glomerula from kidney, and we fixed them. Than the renal glomerula were embedded in DER 732 resin. We prepared sections of various thickness, from thin to ultrathin sections (1,5 mm, 100 nm, 80 nm) and placed them on coverglasses. The sections observed by Snom were unstained or stained with toluidine blue, other ultra thin sections were stained with uranyl acetate and lead citrate. For this study we compare SNOM images, obtained with samples prepared for optical microscope (thin sections coloured with dyes), and TEM images obtained with standard TEM preparation (ultra thin sections metal stained).

The comparison between this two techniques demonstrated that SNOM images (Fig. 1, 2) on thin section of 70-120nm are comparable with the TEM images. Even if the TEM microscopy presents more resolution than Snom, Snom images allow the comparison between the topography and the optical signals, simultaneously acquired. This peculiar SNOM property allows to localize and characterize the structure of the surface of the sample: topographically similar structures often present different optical properties, due to the different chemical composition, or vice versa some optically uniform zone of the surface could be localized by the different particular topography. In particular, in the analysis of the glomerular capillary membrane, Snom Images allowed to evidence a peculiar aspects of the basal membrane, not visible with the TEM microscopy. We must remember that the dark and light zones in SNOM images have a meaning completely different from dark zone in TEM images. In SNOM topography colour scale represents the height, in SNOM optical images dark and light zones are parts with different optical density and composition of the sample, instead in TEM images the contrast is due to the metal staining of the sample. SNOM topography has shown a dark band in correspondence to the basal membrane, localized comparing optical and topographical signals. We could assume that the presence of the dark line could be correlated to the presence of chemical substances that modify the surface of the resin creating a groove. A theory could be the not perfect embedding of the membrane proteoglycan component. This study permitted to obtained useful information by correlating topography and optical signals (both transmitted and reflected) simultaneously measured, and demonstrated the possibility to use Snom on thin sections with the same standard preparation made for TEM, and also on thin section without any staining.

**a) SNOM Topography**



**b) SNOM Optical Signal**

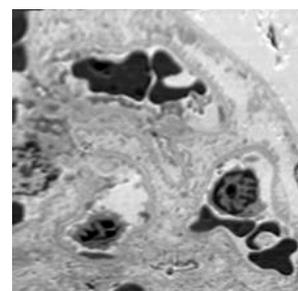


Fig.1 SNOM Images of Ultrathin sections (thickness 100 nm) of renal glomerular capillaries. Scan Area:  $40\ \mu\text{m} \times 40\ \mu\text{m}$  a) SNOM topography b) SNOM optical signal in Transmission mode, wavelength 650nm.

## POSTER A15

### **TPPS<sub>4</sub> J-aggregates formation in the presence of two proteins: comparative study**

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Recently in biotechnology considerable scientific interest has been focused on nanostructures expressing a self-assembling feature under appropriate conditions. J-aggregates with a unique spatial structure and non-linear optical properties represent one of the most interesting types of self-assembling nanostructures. J-aggregates are potential candidates for applications in many promising technological fields like the development of nonlinear optics, design of opto-electric conversion devices, nanodevices and artificial light harvesting systems. Meso-tetra(4-sulphonatophenyl)porphine (TPPS<sub>4</sub>) forms J-aggregates in acid medium due to the interaction of residual negatively charged sulphonic (SO<sub>3</sub><sup>-</sup>) groups with protonated central nitrogen atoms.

In this work J-aggregates formation in the presence of two proteins, lysozyme and serum albumin, was studied by means of absorption and fluorescence spectroscopy. The role of different TPPS<sub>4</sub>-protein interaction in the formation of J-aggregates was discussed.

## POSTER A16

### **Turning Synthetic DNA Oligonucleotides into Designed Nanostructures: Supramolecular Polymeric Chains and Dynamic Objects by Self-assembly**

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DNA is the molecule that encodes the hereditary information in living organisms. In the last years, the specific recognition abilities and the possibility to encode information that are intrinsic in the DNA molecule have been used to assemble nanoscale structures by design.[1] As suggested by Ned Seeman, the recognized pioneer of this field,[2] the Holliday junction is the fundamental structural element around which a great variety of structures can be designed and implemented: this is a branching point where 4 chains of double-stranded DNA meet. By organizing a number of junctions in a proper fashion, it is possible to create rigid structures that overtake the intrinsic flexibility and stochasticity of polymers to create DNA nanoscale objects with the desired size and shape. Using this type of approach, a number of monomeric or polymeric nano-objects can be assembled, with the added possibility of introducing tunable elements, that can change their geometry on an external signal, opening the way towards the construction of nanostructures with controllable dynamics.

Using synthetic oligodeoxynucleotides (ODN), in our laboratory we have assembled parallelogram shaped nanostructures made of 4 blocked Holliday junctions that have “sticky ends” on their side. Programmed assembly of these ends brings to the construction of polymers that can be either flexible or rigid (100 nm of persistence length or more). Proper mixing and assembly of different monomer structures can yield different topologies: we can obtain linear, branched or circular nanostructures up to several hundred nanometers in size. The biochemical and structural characterization of these has been performed using gel electrophoresis and atomic force microscopy.

By proper functionalization of the ODNs used for the assembly, it is possible to include non-DNA objects on the structures: this seems a clever strategy to assemble (a desired number of) objects at a controlled distance on a nanostructure, with the possibility of also modulating their dynamics. As an example of this paradigm, we have assembled interacting fluorophores on a rigid parallelogram made of DNA, and we have

measured a significant FRET. This does not take place if the fluorophores are, instead, free in solution, or even if they are assembled on incomplete (more flexible) parallelogram structures.

Furthermore, by assembling oligonucleotides in a pH-controlled triple helix, we have recently introduced a novel structural motif to the toolbox for DNA-based molecules constructions.[3] This tool is expected to expand further the possibilities of assembling and controlling nanostructures made of DNA.

[1] M. Brucale, G. Zuccheri, B. Samorì, Trends in Biotechnology, May 2006.

[2] N. C. Seeman, Nature 2003, 421, 427.

[3] M. Brucale, G. Zuccheri, B. Samorì, Org Biomol Chem 2005, 3, 575.

## POSTER A17

### **Photocurrent generation by self-assembled peptide monolayers covalently linked to interdigitated gold microelectrodes**

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#### **Abstract**

The miniaturization of electronic devices from microscale to molecular dimensions represents a challenging research topic in modern science. The basic idea of molecular electronics is to use, in a nano-on-micro approach, single molecules as elements of electronic devices. In this aim, photonic activation of electronic functions in nanostructured assemblies may have important applications in designing molecule-based logic gates, optical switches, and more in general new sensors. Photocurrent generating systems based on nanometric films formed by peptide self-assembled monolayers have shown peculiar electronic conductive properties. In this work interdigitated gold microelectrodes were modified by covalently linking a hexapeptide functionalized by a lipoic acid at the N-terminus. The peptide chain [Lipo-(Aib)<sub>4</sub>-Trp-Aib-OtBu] comprises five amino- $\alpha$ -isobutyric acid residues (Aib) and a tryptophan unit (Trp), a fluorescent amino acid with strong absorption properties in the UV region. Due to the number of conformationally constrained Aib residues in the chain, the peptide adopts a fairly regular helical structure. Cyclic voltammetry (CV) measurements show that the peptide forms a homogeneously and densely packed monolayer on the gold surface. Photocurrent generation experiments on the peptide-layered microelectrode reveal interesting modifications of the photocurrent action spectrum with a high photocurrent/voltage response, suggesting that a photoinduced electron transfer process from Trp to gold takes place with high efficiency. These results give basic information on reversible electronic transduction of photonic processes occurring on microelectrodes as a conceptual method to develop molecular and biomolecular optoelectronic systems.

## POSTER A18

### Nanotubes from a Vitamin C-based Bolaamphiphile

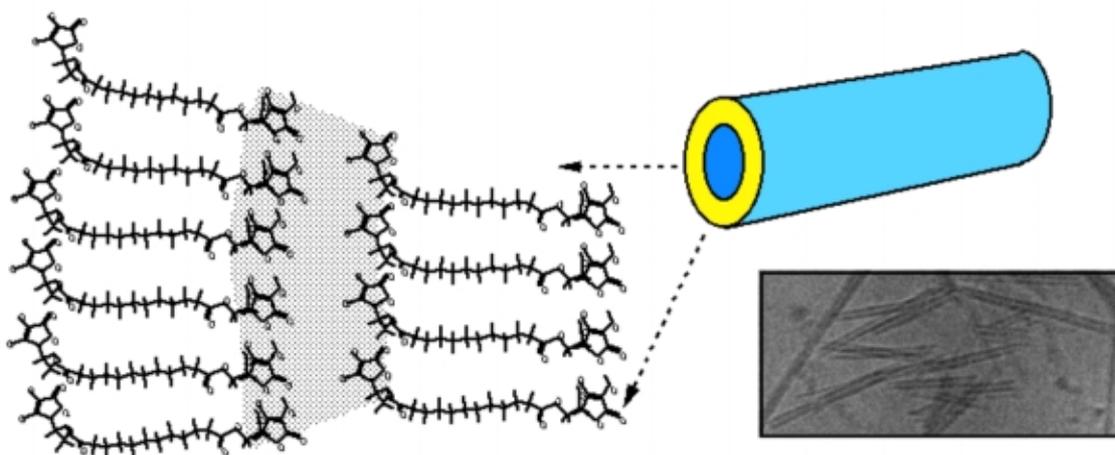
Moira Ambrosi (1), Emiliano Fratini (1), Viveka Alfredsson (2), Barry W. Ninham (1,3),  
Rodorico Giorgi (1), Pierandrea Lo Nostro (1), and Piero Baglioni (1)

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A bolaform surfactant, 1,12-diascorbyl dodecanedioate (BOLA12), with ascorbic acid units as the polar headgroups was synthesized for the first time. Once dispersed in water above 0.5% w/w, BOLA12 forms hollow nanotubes as revealed by cryo-TEM experiments. These nanostructures transform into clear micellar solutions on heating. X-ray diffraction and SAXS experiments were performed both on the pure solid and on its aqueous dispersions. The critical aggregation concentration and the phase behavior were determined by conductivity and DSC experiments. The latter technique provided also the amount of strongly bound, solvating water molecules that surround the polar headgroups. BOLA12 shows the same reducing properties of ascorbic acid, as indicated by the antioxidant activity evaluated with the DPPH method. This feature was used for the reduction of Pd(II) ions on the surface of the nanoassemblies, which lead to the formation of large bundles homogeneously coated with palladium as observed in SEM micrographs.



## POSTER A19

### Biomolecules/CNT conjugates: interaction, patterning and sensing

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Various biomolecules adsorb spontaneously on the sidewalls of purified singlewalled carbon nanotubes. This non-specific binding scheme can be exploited to yield noncovalent biomolecules-nanotube complexes, which are useful prototype for studying biosensing properties in view of device applications.

Here we study the surfactant ability and mechanism of binding of nucleic acids (single and double stranded DNA) and peptides (trypsin, cytochrome c) to understand how biomolecules interact with carbon nanotubes upon different environments and substrates. Topographical images of these complexes by semi-contact mode AFM at ambient conditions are analysed and correlated to the biological activity of the biomolecule/CNT conjugates assessed by biochemical assays.

We then pattern CNTs by soft-lithographic techniques, viz. Micro Molding In Capillaries (MIMIC) and Lithographically Controlled Wetting (LCW), starting from aqueous suspension of tubes in sodium dodecyl sulphate (SDS) as well as directly on the biomolecule/CNT conjugates. Oriented stripes of bundles and individual CNTs are obtained and their electrical interconnection is confirmed by the anisotropy in the electrical current measured along and across the lines. We are in the process of prototyping new sensing device architectures based on these biomolecule/CNT conjugates.

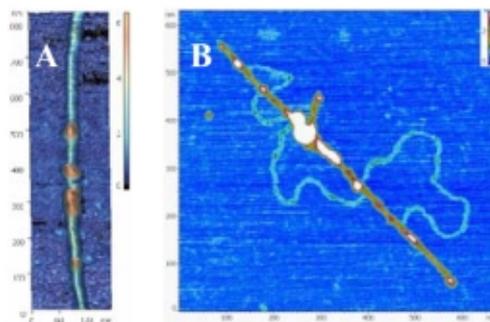
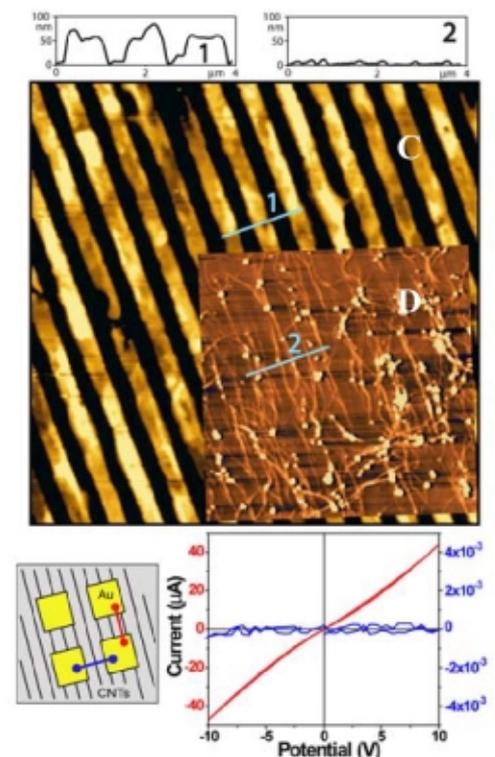


Figure 1 – Examples of biomolecule/CNT conjugates: A) trypsin and B) ds-DNA.

Patterning of CNTs via MIMIC before (C) and after washing (D) the SDS; in graph is shown the I-V characteristic curve of the pattern measured as shown in scheme.



## **POSTER A20**

### **Simple, fast and low cost cantilever technology for DNA analysis**

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In recent years, a new miniaturized sensor technology, cantilever beams technology, was developed to investigate molecular interactions and perform bioaffinity analysis. Adsorption of molecules on the cantilever surface can essentially cause two different phenomena: an increase of the system total mass or stresses on the cantilever upper surface. Consequently cantilever sensors usually work in two different modes: in dynamic mode, when molecules absorption causes a significant increase of the system mass, changing its resonance frequency, and in static mode, when molecules absorption causes a static bending of the cantilever. In this second case, deflection of the free end of the cantilever is typically detected by means of a laser, implying massive damping systems and non user-friendly readout systems. The present work aims to develop a simple, fast and low cost cantilever technology to perform DNA analysis and detect SNPs. Recognition between ssDNA probes, adsorbed on the cantilever upper surface, and complementary targets in solution causes a static deflection of the cantilever. We developed a new technology that involves the dynamic reading out of a static phenomenon, increasing sensibility of the system, improving signal to noise ratio, simplifying and reducing the total device volume.

## POSTER A21

### Growth of III-V nanowires by molecular beam epitaxy

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Semiconducting nanowires (NWs) are the object of numerous research projects, which have the goal to use them as building blocks for nanoscale devices<sup>1</sup>. The fabrication of the nanowires generally occurs via the use of a metal catalyst which induces and dictates the growth. The most accepted model to describe the nanowire growth is the so called vapor-liquid-solid (VLS)<sup>1</sup>, although this model is object of debate<sup>2</sup>.

Another emerging field of research in semiconductor physics is spintronics that plans to make profitable use of dilute magnetic semiconductors. In order to exploit the GaAs technology, one of the most investigated material system is GaAs:Mn. The combination of these two research fields opens the possibility to envisage 1D spintronics.

One important issue regarding the nanowire growth is whether the catalyst diffuses into the wires. The possible diffusion of the catalyst in the nanowires can change their electronic properties. Claims about luminescence related to e-h recombination on catalyst impurities have been published<sup>3</sup>, and very recently direct observation of Au in InAs<sup>4</sup> and ZnSe<sup>5</sup> nanowires has been reported.

In the framework described above we have undertaken a research program on the growth of III-V nanowires (NWs) by solid-state molecular beam epitaxy. GaAs and InAs NWs have been fabricated using both Au and Mn as growth catalysts. In particular, one of our intents is to investigate whether Mn diffuses into the NWs during the growth, with the explicit intent to dope the NWs with manganese as a first step towards the attainment of dilute ferromagnetic semiconducting NW.

The growth of GaAs and InAs NWs has been successfully obtained on a number of substrates. The use of SiO<sub>2</sub> substrates gives rise to the fabrication of a large number of nanowires with both catalysts. Fig. 1 shows the scanning electron microscopy image of a typical GaAs NW yield obtained on SiO<sub>2</sub> (catalyst Mn). Together with the nanowires a number of quasi 2D structures, a kind of nanoleaves, has been also obtained. The growth temperature range useful for the growth of GaAs NWs is 520-620 °C. InAs NWs are instead obtained at a lower temperature. A SEM picture of InAs NWs is reported in Fig. 1(b). The use of other substrates leads to different results with the different catalysts.

The use of oxidized GaAs gives rise to the production of several nanostructures with a larger number of quasi 2D structures than of NWs. These structures appear to be somehow ordered on the substrate surface (Fig. 1 c). Much more difficult appear the Mn-induced NW fabrication on clean GaAs surfaces: within the growth temperature range indicated above and with the deposition of up to 2 nm of Mn on the substrate, NW have been obtained on a cleaved (110) surface, as well as on (100) and (111) epitaxial surfaces. A positive role of cleavage defects for the success of the NWs growth is possible. On the other hand, Au induces the growth of NWs on all the above mentioned substrates as well as on Si(111). In particular, on GaAs(111) surfaces a large yield of regularly shaped and oriented wires has been obtained as shown in fig. 1(d). The growth process and the crystalline structure of the nanowires have been investigated by transmission electron microscopy. The presence of a catalyst droplet at their top is a typical feature of the NWs. The presence of an Au droplet at the top of the GaAs NWs grown with this catalyst is apparent from the TEM picture presented in Fig. 2(a) and the droplet has the same section diameter of the nanowire beneath it. A slightly different situation is found in the case of the Mn-induced wires, although the image analysis in this case is made more difficult by the tip oxidation that occurs when the specimens are taken out of the growth chamber. In this case, indeed, the amount of crystalline material at the top of the wire that can be identified with a-Mn has an apparent diameter smaller than the corresponding wire (Fig. 2(b)). This feature suggests the possibility of a sizeable Mn diffusion into the wires. Mn diffusion is confirmed by extended X-ray absorption fine structure measurements (not reported in this abstract), that show that about 50% of the Mn atoms revealed by the measurements is bound to As, while the rest is bound to oxygen.

Other interesting and common features of Mn- and Au-catalyzed GaAs wires is that the lattices have a wurtzite structures. This is testified by the fast Fourier transform analysis applied to the high resolution TEM images, as shown in Fig. 2 (a).

<sup>1</sup>For a recent review on semiconductor nanowires, see M.Law, J. Goldberger, P. Yang, *Annu. Rev. Mater. Res.* **34**, 83 (2004).

<sup>2</sup>A.I. Persson, et al., *Nature Materials* **3**, 677 (2004).

<sup>3</sup>see, e.g., B. Xiang, et al., *Appl. Phys. Lett.*, **82**, 3330 (2003).

<sup>4</sup>Perea, E.P. et al., *Nano Letters*, **6**, 181 (2006).

<sup>5</sup>Carlino, E. et al., *Phil. Mag. Lett.* in press.

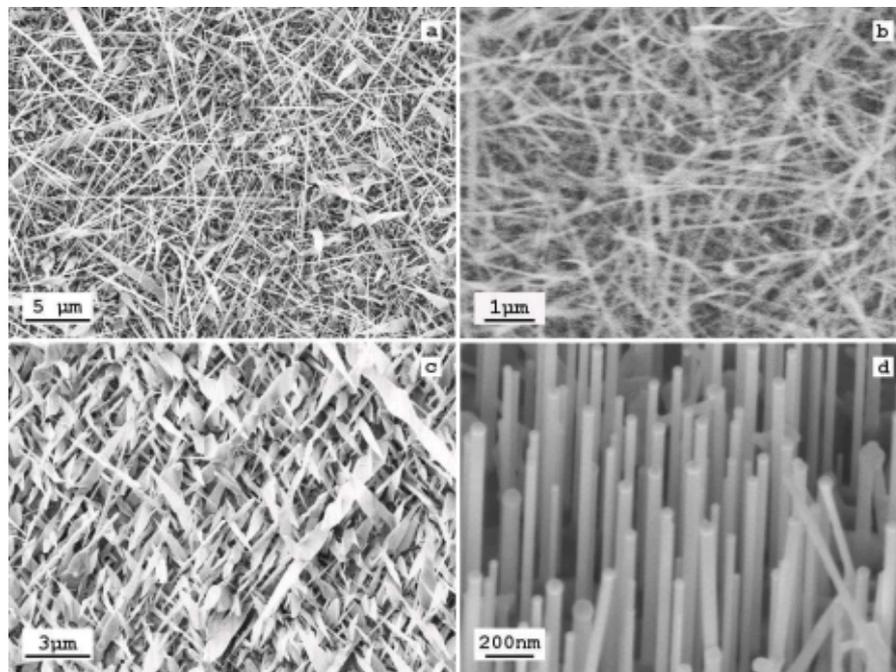


Fig. 1 SEM images of (a) Mn-catalyzed GaAs nanowires grown on SiO<sub>2</sub>; (b) Mn-catalyzed InAs nanowires grown on SiO<sub>2</sub>; (c) Mn-catalyzed GaAs nanowires and nanoleaves grown on oxidized GaAs; (d) oriented Au-catalyzed GaAs nanowires grown on GaAs(111)B.

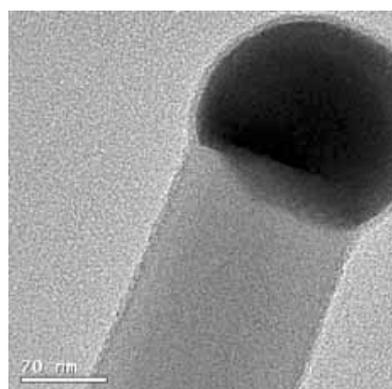


Fig. 2(a). HRTEM image of the tip of an Au-catalyzed GaAs NW.

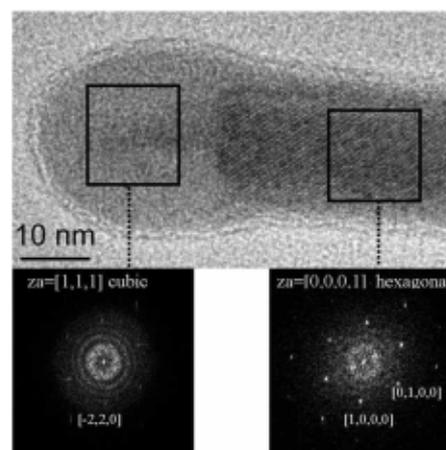


Fig. 2(b) HRTEM image of the tip of a Mn-catalyzed GaAs NW. The insets are the FFT obtained from the marked relevant regions of the nanowire. The FFT from the body indicates wurzite GaAs whereas the FFT from the crystalline region of the tip is due to a-Mn phase.

## POSTER A22

### **Electron beam induced deposition of sub-10 nm freestanding nanowires**

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Electron Beam Induced Deposition (EBID) is a technique of the scanning electron microscopy (SEM) that allows maskless and resistless fabrication of features with sizes ranging from micrometers down to nanometers. Precursor molecules adsorbed on the substrate are decomposed by beam induced surface reactions, resulting in localized deposition of material. The minimum size of EBID objects fabricated on bulk substrate is limited to few tens of nanometers depending on exposure time and electron beam size.

Here we present an approach to obtain sub-10 nm freestanding wires fabricated by EBID from different precursors (Pt-based metallorganic and tetraethyl orthosilicate, TEOS) in a Dual Beam, Focused Ion Beam (FIB)-SEM system. Freestanding growth is obtained with a computer controlled procedure that laterally shifts the electron beam, in spot mode, with a dwell time properly tuned in order to obtain thickness and width uniformity and desired wire length. Only few seconds are needed to grow 200-300nm long wires with a selectivity of the growth site limited by the SEM resolution. Irradiation by 200 keV electron of a conventional Transmission Electron Microscope has been used to further decrease wire width and to reduce the carbon contamination of the deposit.

## POSTER A23

### Improved electrical insulation between FIB-patterned nanogap electrodes by Iodine and HF chemical assistance

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Electrical characterization of nanosized structures like molecules, nanoparticles and nanotubes is fundamental for the development of future electronics and nanotechnology. This requires the fabrication of nanogap electrodes as the contact structure matching the size of these nano-objects and enabling the electrical test.

A new fabrication approach based on Focused Ion Beam (FIB) - Direct Lithography (DL) is attracting increasing interest [1,2]. This technique enables single-step fabrication of submicron- and nano-gap electrodes from a bare metal-on-insulator substrate by sputtering removal of the metal layer with high resolution (few nm) ion beams. The method is quick and flexible, suited for rapid prototyping of nanostructures on any metal/insulator materials combination [3].

One critical aspect of the technique, which is crucial when very low currents (few pA range) are measured, is electrical insulation between the electrodes. In fact, implantation of FIB metal ions (typically Ga<sup>+</sup>) and redeposition of the sputtered material within the gap may generate leakage currents paths.

In this work we present FIB-DL patterning of submicron- (100-200 nm spacing) and nano-gap (15-40 nm spacing) electrodes on Au/Cr/SiO<sub>2</sub> and Au/Ti/SiO<sub>2</sub> substrates, along with room temperature (RT) electrical characterization and elemental microanalysis by Auger Electron Spectroscopy (AES). Typical resistance (R) measured on FIB DL-patterned electrodes was in the 100-400 GOhm range and evidence of Ga implantation in the inter-gap oxide substrate was revealed by AES depth profiling. To reduce this effect and improve electrical insulation, two chemical assistance methods have been followed. By Iodine (I<sub>2</sub>) gas enhanced etching applied in-situ, during FIB processing, R increased up to the 2-40 TOhm range, and Ga concentration was strongly reduced. Similar R values and complete Ga removal was obtained by sample post-processing with HF wet etching.

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## POSTER A24

### SPLIT HOLZ LINES ANALYSIS AS A TOOL TO MAP THE STRAIN FIELD IN PATTERNED NANOSTRUCTURES

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In the last decade it has become evident that one of the major issues for the deep sub-micron integrated circuit technologies regarding yield, device performance and stability is the mechanical strain distribution built up in the layers and the silicon substrate.

Quantitative strain mapping can be obtained from the analysis of the strain induced shift of High Order Laue Zones (HOLZ) deficiency lines present in a Convergent Beam Electron Diffraction (CBED) patterns, acquired in a transmission electron microscopy (TEM). It has been recently proved that the spatial resolution of this technique is in the nanometre range [1]. The strain measurement in a typical unsplit HOLZ pattern can be performed in a semi-automatical way. However, this procedure of analysis requires the sharpness of the CBED pattern, and this occurs when the strain distribution in the analysed region of the cross-sectioned TEM sample is rather uniform. If strain gradients are present along the electron beam direction, the HOLZ lines are split in two components and intermediate fringes can be observed, as evidenced by other authors [2,3]. The closer to the strain source the analyzed point is, the larger the HOLZ band is. In this situation, CBED analysis is still possible, provided a model of the strain field distribution is assumed [4]. A method to extract accurate information on the displacement field distribution from split HOLZ pattern has been developed. We started from the reproduction of the unsplit HOLZ patterns by a recursive simulation of the 2-D many beam dynamical CBED patterns, in analogy with previous works [5,6]. Then we extended the HOLZ pattern simulation to the deformed case, introducing the strain field effects, according to the Peng and Whelan theory [7]. The algorithm of the simulation is based on the Bloch wave calculation, and the strained crystal is treated as an assembly of  $s$  thin perfect crystal slab, according to the column approximation. The  $i$ -th slab is displaced from the equilibrium position by a vector  $\mathbf{R}_i$  orthogonal to the electron beam direction, changing the crystal potential and therefore modifying the eigenvectors. The total electron wave for  $N$  beams at the depth  $z$ ,  $\Psi(z)$ , after each slab can be written by the following eigenvalue equation:

$$\Psi(z) = \prod_{i=1}^s [\mathbf{Q}_i \mathbf{P}_i(z_i) \mathbf{C}_i \Upsilon_i(t_i) \mathbf{C}_i^{-1} \mathbf{P}_i(-z_{i-1}) \mathbf{Q}_i^{-1}] \cdot \Psi(0)$$

where the displacement effects can be accounted by the  $N \times N$  diagonal matrix  $\mathbf{Q}_i$  (whose elements are defined by  $\mathbf{Q}_i = \exp(-2\pi \mathbf{g} \cdot \mathbf{R}_i)$ ).  $\mathbf{C}$  is the  $N \times N$  matrix of the eigenvectors and  $\Upsilon$  represents a  $N \times N$  diagonal matrix, where  $(\Upsilon)_i = \exp(i \cdot \gamma^{(i)} z)$  are the eigenvalues. The displacement field in the investigated nanoregions of the sample is reconstructed assuming a parametrized model of  $\mathbf{R}$  and refined by a best fit procedure which minimizes the differences between simulated and experimental split patterns. This task is done by comparing the corresponding rocking curves of a number of HOLZ reflections, minimizing the equation:

$$\chi^2 = \frac{1}{N-f-1} \sum_{i=1}^N \frac{[(I_i^{\text{exp}} - B_i) - c * I_i^{\text{theor}}]^2}{\sigma_i^2}$$

where  $N$  is the number of points in the profile,  $f$  the number of refining parameters,  $B_i$  the background value and  $c$  a constant.

The method presented here has been applied to the analysis of the strain induced by the formation of Ti self-aligned silicide (salicide) overlayers onto the 0.18  $\mu\text{m}$  wide active silicon areas of shallow trench isolation structures (STI). The TiSi<sub>2</sub> layer is grown on top of the Si active areas, depositing a Ti layer about 30 nm thick on the patterned structures, followed by a sequence of two rapid thermal treatments [4]. The increasing enlargement of the split HOLZ lines that appears in experimental CBED patterns acquired at decreasing depth from the interface is mainly due to the bamboo-like distribution of the grain boundaries along the TiSi<sub>2</sub> stripe, rather than a mere relaxation of the TEM sample.

Applying the fitting procedure to simulate the split HOLZ patterns acquired at different depth from the stressor source, a map of the displacement field components can be obtained, assuming an analytical ellipsoidal model which account the deformation induced by the set of grain boundaries present in the analyzed sample. Based on this reconstruction, the strain field can be determined. The method presented

here is of general validity and, in principle, it can be applied to any sample where strong strain field gradients along the beam direction are present.

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## POSTER A25

### Super intense laser field action on surface and forming the femto-second laser plasma in the nano-structured porous materials

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Using the super short light pulses changes principally a character of interaction of the laser radiation with substance (surface) [1] under laser radiation intensities more than  $10^{15}$  Wt/cm<sup>2</sup>. During the laser pulse electrons get energy of 100-1000eV and it is realized a process of forming the femto-second laser plasma.(FLP) In this paper we consider possibilities of governing by processes, which are taken a place in the FLP in nano-structured porous materials (Si). Nano-structured porous materials consists of the separated clusters set, that forms the fractal structure or regular net. The main mechanism of the hot electrons generation in plasma is provided by oscillation of electron on the border "plasma-vacuum" or resonant absorption of laser radiation. For porous materials one may wait for the sharp increasing the hot electrons generation and X-ray radiation. Under large intensity of laser field it is observed a new type of the hydrodynamic ablation, which has the explosion character. Experimental estimates show that a velocity of the plasma flying of the strongly porous samples Si ( $I \sim 10^{16}$  W/cm<sup>2</sup>) is  $\sim 10^8$  cm/s, that is corresponding to energy  $\sim 2$  MeV [2]. We carried out the modelling of FLP forming in the porous materials on the basis of the energy balance equations and Green's function formalism for non-ordered materials. Special attention is devoted to the modelling the system: nano-structured porous material with clusters, on surface of which there is a great number of bonds with H and OH groups. In a case of the D-and OD group's one can wait for realization of the cluster explosion process and reaction D+D-alpha+n (3,8MeV). In the high density plasma there is possible an excitation of the low lying isomers (level energy less 20 keV) by means of the following channels: photo excitation by own X-ray plasma radiation, the electron impact excitation, electron conversion etc. Atomic numerical code [3] is then used for calculating the stable and long lived nuclei low lying isomers characteristics (time of life, spin, energy, decay channels etc.).

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## POSTER A26

### STEM\_CELL: COMPUTER SIMULATION FOR HAADF SIMULATION AND ANALYSIS

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The simulation of high angle annular dark field (HAADF) images can be tackled by multi-slice and Bloch wave methods [1,2,3,4]. The HAADF image formation is due to the mainly incoherent interaction of the highly focused electron probe along the atomic columns of the specimen. Electron-phonon scattering process strongly contributes to the incoherent nature of the HAADF images. Hence, the thermal diffuse scattering is of particular importance in the HAADF image formation. Within the multi-slice method the role of the thermal diffuse scattering can be treated in the most direct way by applying the so-called “frozen phonon” approximation.<sup>5</sup> This approach is based on the assumption that the high-energy electrons are so fast that each electron sees a snapshot of the atomic thermal movement. The calculated intensity is therefore the incoherent superposition of the images formed for each atomic configuration in the range of positions given by the Debye-Waller factors. According to our test simulations, and in agreement with literature, 20 configurations are necessary to converge to a precision better than 2% in simulating HAADF image contrast. Hence, to this purpose, multi-slice calculation must be repeated for each atomic configuration and for each point of the image. Calculation time depends critically on the TEM sample thickness, scanned area size, sampling frequency of the crystal potential, and of the wave-function, in both direct and reciprocal space [2]. Even with a small scan size (12x16 pixels) the calculation of a single cell image for a GaAs cell in a 10 nm thick TEM sample requires more than 5 hours of computing time. Hence, multi-slice approach produces very accurate and reliable results for the HAADF image simulation but at a cost of very large computer-time.

Here we present a program for HAADF image calculation, based on the routines developed by Kirkland [2], able to reduce of orders of magnitude the computing time. The program has a user-friendly interface and allows a direct access to the parameters necessary for the calculation. The graphic interface, called STEM\_CELL, was written in C++ kylix (BORLAND®) for Linux environment. It allows to control and organize each simulations submitted from this interface as a separate process. Furthermore, within STEM\_CELL, each crystal structure to be simulated can be visualized and modified. Indeed, the main advantage of STEM\_CELL is to speed up simulation by using parallel computing. In fact, the calculation for HAADF image simulation, based on multi-slice approach, has a logical structure suited for being parallelized at two different levels: the simulation is performed for each position of the probe on the specimen structure and repeated for each atomic configuration to take into account of the thermal diffuse scattering in the “frozen-phonon” approximation.

This “embarrassing parallel” scheme allows the adoption of a parallelization strategy based on the MPI message-passing library, via its free implementation MPICH [6]. MPICH message-passing protocol allows the dispatching of arrays of data to different CPU running the same program. At the beginning of the simulation, the image is divided into different sets of non-consecutive pixels, which are assigned to each CPU. Each CPU fills the assigned part of the matrix with the simulation results after averaging over the considered different atomic configurations. At the end of the calculations, MPI protocol sends the data to a single processor that recomposes as a puzzle the final image. The code is scalable up to a very large number of CPU available in many computer clusters of common use. As a result in most of the commonly available computer clusters, more than one order of magnitude of CPU time can be saved. Fig 1 shows the simulation of a ZnSe nano-particle within STEM\_CELL environment. The simulation required, on a 16 CPUs computer, about 7 hours instead of more than 4 days required for standard single processor calculation. HAADF image simulation is necessary to quantify the relevant experiments and to derive detailed atomic resolution information on the structure and on the chemistry of the specimen. The long computing time necessary for the HAADF image simulation makes unpractical the use of simulation in many cases of interest in nanoscience. STEM\_CELL represents a new approach able to reduce the long computing time for atomic resolution HAADF image simulation.

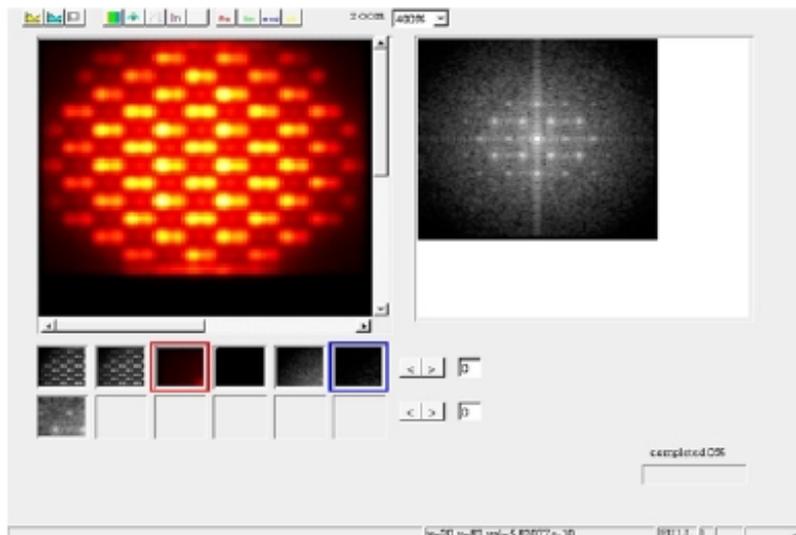


Fig. 1 Snapshot of the program STEM\_PRO showing an HAADF simulation for a ZnSe nanoparticle along the [110] direction.

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## POSTER A27

### ATOMIC RESOLUTION QUANTITATIVE COMPOSITION ANALYSIS BY ANNULA DARK FIELD STEM Z-CONTRAST EXPERIMENTS

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In the last years High Angle Annular Dark Field (HAADF) experiments have received an increasing attention in the study of solid-state materials for the high spatial resolution, chemical sensitivity and flexibility to be used in combination with spectroscopic experiments at atomic resolution. Detailed information on the structure and the chemistry of the specimens can be achieved from a HAADF image even without any image simulation [1,2]. However, by means of a proper use of simulations, it is possible to achieve further quantitative chemical information [3,4]. Here a general approach to derive from the intensity distribution of a HAADF image the distribution of a chemical species in a host matrix is derived. As case study the method has been applied to measure at atomic resolution the composition profile of a Si layer buried in a GaAs matrix. The experimental images have been simulated by multislice method in the frozen phonon approximation [5].

Indeed, to quantify the chemistry from the HAADF images it was necessary to take into account some aspects usually not considered. As an example, the use of virtual crystal approximation has been shown to produce unreliable results when applied to the simulation of the HAADF image contrast of an alloy [6]. To overcome this inconvenient it has been found that the image contrast calculated as average over different atomic configurations allows a satisfactory concentration measurement derived from HAADF image intensity. For example, in the case of Ga(Si)As system, the average over different atomic configuration introduces an uncertainty in the concentration measurement of the order of about 2% molar fraction. However, an average along the interface direction further reduces the error on the experimental measurement. Other aspects have to be taken into account for an accurate quantification: the TEM specimen thickness, the strain status of the material and the electron-optic configuration. Fig. 1 shows the results of simulations for different sample thickness. It is worth noting that in the case of Si buried in GaAs results: (i) HAADF image intensity depends quasi-linearly on composition  $x$ ; (ii) the ratio between the SiAs and GaAs intensity is weakly dependent on thickness. Indeed, it can be regarded as constant, in the range of thickness of TEM specimen between 10-40 nm, introducing an error of 0.7% in the Si molar fraction measurement. Due to this behavior it is straightforward to derive the Si composition from experimental intensity measurements and draw the composition profile shown in fig 2. The error bar accounts for the different atomic configuration considered, the uncertainty on the TEM sample thickness and experimental noise. These data are in excellent quantitative agreement with the experimental composition obtained by XSTM experiments on the same specimens [6]. This quantitative approach can be applied in principle to all the materials systems and it is a new powerful tool to study the chemistry of the materials at the atomic resolution.

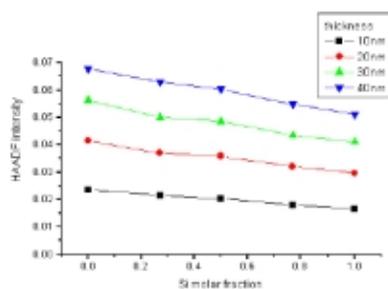


Fig. 1: Simulated HAADF Intensity vs Si molar fraction for different TEM sample thickness. The intensity is expressed as the ratio between the incident beam intensity and the measured HAADF image intensity.

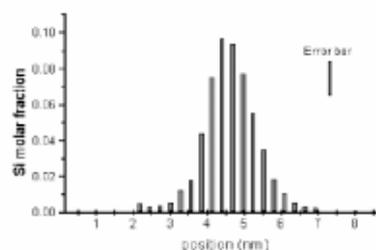


Fig 2: Compositional profile of the thin Si layer buried in GaAs matrix according to HAADF analysis.

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## POSTER A28

### Combination of top-down (microcontact print) and bottom-up (electrodeposition at nanometer scale) fabrication for the growth of confined CdS.

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The attainment of ultrathin films of well ordered II-VI and III-V compound semiconductors has been an active research area of the Electrochemical group in Florence. The method employed was the Electrochemical Atomic Layer Epitaxy (ECALE) which is based on self limiting reactions such as underpotential deposition. Recently, the possibility of combining the electrodeposition at nanometer scale and the self assembling phenomena has been investigated. In particular, the ECALE method was used to deposit CdS on Ag(111) covered by a patterned hexadecanethiol, C<sub>16</sub>SH, SAM. In fact, the deposition of CdS takes only place on the uncovered silver substrate whereas it is prevented on the thiols monolayers, yielding CdS patterned according to the used stamp.

The patterned Ag(111) was obtained by using the microcontact printing technique of a PDMS stamp previously immersed in C<sub>16</sub>SH. Figure 1 shows the AFM image of the stamp used in this work. The thiol strips are approximately 300 nm large, with a 850 nm pitch. The final product consisted of 530 nm CdS strips alternated to 320 nm C<sub>16</sub>SH strips (Fig.2). Electrochemical measurements performed on the deposition of CdS on these modified Ag(111) surfaces showed that the deposition process is similar to that performed on the bare Ag(111), with the obvious decrease in the amount of material obtained due to the reduced electrode surface. In particular the right 1:1 stoichiometric ratio between Cd and S and linear increase of the deposit with the number of deposition cycles still indicate the layer-by-layer growth mechanism that is the aim of ECALE method.

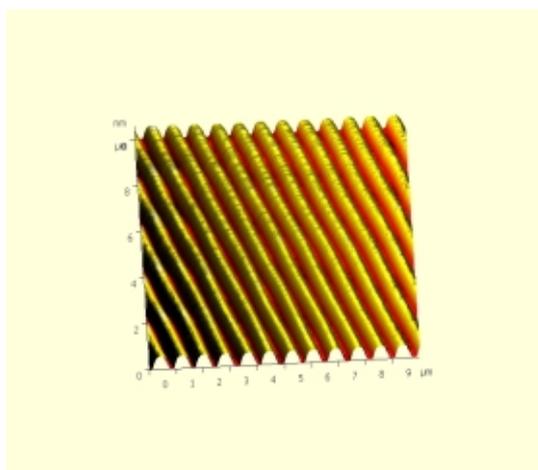


Fig. 1

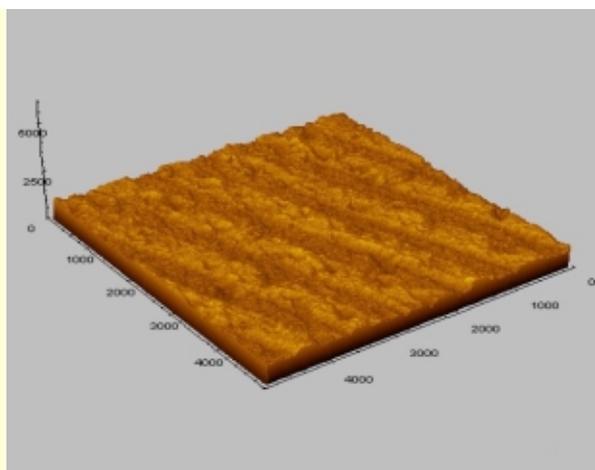


Fig. 2

## POSTER A29

### Long-wavelength emitters based on InAs(N)/Ga(In)As(N) quantum dots

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The goal to reach the telecommunication wavelength of 1.31 and 1.55  $\mu\text{m}$  on GaAs substrates is being investigated by several laboratories via the growth of In(Ga)As/GaAs quantum dots (QDs) or InGaAsN/GaAs quantum wells (QWs). Both systems have demonstrated to be able to produce device quality materials for laser emission at 1.31  $\mu\text{m}$ , while the insurgence of structural defects for large QDs or high nitrogen content is responsible for the low emission efficiency shown at longer wavelengths. A possible way to reach longer wavelengths is the combination of those two methods, that is the fabrication of In(Ga)AsN QDs [1].

We present here our results about the optical properties of InAs(N)/GaAs(N) quantum dots. We have followed two main roads toward the achievement of long wavelength emitters: the introduction of nitrogen in the dots and the use of InAs dot in combination with N-containing GaAsN barriers. High quality QDs with photoluminescence at room temperature exceeding 1.4  $\mu\text{m}$  have been obtained. The results is the combination of the choice of proper growth conditions and band-gap engineering. The structures are grown by molecular beam epitaxy by the combination of low growth-rate, the use of a dispersive nitrogen plasma source used at low power (60-80 W), and a proper design of the samples which makes use of stepped barriers to improve carrier trapping efficiency and to reduce the emission energy.

First we will compare the luminescence from InAsN/GaAs and InAsN/GaAsN quantum dots with that obtained from InGaAsN/GaAs quantum wells grown in the same experimental system. All structures were engineered to emit near 1.3  $\mu\text{m}$  at room temperature. Quantum-dot emitters were found to exhibit higher thermal stability and did not require post-growth annealing. The use of GaAsN barriers as opposed to GaAs barriers provided for narrower and more intense quantum-dot luminescence. The amount of N in the QDs is about 1%. The simple increase of N content into the QD cannot be however the method to reach the goal of emission at 1.55  $\mu\text{m}$  because the optical quality of the dots rapidly degrades. In order to avoid quality degradation through direct incorporation of N in the QDs, further improvement has been achieved by combining the optimized growth of InAs dots and the use of GaAsN and/or InGaAsN barriers. First, InAs quantum dots have been grown at high temperature (540  $^{\circ}\text{C}$ ) on a GaAs buffer layer, and then, after having reduced the growth temperature to 500  $^{\circ}\text{C}$ , a GaAsN or InGaAsN barrier has been grown on top of the InAs layer. In order to hinder the direct impinging of energetic ions on the layer surface and to reduce the ensuing generation of damage-induced defects, we have kept the shutter of the N-plasma-source closed to grow some of the structures. The low growth-rate is then used to increase the nitrogen incorporation into the layers. Efficient room temperature emission above 1.41  $\mu\text{m}$  (0.88 eV) has been obtained and further red shift of the emission wavelength can be envisaged by a further tune of the growth conditions and with the use of stepped barriers.

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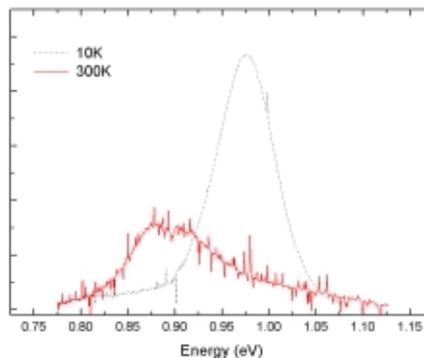


Fig. 1 Photoluminescence of InAs/GaAs<sub>0.979</sub>N<sub>0.021</sub> quantum dots. The InAs nominal coverage is 2.7 monolayers. The RT spectrum is distorted at its peak by light absorption from the environment humidity.

## POSTER A30

### Fabrication and transport of large-scale molecular tunnel-junction arrays

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Until now, miniaturization in electronics has been achieved by top-down approaches thanks to the improvement of lithography techniques. However, the current trend is not further sustainable using this strategy due to fundamental limits. Gaining the nanometer scale requires a turning point and conceptually new devices [1]. Molecular electronics [1] is emerging as an alternative to Silicon based nanoelectronics for building integrated devices. Its major challenge is to interconnect molecules by fabricating nanometer spaced electrodes. Due to the physical limitations of optical lithography, new techniques have been developed for patterning below 100 nm but none of them equals the advantages of photolithography for low cost and high throughput. Moreover, most of the proposed methods are appropriate for contacting only single devices.

Recently, Krahné R et al. [2] succeeded in the fabrication of a network of nanojunctions using only optical lithography and wet etching of an AlGaAs/GaAs quantum-well (QW) structure. In such method, the thickness of the quantum well and of the deposited metal layer control the gap size on a sub-nanometer level. However, this very innovative approach to nanoscale electronics has some intrinsic drawbacks, since the fabricated nanojunctions can be employed to implement devices only at cryogenic temperature (4K) and in the dark because of the bulk currents through the semiconductor substrate. In this work, we improve this method by means of a selective oxidation of the two AlGaAs barriers above and below the QW in order to reduce the leakage current through the semiconductor layer and fabricate room-temperature nano-scaled devices.

The AlGaAs/GaAs quantum-well structure was grown on a GaAs substrate in a horizontal low pressure MOCVD system with the following layer sequence: 200-nm-thick GaAs buffer layer, 300-nm-thick  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  lower barrier-layer, GaAs quantum well, 100-nm-thick  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  upper barrier-layer, a 10-nm-thick GaAs cap layer. All layers were undoped and grown at 750 °C. The thickness of the embedded GaAs layer was 15 or 20 nm, while the Al concentration in the two AlGaAs barriers was varied between 35% and 90% in various samples. The selective oxidation of the Al-rich layers was carried out in an oven by means of a nitrogen flow, which was allowed to bubble into deionized water and flow in the chamber as the oven reached the established temperature. The temperature was varied from 100°C to 450°C, while the oxidation time from 5 to 240 min. Using such approach, the bulk open-circuit current at room temperature was reduced to values as low as few pA (from tens of  $\mu\text{A}$  in the case of the non oxidized structure). Since only photolithography is used to define the electrode pattern, this approach enables the simultaneous, cheap fabrication of large arrays of nanospaced electrodes (all processes described are wafer scale). This opens the way to the fabrication of complex circuits consisting of nanodevices with different functionalities.

In such nanogaps, molecules can be positioned between electrodes by electrostatic trapping or by specific immobilization procedures, enabling the fabrication of complex circuits consisting of different integrated nanodevices. In particular, we investigated transport in molecular tunnel-junctions based on the blue copper protein Azurin under ambient conditions with typical molecular features (such as NDR) observed in the I-V characteristics. Notably, our results are in good agreement (for both current values and peak positions) with the signatures of resonant tunneling (and NDR) recently reported in the current-voltage characteristics of Cu-Azurin metalloprotein CP-AFM junctions at low applied forces by the Davis group at the Oxford University [3]. This approach opens the way to the fabrication of complex circuits consisting of nanodevices with different functionalities.

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## POSTER A31

### The fluctuations of ionization leakages of charged particles in a nano - micrometer thickness detectors

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The affectivity and sensitivity of detectors against the flow of charged particles and against the ionizing radiation in general are one of the important characteristics of detectors in measuring the density of the flow of charged particles. It depends on the material of detector, how the detector will interact with the charged particle, how much is the thickness of the detector expressed in  $\text{g}/\text{cm}^2$ . The differences in thickness of the detector has it's own impact in the affectivity of the detector. In case of thick detectors, not precise measurements conditioned by the thickness fluctuations are not important and can be thrown away. The situation is different in case of "thin" detectors.

The main aim of this research is to find out the possible usages of MOSFET IMPATT semiconductor devices made by planar technology, as a detectors for charged particles.

For doing that the calculation is made, by using the formula of Bete - Bloch, to find out the ionization leakages of the charged particles in the MOSFET IMPATT devices and to determine the expected measure of registered signal.

$$-\left(\frac{dE}{dx}\right)_{T_0} = \frac{2\pi z^2 e^4 n}{mv^2} \left[ \ln \frac{2mv^2 T_0}{I^2 (1 - \beta^2)} - \beta^2 - \delta \right]$$

Also the detailed study is done to find out the impact of fluctuations of ionization leakages and materials in "thin" detectors ( $200\text{nm} < d < 100\text{mkm}$ ) by using the following formula.

$$\frac{\partial f(x, \Delta)}{\partial x} = \int_0^R W(\varepsilon) f(x, \Delta - \varepsilon) d\varepsilon - f(x, \Delta) \int_0^{\varepsilon_{\max}} W(\varepsilon) d\varepsilon$$

There is a parameter in the formula that is added by us and is conditioned by the smoothness of the thickness of the detector.

## POSTER A32

### Nanofriction and Wear of Dry Solid Surfaces Near the Melting Point

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In many practical nanofriction problems that involve hard contact and wear the local temperature may easily reach the melting temperature, but there is to date no adequate theoretical or physical description of the phenomena to be expected in this regime. We have addressed this general problem and attempted a first assessment of the main concepts by simulating the nanofriction of a tip on a NaCl(100) surface near the bulk melting point. This particular surface is a benchmark case whose nanofriction and wear is well investigated at room temperature [1], and more importantly it was chosen because it is predicted not to undergo surface melting at the bulk melting point[2].

This nonmelting avoids the jump to contact and tip wetting that will otherwise spoil dry friction.

We conducted molecular dynamics simulations of a hard sharp tip sliding at various velocities and penetrations on NaCl(100) close to the and beyond the bulk melting temperature,  $T_m \sim 1070$  K. Preliminary results reveal the existence, beside hard surface furrowing at  $T > T_m$ , of a new intermediate regime near  $T_m$ . In this regime the surface is still definitely crystalline and not liquid. Nevertheless it is plastically deformable around the ploughing tip, the resulting furrow and debris healing spontaneously on a microscopic time scale. There is a sharp drop of wear frictional force with temperature that can be partly explained in terms of the dropping free energy cost of the furrow and debris surfaces, and partly in terms of fast healing of the furrow... This results in an effective self-lubrication against wear near the bulk melting point.

These results should remain conceptually applicable to nonmelting metal surfaces.

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