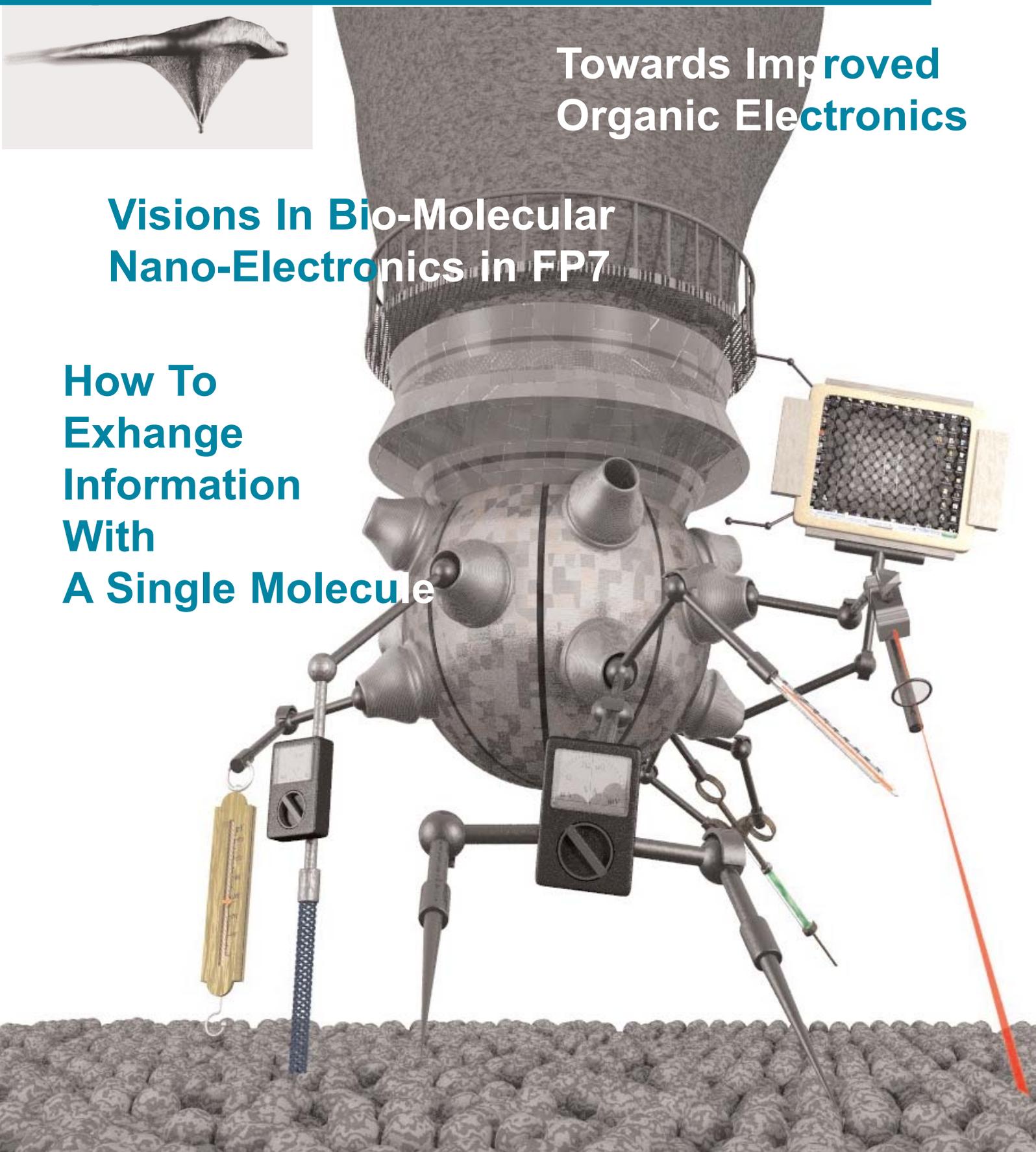




## Towards Improved Organic Electronics

### Visions In Bio-Molecular Nano-Electronics in FP7

### How To Exchange Information With A Single Molecule





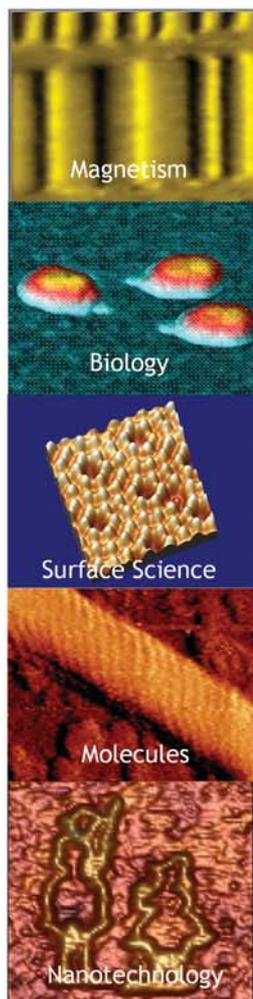
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Nanoelectronics is potentially one of the branches of Nanotechnology with the most significant commercial impact and covers a very wide range of interdisciplinary areas of research and development such as telecommunications, automotive, multimedia, consumer goods and medical systems.

The emergence of new research directions such as Hybrid molecular electronics, One-dimensional structures such as nanowires, Nano-electro-mechanical-systems (NEMS) or Carbon Nanotubes (CNT) will strategically impact on future developments in the nanoelectronics domain and their long-term applications. These opportunities for alternative nanodevices (molecular-based technologies, nanomechanics, etc.), required by miniaturisation, still required a number of technological challenges to be tackled such as interconnections.

Research articles providing insights on these issues i.e. Composite Materials based on Carbon Nanotubes and Intrinsically Conducting Polymers for Organic Electronics, Bio-Molecular Electronics and Interconnection problems ("How to exchange information with a single molecule") are proposed in this E-NANO Newsletter n°03.

We would like to thank all the authors who contributed to this issue as well as the European Union (IST/FET/NANO) for its close collaboration.

Dr. Antonio Correia (Editor)  
PHANTOMS Foundation

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**Editorial Information** 4


---

**Research**  
**Towards Improved Organic Electronics** 5


---

Intrinsically conducting polymer-carbon nanotube composites.  
*Wolfgang K. Maser, Raquel Sainz, M. Teresa Martinez, Ana M. Benito*

**Research**  
**Visions In Bio-Molecular Nano-Electronics in FP7** 10


---

*Rosa Di Felice, Danny Porath*

**Highlight**  
**IST Future and Emerging Technologies Programme** 14


---



---

**NANO News** 16


---

**NANO Conferences** 18


---

**NANO Vacancies** 19


---

**Pico-Inside Integrated Project**  
**How To Exchange Information With A Single Molecule** 21


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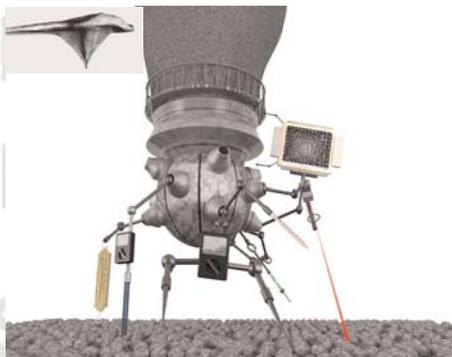
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Vision of a SPM tip used to visualise, characterise and manipulate nanoscopic environments (Courtesy: Enrique Sahagun, MOLE Group, Universidad Autonoma de Madrid, Spain)

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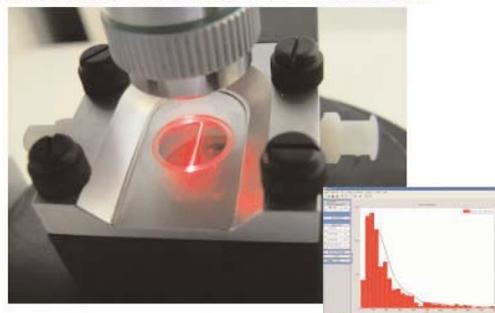
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## Intrinsically conducting polymer-carbon nanotube composites: Towards improved organic electronics

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Instituto de Carboquímica (CSIC), Zaragoza (Spain)

**Abstract.** Carbon nanotubes combined with intrinsically conducting polymers are considered to contribute to further progress in nanoelectronics and to the development of improved electronic and optoelectronic devices. This article resumes our work on highly functional and processible polyaniline-carbon nanotube composite materials and shows the close relation between functionality and processing behaviour on one side and nanotube-polymer interactions on the other side.

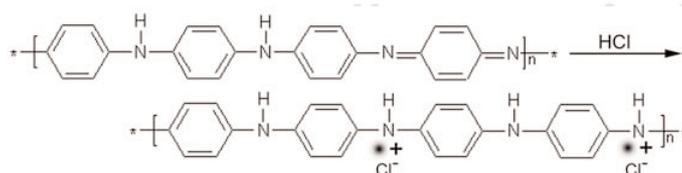
**Keywords:** Carbon Nanotubes, conjugated polymers, nanocomposite materials, interface interaction, self-alignment, characterization, processing.

### Introduction

The electronics industry of the future must satisfy the demands of an increasingly complex society for pervasive computing: access to instant information, data handling, and communication. For the past forty years inorganic silicon and gallium arsenide semiconductors, silicon dioxide insulators and metals have been the backbone of the semiconductor industry. On the other side, "organic electronics", a growing field of research, is a complementary approach to improve the semiconducting, conducting, and light-emitting properties of organic materials through novel synthesis and self-assembly concepts. Performance improvements, coupled with the ability to process these "electroactive" materials via more traditional solution casting/printing/stamping techniques over large areas on materials such as plastic or paper, could be used to create products such as low-cost information displays on flexible pastic for e-newspapers, and low cost memory and logic for smart cards. These types of novel products certainly will contribute to meet the society's demands. Today, two classes of families, both Nobel-prize decorated, are of paramount interest to "organic electronics": Intrinsically conducting polymers [1] and carbon nanotubes [2].

An intrinsically conducting polymer (ICP), also called electroactive polymer or "synthetic metal", is an organic polymer that possesses the electrical, electronic, magnetic, and optical properties of a metal while retaining the mechanical properties (flexibility and toughness), processibility, etc. commonly associated with a conventional polymer. Its properties are intrinsic to a "doped" form of the polymer. In the "doped" state, the backbone of a conducting polymer consists of a truly conjugated and delocalized  $\pi$  electron system providing its semiconducting, conducting and other electroactive properties. "Doping" may be

carried out chemically or electrochemically and always involves "dopant" counterions which stabilize the "doped" state.



**Figure 1:** Non-redox doping process in polyaniline resulting in the transformation from its insulating into the conducting state.

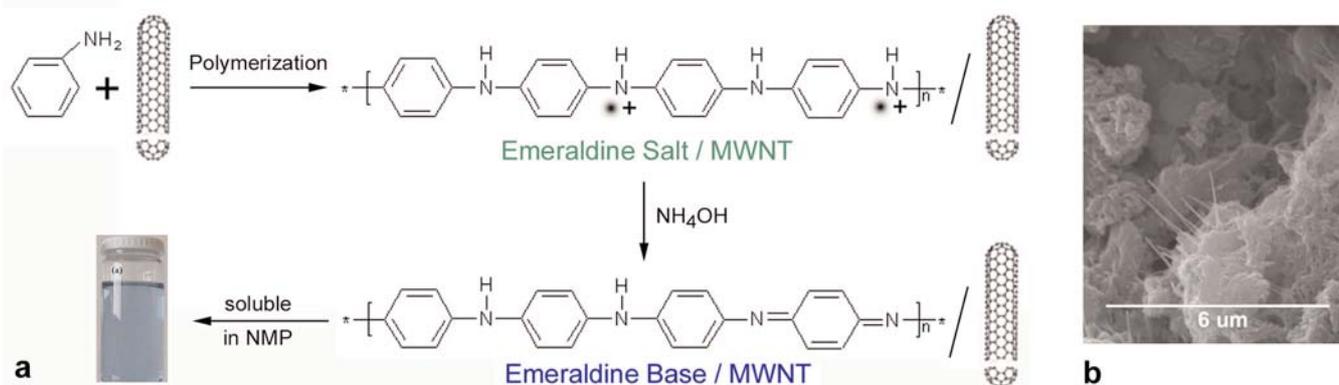
The concept of "doping" is illustrated in Figure 1 which shows an example for a non-redox "doping" process in polyaniline using protonic acids. During this "doping" process the number of electrons associated with the polymer backbone does not change. However, the energy levels are rearranged and a stable polysemiquinone radical cation (a polaron) is produced leading the polymer into the highly conducting regime. The highly conducting form of polyaniline, which corresponds to a salt, can be reversibly "undoped" into its non-conducting base form. Moreover, the whole process is accompanied by very beautiful and reversible changes in color. Some other typical representatives of intrinsically conducting polymers are polypyrrole, polythiophene, poly-3,4-ethylenedioxythiophene (PEDOT) and poly-(para-phenylene). Only a bit more than 10 years after the discovery of intrinsically conducting polymers [3] the development of the first organic light emitting devices (OLEDs) [4] has become a tremendous boost for the further development of various types of electronic and optoelectronic devices made out of electroactive polymers [5]. The key to further progress relies on improvements in the charge carrier mobility and the processibility. This is closely related to conformational changes, chain interactions, self-assembly and ordering of the backbone of the electroactive polymers in question. Here, novel nanoscale concepts will play an essential role and thus, the field of intrinsically conducting polymers and organic electronics goes hand in hand with nanoscience and nanoelectronics.

The other highly attractive building block for a future nanoelectronics are carbon nanotubes (CNTs) [6]. These are nanoscale objects consisting of one or several graphene sheets, seamlessly closed to form cylindrical structures in the form of single-wall or multi-wall carbon nanotubes (SWNTs, or MWNTs, respectively). With their unique structural, mechanical, thermal, electronic and optical properties [2,] they offer a broad range of applications in various fields of science and technology [7] such as nanoelectronics (from conducting wires to semiconducting logic switches), field emitting devices (flat panel displays, movable X-ray scanners) and NEMS (nanoactuators as well as chemical and biochemical sensors). Furthermore, carbon nanotubes blended into common plastic materials yield highly reinforced, supertough and/or conducting composites, i.e. new classes of advanced materials. On the other side, carbon nanotubes can be considered as a natural partner for intrinsically conducting polymers. Their dimensions and electronic structure combine well with the chain structure and the delocalized electron system of

these electroactive polymers. Their mutual interactions thus let expect highly favorable synergetic effects between both constituents which might contribute to further improvement of organic electronic devices.

Bearing these considerations in mind, we carried out intensive research on novel composite materials based on carbon nanotubes and intrinsically conducting polymers. Hereby we were focusing on two key issues: Enhanced functionality and processibility of the obtained materials. Both points are directly linked to favorable interactions between carbon nanotubes and the polymer chains and thus intimately related to the synthesis approach and self-assembling processes. In the following we will describe our research approach – a journey from chemistry via fundamental understanding of interactions towards practical consequences for processing - and resume our main findings.

was added to initiate the polymerization process rapidly resulting in a dark green suspension. After several washing filtering cycles we obtained powder of PANI in its primary doped form, i.e. emeraldine salt (ES). In a next step, we transformed ES into its soluble emeraldine base (EB) form [9]. Therefore, we dedoped both ES and ES-MWNT composite with ammonium hydroxide (NH<sub>4</sub>OH). After several washing and filtering cycles EB and EB-MWNT composite were obtained as powder materials. Assuming that no MWNTs got lost in washing and filtering cycles and taking into account the process yields, we estimated the content of MWNTs in the final EB-MWNT composite at about 50 wt%. SEM microscopy shows that the MWNTs are nicely embedded in the polymer matrix (Figure 2b).



**Figure 2:** (a) Synthesis of PANI-MWNT composite. In-situ polymerization yields in the green emeraldine salt-MWNT composite which subsequently is transformed into the blue and soluble emeraldine base-MWNT composite. (b) SEM image of the emeraldine base-MWNT solid powder.

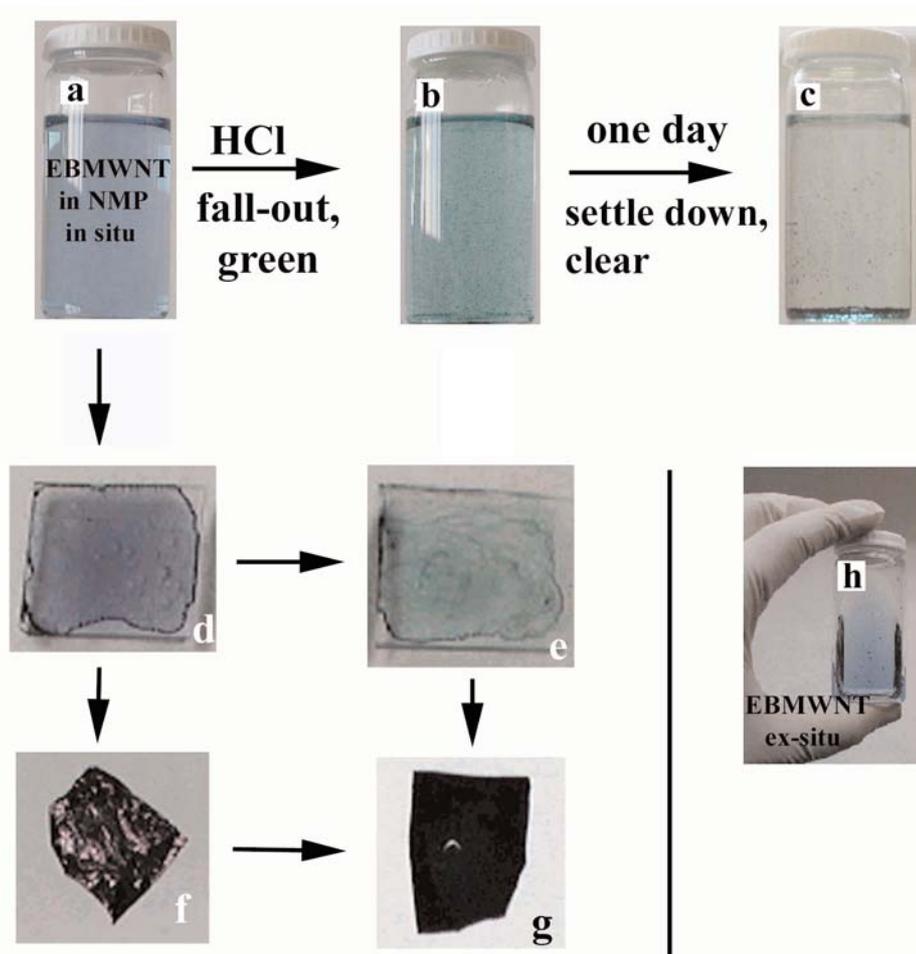
### 1. PANI-CNT composite: Synthesis and processing

As intrinsically conducting polymer we have chosen polyaniline (PANI) for several reasons: The monomer is inexpensive, the polymerization reaction is straightforward, and it can be processed from solutions into films. Its electric and optical properties can be reversibly controlled over a wide range by both charge-transfer doping and protonation. With a high environmental stability PANI possesses many advantages to meet the requirements for optoelectronic devices. Furthermore, its non-planar chain architecture (the three PANI amine-benzenoid units acquire certain ring-torsion angles with respect to its flat imine-quinoid units) should, in principle, reduce opportunities for strong interactions with CNTs and thus deserves some more scrutiny. As carbon nanotubes were chosen straight and well-graphitized multi-wall carbon nanotubes of micrometer length and diameters of 20-40 nm produced in our own electric arc-discharge system.

For the synthesis of PANI-MWNT composites we applied for the first time an in-situ approach, i.e. we carried out the polymerization of aniline in the presence of MWNTs (Figure 2a) [8,9]. An aniline monomer solution in HCl 1M was added to MWNTs suspended in HCl 1M and the oxidant (NH<sub>4</sub>)<sub>2</sub> S<sub>2</sub>O<sub>8</sub> (ammonium peroxodisulphate, APS)

To our surprise, like pure EB itself, EB-MWNT containing about 50 wt% of MWNTs (which do not dissolve in any solvent) was completely soluble in n-methylpyrrolidinone (NMP) and results in a blue and stable solution. Intents to transform the EB-MWNT solution into an ES-MWNT solution by adding a few drops of HCl immediately led to the fall-out of small agglomerates. After one day, the solution was completely colourless while all agglomerates settled down at the bottom of the flask. Curiously, when applying an ex-situ synthesis in which MWNTs were added directly to ES and then transformed to EB, the resulting EB-MWNT material does not dissolve as well as the in-situ material. Agglomerates form and fall out with time (Figure 3).

Blue colored films we obtained by casting NMP solutions of EB-MWNT and EB onto glass substrates followed by vacuum drying at 70°C for 24 h. Subsequent immersion of these films in distilled water resulted in free-standing blue films of EB and EB-MWNT which easily could be transformed into corresponding green films of ES and ES-MWNT when exposed to HCl vapour for a few seconds (Figure 3). All in all, it became clear to us that the starting point for any further processing only can be in-situ polymerized EB-MWNT.



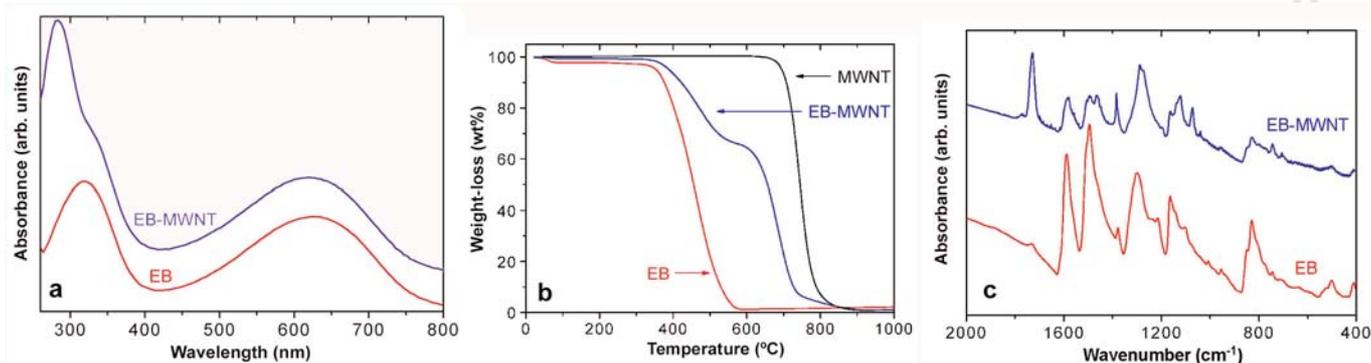
**Figure 3:** Processibility of EB-MWNT. (a) solution in NMP. Addition of HCl results in (b) fall out and (c) settle down of solid material. The solution becomes clear. (d) casted film from EBMWNT blue solution onto glass. (e) exposure to HCl vapor results in green film. (f) free-standing film from (d). (g) free standing film from (e). (h) Ex-situ polymerization results in agglomerates and non-stable solutions.

## 2. Composition and structure

Directly after synthesis we took a UV-Vis spectra of EB and EB-MWNT solutions in NMP (Figure 4a). Maxima at 320 nm and 624 nm correspond to the  $\pi$ - $\pi^*$  transition centred on the benzenoid unit of EB and to the quinoid excitation band, respectively. However, it was striking that the EB-MWNT solution shows a new and very strong band with its maxima at 283 nm. We could relate this band to the  $\pi$ - $\pi^*$  transition centred on the quinoid unit. Apparently the presence of MWNTs leads to an enhanced response

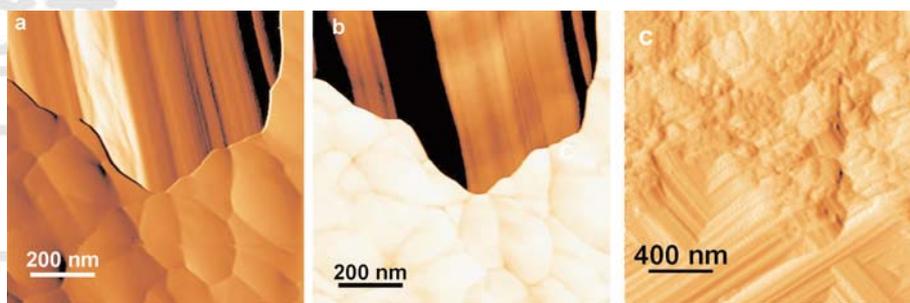
of quinoid related rings. On the other side, the rest of the features are identical to pure EB. This lead us to the assumption that we have to deal with a two phase system: free EB and a new phase of EB having a more planar conformation which is related to MWNTs. Thermogravimetric analysis (TGA) (Figure 4b) clearly confirmed the existence of an additional MWNT related EB phase which starts to decompose at about 150 °C higher temperature than the backbone of pure EB. Also infra-red spectroscopy (figure 4c) witnessed significant changes in the EB-MWNT composite and most of them were directly related to a relative increase of the vibration strength of C-C bonds of the quionoid versus benzenoid groups (range between 1585-1380  $\text{cm}^{-1}$ ) as well as changes related to ring-deformations for quionoid and benzenoid groups (range 1105-950  $\text{cm}^{-1}$ ).

Deeper inside in the composition and structure we obtained by atomic force microscopy (AFM) surface studies (topography, phase, and adhesion) on solution-cast films of EB and our new EB-MWNT composite (Figure 5). The composite shows two features: a granular structure, which is typical for pure EB, and well-aligned structures. The sizes of the individual aligned objects are usually between 20-40 nm. The phase response clearly reveals that the aligned structures are related to MWNTs. However, the adhesion response (not shown here) does not reveal any difference between the aligned and grain-structured objects. This let us to the assumption that the surface the the aligned MWNT bundles must be covered by the same material as the surrounding grains, i.e. EB. Therefore, AFM further corroborated the co-existence of "free" EB and aligned bundles of EB-coated MWNTs. This finding further is supported by TEM images of the EB-MWNT composite showing a good



**Figure 4:** (a) UV-Vis spectra; (b) TGA, (c) FTIR spectra. From Ref. [9]

polymer wetting of the MWNTs. Furthermore, we observed that the EB-covered MWNTs form a three-dimensional network throughout the EB matrix.

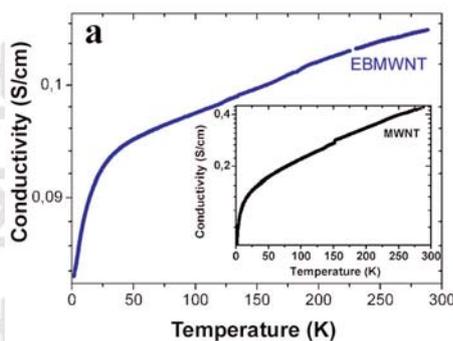


**Figure 5:** AFM images of EB-MWNT films. (a) Topography image showing granular EB and aligned MWNT structures. (b) Phase response on the same area. (c) Topography image showing the network formed by EB covered MWNTs. From Ref [9].

### 3. Functionality

Knowing about the fundamental differences between EB and the new EB-MWNT composite we wanted to test for the functionality of this material and performed temperature-dependent conductivity measurements (Figure 6a) on the bulk powder materials. The room temperature value for EB falls below the experimental limit (below  $10^{-10}$  S/cm) and therefore no temperature dependence could be measured. However, with about 0.1 S/cm, the room temperature conductivity for the EB-MWNT powder has drastically increased at least by nine orders of magnitude compared to EB. Its temperature dependence resembles the one for MWNTs indicating that the conduction occurs through a percolated three-dimensional network of MWNTs. However, the room temperature value of the EB-MWNT composite does not reach the value of a pure MWNT network, which is expected to be one or two orders higher in magnitude. This points to the existence of additional tunnelling barriers between the MWNTs formed by the EB coating layer around the MWNTs. As a further functionality we could see the enhanced thermal stability of the composite which decomposes in air at 150 °C higher temperatures than the backbone of pure EB. Finally, we investigated the photophysical properties of the composite and measured its photoluminescence behaviour

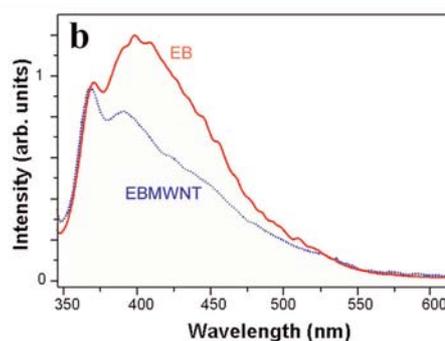
( $\lambda_{exc}=330$  nm) [10] (Figure 6b). Firstly, EB itself shows a broad emission maximum at about 400 nm caused by reduced benzenoid/amine groups. It usually gets suppressed drastically when EB is transformed by chemical doping into a highly conducting state. Secondly, EB-MWNT also luminesces and essentially maintains the features of EB. Here the reduction of the long-wave emission band is in agreement with a more planar conformation of EB on MWNTs. Finally, it is highly remarkable that the presence of 50 wt% of MWNTs in the EB-MWNT composite, which make it highly conductive, does not result in a quenching of luminescence. Thus we



**Figure 6:** (a) Temperature dependent electrical conductivity. (b) Photoluminescence. From Ref. [10].

### 4. PANI-CNT interactions

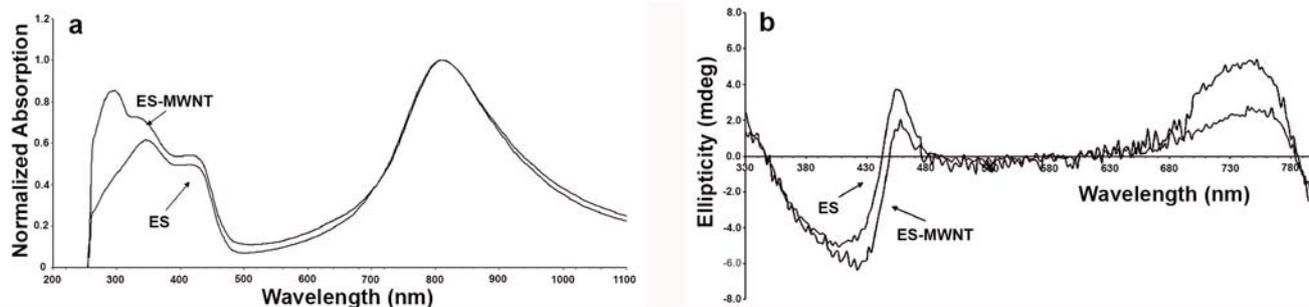
Taking all results together, we now obtain the following picture. Polymerization of alinine in the presence of MWNTs (in-situ polymerization) leads to the growth of an EB-MWNT composite completely soluble in NMP. This is composed of a pure EB matrix and of EB-coated MWNTs. Here, the MWNT-coating EB layers have adopted a more planar conformation of EB, thus optimizing the interaction between EB and the MWNTs. The new planar form further might be stabilized self-organization processes which sandwich EB between adjacent MWNTs resulting the the alignment of EB-covered MWNTs. The strong  $\pi$ - $\pi$  interaction between EB and MWNTs is responsible for the solubility of the whole composite material and allows its further processing into coloured films to which the rich doping chemistry of polyaniline fully can be applied. The EB-coated MWNTs also are responsible for the drastic increase in the electrical conductivity, which is even higher than that of the insoluble conducting form of PANI in its emeraldine salt form (ES), as well as for the enhanced thermal stability of the EB-MWNT composite. On the other side, luminescence is still provided by the “free” EB phase and not



disturbed by the conducting EB-MWNT network. All in all, the key towards highly functional nanocomposite directly is related to strategies of achieving favorable interactions between the intrinsically conducting polymer and carbon nanotubes.

### 5. Advanced solution processing: Optical activity

We recently investigated if it would be possible to further influence the polymer chain conformation and add another property of great scientific and technological interest, namely optical activity. It is well known that the addition of chiral acids transform EB into the corresponding emeraldine salt (ES) whose backbone then adopts a chiral structure which is responsible for its optical activity. Therefore,



**Figure 7:** HCSA doped ES and ES-MWNT in NMP. (a) UV-Vis spectra. (b) Circular dichroism spectra. From Ref. [11].

starting point in our case was the blue and stable EB-MWNT solution. To this solution we added the chiral S-(+)-10-camphorsulfonic acid (HCSA). In contrast to the addition of HCl which results in the precipitation of the MWNTs, using HCSA resulted in green and stable solution of the corresponding emeraldine salt (ES-MWNT). Figure 7a shows the UV-Vis spectra of the resulting ES-MWNT composite and ES for comparison. The three characteristic bands at 345, 415, and 810 nm are associated with  $\pi$ - $\pi^*$ , polaron- $\pi^*$  and  $\pi$ -polaron band transitions of ES. The broad  $\pi$ -polaron band at 810 nm is typically for the arrangement of the polymer chains in the "compact coil" form [11]. ES-MWNT essentially shows the same features, and additionally a dominant band at 295. As in the case of EB-MWNT this band corresponds to the p-p\* transition centred on the quinoid unit and is related to the coating of EB onto MWNTs. Furthermore, both solutions have become optically active (figure 7b). These observations are consistent with the polymer adopting a "compact coil" formation. The circular dichroism spectrum for ES-MWNT showed that the polymerization of aniline in the presence of nanotubes and doping does not inhibit the polymer's ability to become optically active. The effects of introducing optical chirality into PANI-CNT composites and its technological implications currently is investigated in more detail in our group in a joint research programme with the group of Dr. Marc in het Panhuis at the University of Hull (UK).

## 6. Conclusions

In this article we have described the formation of a highly functional and completely soluble polyaniline-multi-wall carbon nanotube composite. It possess enhanced conductivity, improved thermal stability, is luminescent and optically active. While the first two properties as well as the solubility and processibility are genuinely related to a new PANI-MWNT phase in which EB has adopted a more planar conformation strongly linked to the MWNTs via  $\pi$ - $\pi$  interactions, the two latter properties are more related to the co-existing "free" PANI phase which apparently is not influenced by the new PANI-MWNT phase. In our future work we further will focus on the understanding of the interactions between intrinsically conducting polymers and carbon nanotubes and their controlled manipulation, as well as on advanced processing of the resulting composites and their use in electronic and electro-optical devices.

This work has been supported in by the Spanish MEC project NANOSIN (MAT 2002-04540-C05-04) as well as by the Diputación General de Aragón under its programme Grupo Consolidado (Grupo de Nanoestructuras Carbonosas y Nanotecnología. CNN).

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## Visions in Bio-Molecular Nano-Electronics in FP7

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*This document includes future visions from scientists active in the field of (bio)molecular electronics. It attempts to provide answers to questions such as the following: Why should we have advanced research in molecular-based nanoelectronics? What research can be envisaged in the future? What are the key issues, goals and obstacles that we are facing? The document is intended to contribute to the definition of research programmes, in particular in the Framework Programme 7 of the European Union*

### Abstract

*The primary goal of molecular nanoelectronics is the storage, transfer and processing of information at the nanometre-scale. This can be materialized in the form of molecular wires, devices, sensors and ideally a molecular computer. While this goal is standing up-front, other scenarios are open and waiting to be discovered along the way. Bio-molecules offer yet more possibilities based on the structure-function relation and on self-assembly.*

### 1. Objectives and approaches of research.

One of the most recurring questions in deciding future plans is: "Are the envisaged molecular devices expected to operate as the devices we know today, or should they bring completely new functions, principles of operation and new technology?"

It is clear that the whole field of nanoelectronics arose from the aim to scale down devices, increasing their surface density, and computing performance while decreasing costs and circuit power consumption. This intrinsically contemplates shrinking mind the standard device functions. However, when the "bottom-up" approach came into play making use of molecular building blocks, it became clear that, while we want to elicit currents from molecules, these molecules may want to give us something else. The problem is that we do not yet have that kind of understanding of the "molecular materials science" that would allow us to design novel functionalities and novel architectures in an optimized way. Therefore, all the doors should be left open.

In other words, the most reasonable approach seems to maintain the current *two-fold strategy*: on one hand, to explore molecule-based new materials having in mind the conventional types of functions that we already know (wires, diodes, transistors, sensors, actuators, etc.); on the other hand, to capture revolutionary potentialities that the new building blocks offer. For instance, along the latter line, one possibility that is already pursued is to exploit the intrinsic computational capabilities of some molecules, without the need for intermediate devices as pieces to build a computer. Other viable strategies may be suggested by upcoming results.

Two explicit suggestions emerge from these considerations: (i) flexibility in the topics for future research programmes, because the field may (continuously or discontinuously) develop along the way; (ii) from the point of view of selection criteria, not to use existing device paradigms too narrowly to judge the quality of proposals, because scientists may be able to reach far beyond conventional functionalities, being open to learn in an evolutionary/revolutionary way as things develop. After all, openness can be the source of the real scientific revolution that we are all looking for.

### 2. Contents of research.

#### 2.1. Molecule-based information storage, transfer, and processing

As stated above, the minimal objective of research in (bio)molecular electronics is to continue realizing the same functions that we know how to do (in other words, think of the same device operations), but in a better (smaller, denser) and faster way. So molecules would carry us (by themselves – through self-assembly and natural functionality?) along the way towards "better" and "faster".

However, even within this conventional attitude, we are faced with the fact that molecules are intrinsically NANO-sized. This fact has two main consequences: (i) molecules represent one way to access the real NANO scale, without constraints at the NANO-MICRO scale; (ii) every molecule is a very complex entity by itself and we must acquire the capabilities to study, understand, control and integrate it.

(i) *Embedded molecular devices.* The popular way of measuring the electrical response of molecules is to position them between electrodes, apply voltage and try to measure current. When this is done, the NANO scale of the whole circuit is already compromised, because usually the electrodes or interconnects are much bigger than the molecule and the resulting complete device is huge. In addition, in the current technology, even if it is still possible to down scale the dimensions of a single device, the distance between computational elements remains large and there is no way to get to the real NANO scale for a computational frame in this way. The key-word towards a

breakthrough in scaling is *embedding*. A device must be embedded, for example in the wire itself. Metal gating remains anyway an open issue even for embedded devices. Embedded operation can be achieved by complexation with other objects (ions, functional organic molecules, proteins, inorganic nanoparticles).

(ii) *Control*. We do not really know how a single specific molecule looks like at the atomic scale. We need to develop tools to access this information. As a comparison, huge progress has been achieved after the development of scanning probe instruments in terms of “visualizing” surfaces in real space, and “visualizing” (or probing) atoms and molecules. Developing the tools for the above goal will open the way to much better characterization and control of single molecules have sizes of 0.5 to 10 nm. In all the current measurements on junctions, we do not really know the structure and configuration of a single molecule and we are mostly guessing. For instance, what is B-DNA? One can elicit an exact structure only when performing X-ray measurements and averaging over a large number of molecules. It represents an average structure, but not the realistic appearance of an individual molecule. No single molecule can be really given an assigned category name (B-DNA, Z-DNA, etc.). The need for controlling single molecules is apparent.

## 2.2. Molecular Computing

Some bio-molecules may function as computational elements by themselves by using different set of states that are different at variable configurations. They are not only the potential basis to develop devices and circuits that are then assembled in computers, but can directly perform the computing operation. In addition some molecules such as DNA are used for direct computing using its sequence and recognition capabilities – DNA computing. This avenue of research is already explored and should be assessed and continued.

## 2.3. Structure-Function

The molecular structure and its dynamics are main factors governing the function.

There is a need for sophisticated tools to observe the structure at the nano-scale, and the dynamics of any given structure. The investigation techniques in the field of molecular electronics, both experimental and theoretical, need to be developed in order to probe (and account for) structure and structural changes.

The old paradigm “structure makes the function” should indeed be evolved to “dynamic structure and dynamic response make the function”. *Structure* research has to encompass *dynamic time-resolved structure*. In fact, in order to understand the function one must understand the dynamics at the nano molecular level and possibly at the single molecule level. Examples are all the processes of storage or disposal in complex systems, from energy/charge transfer in photosynthesis to charge transport in DNA.

In order to understand the function one must also elucidate the nature of the response (e.g., to electric/magnetic fields or to radiation) of molecular nano-systems.

## 2.4. Self-assembly

What do bio-molecules teach us? Self-assembly is one feature that we can learn both to exploit naturally and to manipulate.

A direct exploitation is to use spontaneous recognition and structuring capabilities of biomolecules to pursue nanoelectronic systems that auto-organize.

The capability can also be manipulated for our own purposes by learning the operating principles/mechanisms of self-assembly and by applying them to arrange other complex objects (e.g., inorganic, or organic/inorganic hybrids).

Other candidates that offer self-assembly may also be developed in general for nanoelectronics.

## 2.5. Dynamically controlled interfaces

How do molecules recognize each other and other materials or interfaces? We should learn how to realize controlled interfaces and in particular dynamically controlled interfaces (e.g., electrically or optically controlled).

We could define new ways to impart specificity to surfaces, nanostructures, and nanodevices. This, as well as control, is important even immediately, before maturing to real biomolecular electronics, and not only in the long term.

Control of interactions (non-covalent; e.g., electrostatic specificity) more similar to those occurring in proteins and antibodies.

Architectures that need also inorganic components, such as interfaces with inorganic substrates (metals, semiconductors, oxides), coupling with nanoparticles, etc.

Interfaces with the bio-world in terms of devices for sensing, diagnostics, etc. How can these devices be integrated with electronic devices? Read-out schemes.

## 2.6. Wet nanoelectronics

Proteins are able to perform electron transfer (e.g., Azurin). Devices have been demonstrated and more complex architectures working in solution have been shown.

Wet “nanoelectronics” may also work with ions (e.g., ion channels).

Nanoelectronics could be realized in a wet environment, where enzymes may be active and collective gating can be done through the solution.

Operation in a wet environment plays a strong role for biosensors. However, the variety of possible wet bio-devices extends to diodes and transistors, and possibly to novel functionalities.

Nanosensors, not necessarily based on bio-molecules, may be devised to work in both dry and wet environments.

### 2.7. New versus conventional devices

With conventional devices and circuits, the designers know the exact location of any device in a given circuit.

On the contrary, the fabrication of molecular devices would likely introduce lots of errors, due to the way the molecules that must interact find each other, recognize each other and find their final site and configuration in the product (self-assembly, auto-organization). Therefore, error tolerant architectures must be developed.

A self-assembled system may have many defects that may be incompatible with current circuit operation architectures. To implement molecular electronics, one should search ways to exploit the defects in a constructive way. Hence, it may be useful to mature completely new concepts for devices and networks.

Repair mechanisms should be developed to cope with run-time errors.

The above concepts must be developed in a holistic way, from devices to computing units to complete systems.

### 2.8. Molecular magnets

Molecular magnetism is a rather mature field that has run in parallel to research in molecular electronics. They have been addressed up to now mostly from the materials point of view. A strong cooperation between chemistry, physics and engineering is encouraged for this

field. These molecular magnets could be the protagonists of next generation memory devices, which are within the IST thematic area.

Most keywords are common: molecules, well controlled and defined molecules, production by chemical synthesis, nano-scale.

Molecular magnets are mostly interesting for their magnetic properties, and applications in information storage.

Other aspects are also investigated e.g., interaction with light or application in quantum computing. For quantum computing, a central issue is to control electronic states and decoherence.

Applications of Molecular Magnets are currently operated at very low temperatures (to reduce noise) but research is going on to check their operation at room temperature, with encouraging signs.

The field shows a long standing collaboration between theory and experiment, between physics and chemistry.

### 2.9. Role of theory, integration between theory and experiment

Several issues may sound at first very fundamental and pertaining to the area of basic research, but indeed play an important role at the nano-scale and cannot be neglected when going towards applications. An example is given by "Ab-initio theory of *excited states* and of *correlation*", which sounds very basic but is related to the development of new technologies.

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In the case of a very few electrons device, adding one more electron in a confined object is going to be very much affected by *correlations*. The theoretical models that are developed to describe these effects are going to be really important to describe the behavior of some devices, for instance atomic chains, beak-junctions, some kinds of molecular junctions. They are also identifying radically new phenomena. Beyond the need for basic research in this field, it is important to envisage the development of such research in close connection with applied projects as it may open the way to inventing the most innovative devices.

*Excited states* in biomolecules: the theoretical description is still in its infancy, but the theory community is working in that direction. These may be important in applications such as: powering a bio-device, harnessing energy from light, etc.

Simulations at different time and length scales: this is another very basic but at the same time an essential tool to investigate the properties of biomolecules (or even smaller organic molecules on inorganic substrates). They could help understanding recognition and self-organization, aggregation and discomposure of hybrid materials, environmental effects.

### 3. Instruments/Methods for research.

#### 3.1. Multidisciplinarity

In order to implement molecular electronics, true multidisciplinarity is needed. Researchers with backgrounds in physics, chemistry, biology, engineering, computer science, must really work together to solve problems and get useful results/products.

The way multidisciplinarity is currently implemented in many cases is instead rather limited: in some projects that involve research groups with expertise in different disciplines, each group proceeds with its independent research, and the collaboration is limited to meetings and discussions once in a while but without really implementing multidisciplinary collaboration. The results are mostly obtained independently and then communicated.

Multidisciplinarity implies learning the research instruments typical of other disciplines, and requires the development of mutual understanding and of a common language.

Multidisciplinarity really emerges when interdependency is needed to attain the desired goal. The interdependency induces new potentialities although it also adds many difficulties.

In molecular electronics bio-chemical synthesis (bio-chemistry) needs to be optimized to design and produce a new molecular species. If the molecule must be measured on a substrate or between electrodes (physics, engineering), its characterization in such conditions is an essential feedback to improve the synthesis protocols. The only way to implement such a collaboration is to learn from each other, doing the experiments partially together and interpreting the results together.

This attitude does not really need dedicated research funding, but rather it does require funds to foster multidisciplinary *education* and *true* multidisciplinary projects.

#### 3.2. Relationship between academia and industry

A widespread feeling is that industry, as well as many potential funding agencies and sources, are currently not ready to cope with the field of molecular electronics. There are still too many open issues for fundamental understanding. Molecular electronics started about 10 years ago but the understanding that we reached is still limited. The following basic issues are fundamental to eventually reach device production: (i) Nature of the connection of the molecules with metals; (ii) How much voltage can a molecule sustain and how is the heat dissipated? (iii) How do the energy levels of the molecule change in an electric field or upon contact to other molecules or surfaces?

Part of the research community encourages an enlargement of collaboration and multidisciplinary also to industrial groups, besides academic groups, to be implemented for instance through stages and visits. This academy-industry link would be useful to widen the careers of young scientists and to enrich the scientific quality of the industrial scene in European countries. Beyond this, learning the industrial viewpoint ("non-optimal" but "market-competitive" products) could also help scientists to design new electronic products that will be able to meet the market in the future, thus marking the most promising research avenues for the present.

Another cited strategy is to encourage start-ups, along the USA example. Invest money to start launching new ideas and products.

### 4. Conclusion.

In summary, research in the field of bio-molecular nano-electronics bears a huge potential for both fundamental understanding and technological exploitation in several aspects related to human development, from medical diagnostics/therapy to computation and a variety of (opto)electronic devices.

*Please send your comments and suggestions to the authors of this document; the aim is to consolidate different views to produce a vision paper for the future of the domain.*

## Future and Emerging Technologies

<http://www.cordis.lu/ist/fet>

FET is the IST Programme nursery of novel and emerging scientific ideas. Its mission is to promote research that is of a long-term nature or involves particularly high risks, compensated by the potential of a significant societal or industrial impact.

As such, FET is not constrained by the IST Programme priorities but rather aims to open new possibilities and set new trends for future research programmes in Information Society Technologies.

### Emerging Nanoelectronics (ENANO)

Proactive Initiative in the 6th Framework Programme

<http://www.cordis.lu/ist/fet/nid.htm>

This initiative complements mainstream IC developments with advanced research in hybrid and molecular electronics, and prepares the bases for an extension of integrated circuit technology beyond the limits of CMOS scaling. This initiative covers a time horizon beyond 2009, corresponding to that covered in the "Emerging Research Devices" (ERD) section of the ITRS roadmap. The scope is however limited to a number of non-CMOS options listed in the ERD document.

## LITHO 2006

# Ultimate Lithography and Nanofabrication for Electronics and Life Science

**LITHO2006 - Marseille (France): June 26-30, 2006**

The **LITHO2006** conference will take place at the **Marseille World Trade Center**, located in the heart of the Phocian city, a short distance from the Old Port.

### Industrial Day:

A full day will be devoted to speakers from private companies, IC producers or equipment suppliers.

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Around **15 student grants (covering travel expenses up to 150 Euros)** will be available for this event

<b>Abstract Submission (Oral request)</b>	<b>April 14, 2006</b>
<b>Student Travelship Bursary Request</b>	<b>April 14, 2006</b>
<b>Early bird fee deadline</b>	<b>May 12, 2006</b>
<b>Abstract Submission (Poster Request)</b>	<b>June 08, 2006</b>

#### Micro / Nano fabrication

EUV Lithography  
SPM Lithography  
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Ion-beam Lithography  
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Self-organisation  
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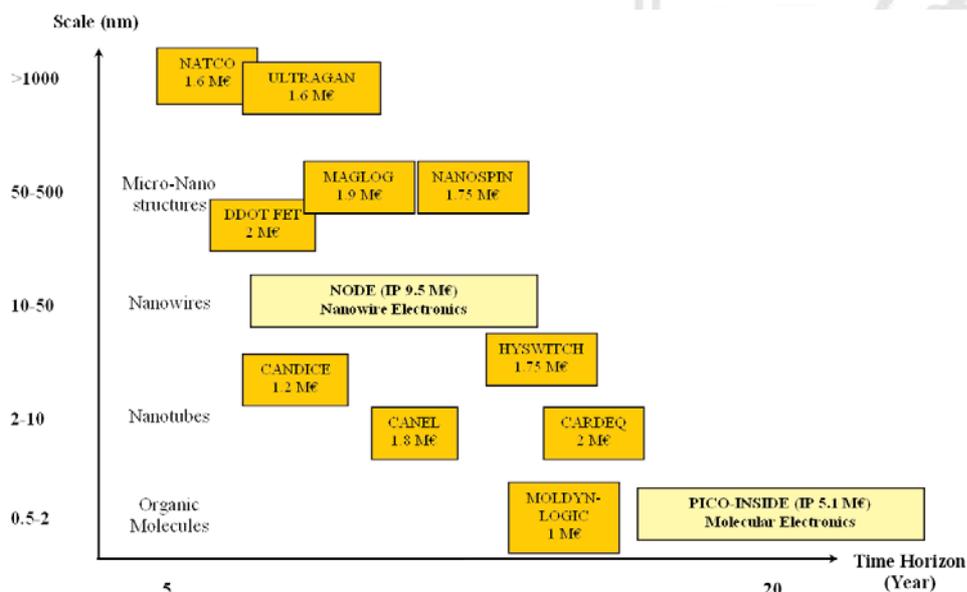
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Each proposal is expected to include elaboration of recent breakthroughs into reproducible physical prototypes and accurate simulations, forward looking research into circuits and architectures, as well as more basic research into topics such as self- or directed assembly. Proposals should identify long-term aims and expected objectives within the duration of the project. They should propose merit criteria where the proposed developments would compete with mainstream approaches or complement these.



Contact

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Useful Link

FP5 Projects - Final Reports:  
<http://www.phantomsnet.net/Enano/euprojectreports.php>

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- Adrian Bachtold (ICN-CNM, Spain)
- Flemming Besenbacher (iNANO, Denmark)
- Jean-Philippe Bourgoin (CEA Saclay, France)
- Dan Dahlberg (University of Minnesota, USA)
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- Gerald Dujardin (Universite Paris Sud, France)
- Jose-Maria Gomez Rodriguez (UAM, Spain)
- Michael Heckmeier (Merck KGaA, Germany)
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Trends in NanoTechnology

**NANO News - <http://www.phantomsnet.net/Resources/news.php>****DNA-wrapped carbon nanotubes serve as sensors in living cells [26-01-2006]**

Single-walled carbon nanotubes wrapped with DNA can be placed inside living cells and detect trace amounts of harmful contaminants using near infrared light, report researchers at the University of Illinois at Urbana-Champaign.

*Nanotubes / Nanosensors & Nanodevices*

**Applied Materials, IMEC Team to Develop Innovative 32nm, 22nm Interconnects [24-01-2006]**

Applied Materials and IMEC announced a significant joint effort to develop 32nm and 22nm-node copper/low k interconnect processing technologies using a suite of Applied Materials' most advanced systems.

*Nanoelectronics*

**Towards Molecular Electronics: New Way of Making Molecular Transistors [20-01-2006]**

Researchers at Columbia University's Nanoscience Center are on the verge of solving one of the most vexing barriers facing advances in molecular electronics: incorporating individual molecules into functional nanoscale devices and exploiting their electrical and chemical properties.

*Molecular Electronics*

**New theory explains electronic and thermal behavior of nanotubes [20-01-2006]**

Researchers at the University of Illinois at Urbana-Champaign have made an important theoretical breakthrough in the understanding of energy dissipation and thermal breakdown in metallic carbon nanotubes.

*Nanotubes / Theory & Modeling*

**Photonics21 Technology Platform Launched [16-01-2006]**

Photonics21 is a Technology Platform for all stakeholders in photonics. It will have the responsibility to determine a strategic research agenda. This agenda will provide the basis for a common strategy to achieve a strong European leadership in Photonics.

*Nanophotonics & Nano-Optoelectronics*

**STMICROELECTRONICS LEADS CLEAN [13-01-2006]**

STMicroelectronics will coordinate CLEAN (Controlling Leakage power in NanoCMOS SoCs), a European Integrated Project involving 14 European partners. The three-year, €4.5 million research project aims to extend battery life and reduce the power consumed by electronics by finding solutions to controlling leakage currents in CMOS designs below 65nm.

*Nanoelectronics, Scientific Policy*

**Propagation of avalanches in magnets assisted by quantum law [10-01-2006]**

A new macroscopic physical phenomenon governed by quantum law, quantum magnetic deflagration, has been unveiled by a team of European researchers. The discovery could lead to future quantum and nano-information technology applications.

*Nanomagnetism*

**Purdue center working to speed research in nanoelectronics [10-01-2006]**

The National Science Foundation and a consortium of companies seeking to accelerate nanoelectronics research announced they are providing \$2 million to five university centers, including one based at Purdue University's Discovery Park.

*Nanoelectronics, Scientific Policy*

**Winners of the 2005 Feynman Prizes in Nanotechnology [04-01-2006]**

The Foresight Institute Feynman Prizes are given in two categories, one for experimental work (Dr. Christian Schafmeister) and the other for theory in advances in nanotechnology (Dr. Christian Joachim).

*Theory & Modeling, Scientific Policy*

**Olivier Kahn International Award [03-01-2006]**

The award an "Olivier Kahn Medal" will be accompanied by a prize of 10,000 euros, to allow the laureate to develop his/her research and to participate to major international conferences. Furthermore, the laureate will receive help from professional experts to communicate on her/his win, to present her/his results at main conferences/ exhibitions in the domain.

*Scientific Policy*

**Stamps create DNA nanoarrays [02-01-2006]**

US researchers have come up with a modified molecular combing technique for creating arrays of stretched DNA molecules over a millimetre scale. The arrays could have applications in nanoelectronics, biological or chemical sensors, and genetic analysis and medical diagnosis.

*Nanoelectronics, Nanobiotechnology, Nanofabrication*

**DNA self-assembly used to mass-produce patterned nanostructures [02-01-2006]**

Duke University scientists have used the self-assembling properties of DNA to mass-produce nanometer-scale structures in the shape of a 4x4 grids, on which patterns of molecules can be specified.

*Nanoelectronics, Nanobiotechnology, Nanosensors & Nanodevices*

**NANO Conferences - <http://www.phantomsnet.net/Resources/cc.php>**

**(March 2006)**

**3rd NanoSpain Workshop**

20-23 March, 2006 - Pamplona (Spain)

<http://www.nanospain.org/Workshop3>

*Nanoelectronics, NanoMaterials, NanoBiotechnology*

**International Conference on Nanoscience & Technology (ICONSAT2006)**

16-18 March, 2006 - India Habitat Center, New Delhi (India)

<http://www.iconsat2006.com/>

*NanoBiotechnology, NanoSensors & NanoDevices*

**EUROSOI Workshop**

8-10 March, 2006 - Grenoble (France).

<http://grenoble2006.eurosoi.org/index.asp>

*Nanoelectronics, NEMS & MEMS*

**(April 2006)**

**ChemOnTubes - International Meeting on the Chemistry of Nanotubes : Science and Applications**

02-05 April, 2006 - Arcachon (France)

<http://chemontubes.crpp-bordeaux.cnrs.fr/>

*Nanochemistry, Nanotubes*

**2006 Materials Research Society Spring Meeting**

17-21 April, 2006 - San Francisco, California (USA)

[http://www.mrs.org/s\\_mrs/doc.asp?CID=2072&DID=89943](http://www.mrs.org/s_mrs/doc.asp?CID=2072&DID=89943)

*Nanomaterials, Molecular Electronics, Nanotubes*

**7th European Workshop on ULtimate Integration of Silicon (ULIS2006)**

20-21 April, 2006 - Grenoble (France)

<http://www.minatec.com/ulis2006/>

*Nanoelectronics, NanoMaterials, NanoBiotechnology*

**(May 2006)**

**International Conference on Nanoscience (ICON2006)**

07-11 May, 2006 - Choroni (Venezuela)

<http://icon2006.phantomsnet.net>

*NanoMaterials, NanoPhotonics & Nano-Optoelectronics, NanoBiotechnology*

**Nanotechnology in Northern Europe (NTNE 2006)**

16-18 May 2006 - Helsinki, Finland

<http://www.nano.fi/ntne2006/index.htm>

*Nanoelectronics, NanoPhotonics & Nano-Optoelectronics, NanoMetrology & Standards*

## NANO Vacancies - <http://www.phantomsnet.net/Resources/jobs.php>

### PhD position: "Magnetic Nanoparticles for Biotechnology Applications"

Applications are invited from graduates in Chemistry and related disciplines to pursue research towards a PhD on Magnetic Nanoparticles for Biotechnology Applications. The project (ongoing Spanish Research Project) involves the preparation and functionalization of magnetic nanoparticles, and finally the characterization of the resulting materials with the aim to be used in bioapplications. The candidate should preferably have experience in preparation techniques and have good undergraduate scores.

Applications should be e-mailed to:

Dr Pedro Tartaj (ICMM, CSIC - Madrid, Spain). E-mail: [ptartaj@icmm.csic.es](mailto:ptartaj@icmm.csic.es)

### Post-doctoral position: "Theoretical Nanophotonics: Light Emission Induced by Fast Electrons"

Applications are invited for the post of a Postdoctoral Research Assistant to work on a project carried at the Spanish Scientific Research Council (CSIC) in Madrid under the supervision of Dr. J. García de Abajo. The successful candidate will undertake research into theory of interaction of fast electrons with nanostructures.

The main aim of the project is to investigate theoretically cathodoluminescence arising from bombardment of nanoparticles and nanophotonic environments in general by fast electron beams as those available in scanning and transmission electron microscopes. The theoretical research to be undertaken is part of an international collaboration that involves as well the University of Southampton and the University of Paris-Sud in the join European STREP project SPANS.

A PhD in a relevant area of theoretical physics or materials modelling is required and experience in using/modifying/developing electromagnetics and/or electronic structure codes is highly desirable.

The position is for two years with a salary of 42,000 euros per year.

Informal enquiries should be addressed to Dr. J. García de Abajo at [jga@sw.ehu.es](mailto:jga@sw.ehu.es)

### Post-doctoral position: "Technology and Planarisation of Silicon Nanowire arrays for Nanoelectronic and Nanophotonic Devices"

Within the frame of the French CEA program "Chimtronique" we offer a post-doc position in the field of nanowires technology.

The candidate will have the opportunity to use state of the art equipments and interact with a number of scientist within CEA/Grenoble area. This Work will proceed within the framework of a collaboration between CEA/LETI/DOPT, CEA/LETI/DIHS, CEA/DRFMC and CNRS/LTM. Profile

A PhD in material science, electrical engineering or physics is required. Experiences and knowledge in semiconductor processing, surface science and structural characterization would be appreciated. The candidate should have team spirit with coordination, communication and reporting skills. The position is available for one year, beginning January 2006, with a one year extension option.

If you are interested, send a CV + motivation letter + recommendation (preferably by e mail) to :

Pierre Ferret: LETI/DOPT/LCDO (CEA/Grenoble, cedex 9 F-38054 Grenoble, France) [pierre.ferret@cea.fr](mailto:pierre.ferret@cea.fr)

Pascal Gentile: DRFMC/SP2M/Sinaps (CEA/Grenoble, cedex 9 F-38054 Grenoble, France) [pascal.gentile@cea.fr](mailto:pascal.gentile@cea.fr)

### PhD position: "Molecular Light Emitting Devices"

Applications are invited from graduates in Chemistry, Physics and Materials science disciplines.

A letter of interest with a concise CV and the name and contact details of at least 1 reference should be sent to the e-mail below.

Closing date for receipt of applications: February 28th 2006.

Further information: Dr Henk Bolink. ICMol-University of Valencia (Spain) ([henk.bolink@uv.es](mailto:henk.bolink@uv.es))

**Keynotes:**

- |                               |   |
|-------------------------------|---|
| <b>Nicolas Agrait</b>         | UAM, Spain  |
| <b>Carlos Balseiro</b>        | Centro Atomico Bariloche, Argentine                       |
| <b>Remi Carminati</b>         | Ecole Centrale Paris, France                              |
| <b>Fernando Flores</b>        | UAM, Spain  |
| <b>Francisco Garcia Vidal</b> | UAM, Spain  |
| <b>Uzi Landman</b>            | Georgia Tech, USA   |
| <b>Alfredo Levy</b>           | UAM, Spain  |
| <b>Horacio M. Pastawski</b>   | Universidad Nacional de Cordoba, Argentine                |
| <b>Jorge Ripoll Lorenzo</b>   | Institute Of Electronic Structure & Laser (FORTH), Greece |
| <b>Daniel Sanchez-Portal</b>  | DIPC, Spain   |
| <b>Frank Scheffold</b>        | Fribourg University, Switzerland                          |
| <b>Daniel Ugarte</b>          | UNICAMP, Brasil   |
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**Deadlines:**

**Student travel bursary applications:**

24 March , 2006

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## How to exchange information with a single molecule

By Pico-Inside project partners ([www.picoinside.org](http://www.picoinside.org))

At the laboratory scale, there is an urgent technological problem to be solved: how to interconnect a molecule with the prospect to exchange information in a multi-channel configuration with this molecule? Starting from a surface science point of view, one of the Research Unit aims of the new IST-FET "Pico-Inside" project is to explore the solutions of this problem. Whatever the type of information to be exchanged, connecting a molecule to electrodes or dielectric waveguides means creating an interaction between a few parts of this molecule and the surface-end of each interconnect. From the surface science point of view adopted in Pico-Inside, any change of the detail atomic ordering at the "molecule-surface-end" junction or any change in the adsorption site of the molecule in interaction with the interconnects will modify the orbital mixing between the surface and the molecule. Then, the quality of the information exchange will be degraded.

In the following, research work of Pico-Inside partners is presented in a way to indicate the starting point of the Pico-Inside exploration of this interconnection problem. Pico-Inside is concentrating its efforts on electronic interconnects meaning that only metallic electrodes issues are discussed. They are also concentrating on the physical and technological aspect of the interconnects and not of the type of information to be exchanged (classical, quantum) nor on the chemical aspect of the interconnection problem.

In a fully planar technology, a maximum of 5 levels of interconnection is required to pass from the molecule to a macroscopic amperemeter (see Figure 1):

1- From the molecule to the atomic wires. This is

the atomic scale level of the interconnects.

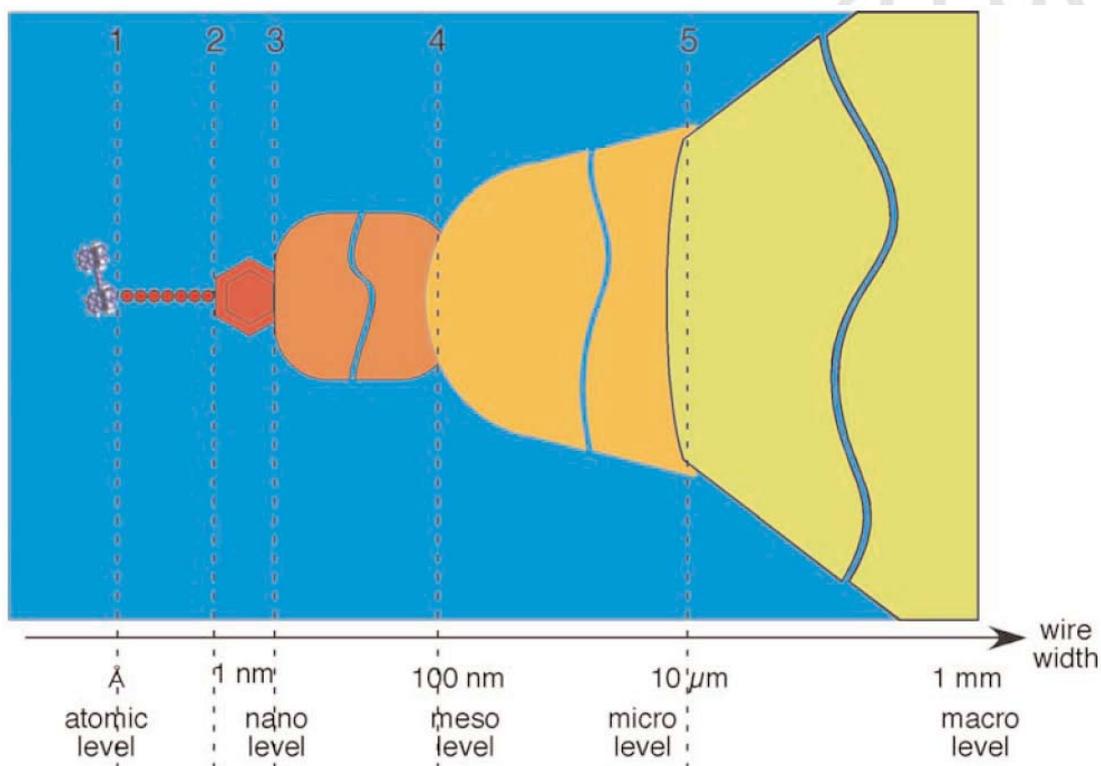
2- From the atomic wires to nano metallic islands, only a few mono layers in height. This is the nano scale level of the interconnects.

3- From those nano metallic islands to mesoscopic metallic wires with a width below 100 nm. This is the mesoscale level of the interconnects.

4- From those mesoscopic wires to micron scale metallic pads. This is the microscale level of the interconnects. The lateral size of those pads depending of the next level.

5- From the micropads to macroscopic wiring which links the micro level and the macro level and then to the amperemeter.

At all the levels, a major point is to preserve the cleanness of the others level of the interconnection sequence. This means that the difficult task is to determine a succession of technologies which will preserve the initial atomic scale precision of the atomic scale level of the interconnect. This requires the exploration of fabricating metallic atomic scale mesa islands on semi-conductor and insulating surface, of molecular molding and stabilisation of atomic wires, of self-assembling molecule on an insulator in a systematic way, of developing a nanostencil technique down to 10 nm and of using metallic cantilevers for the interconnect to the macroscopic level. In Pico-Inside, we will also take care of the possibility to suppress one or more of those interconnection levels to increase the reproducibility of the final interconnection chain.



**Figure 1.** The aim of Pico-Inside is to multiple connect a single molecules to the macro world under ultrahigh vacuum conditions. Different interconnections will be studied: 1) molecule to atomic wire (atomic level) 2) atomic wire to a metallic island of a few monolayers high which links the atomic level and the nano level 3) metallic island to a thin metallic ribbon which links the nano level and the meso level 4) thin metallic ribbon to micro-electrode which links the meso level and the micro level 5) micro-electrode to macroscopic wiring which links the micro level and the macro level.

The need for a first atomic scale level of interconnect is explained by a very hard geometric constrain in this multi-interconnection problem. To illustrate this point, let us remind the past tentative in another FET-IST project BUN which end in year 2003. The problem was to use the e-beam lithography technique for the fabrication of a maximum of nanoscale metallic wires on a circle. A maximum of 20 nanoscale metallic electrodes terminated each by a 20 nm apex diameter were fabricated on a SiO<sub>2</sub> surface. On this surface, those 20 electrodes open the access to an area of a diameter not smaller than 200 nm. This diameter is clearly too large as compared to the size of conjugate molecules available in our days. This geometrical constrain forces to fabricate local access on the molecule using atomic wires. But this can be considered as positive because it will force the molecular designer to integrate as much as possible the electronic functions to be performed in a small molecule. This part is worked out in the research Unit 1 of Pico-Inside.

The 5 interconnection levels can be separated in two groups. One group for the first and the second interconnect levels is relevant to surface science. The second group for the three last, can be considered as technological interconnects. Notice that these electrical contacts will be used under or near an UHV-STM or NC-UHV AFM head. Therefore, the way to fabricate the second group will depend strongly on the geometrical environment around the local STM or AFM probe. The realization of the first group will depend on the nature of the substrate (semiconductor or insulator) to be used.

In this article four aspects of the Pico-Inside research will be described in more detail:

- 1) The positioning of suitable molecules on insulators. As described by Socoliuc et al. (part 1), it was found that many organic molecules are loosely bound on insulators, which leads to diffusion at room temperature. A major goal is to immobilize these molecules on suitable substrates, such as modified insulators or wide-gap semiconductors with small doping concentrations.
- 2) The molecular molding of atomic wires on metallic and on insulating substrates. The technique of molding will be described by Linderoth et al. (part 2).
- 3) The metallurgy of nanopads. The preparation procedures for metallic nanowires and metallic nano-pads will be developed for semiconductors and insulators. An example of a possible procedure will be given by Goryl et al. (part 3).
- 4) The development of the nanostencil technique is one very important solution to interconnect the nano-pads or nano-wires to the micrometer scale. The experimental setup is complex, because all functions have to be performed under ultrahigh vacuum conditions as described by Martrou et al. in part 4.

## Part 1 - Immobilization of organic molecules on insulators

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Silicon microelectronics has undergone continuous miniaturization during the last three decades leading to dramatic improvements in computational capacity and speed. As fundamental limit of electronic devices, individual molecules have been foreseen as functional electronic structures. The wide variety of organic molecules would seem to make viable the hope that single molecules will be able to perform for instance the logic functions [1]. With this goal in mind, absorption of organic molecules on flat and patterned surfaces has become a subject of intensive studies [2]. Such studies have been performed mainly using metallic substrates, although the coupling between the electrons of the molecules and the surface could prevent their use. In order to separate the functional electronic systems from the substrate, molecules with spacer legs have been designed [3], adsorption on thin insulating spacer films [4] and in pits produced on an alkali halide sample by electron irradiation have been explored [5].

### Non-contact atomic force microscopy (nc-AFM)

Since its invention, the non-contact atomic force microscope (nc-AFM) has proven its capability of yielding images with atomic resolution on a wide variety of surfaces [6], ranging from metals to semiconductors to polymers to biological materials [7]. The nc-AFM offers unique advantages compared to other scanning probe techniques, such as contact atomic force microscopy (c-AFM) and scanning tunneling microscopy (STM). The absence of repulsive forces in nc-AFM permits its use in the imaging of "delicate" samples [5] and, the nc-AFM does not require conducting samples. This technique relies on a microfabricated tip at the end of a cantilever excited at its fundamental bending eigenfrequency. After approaching the surface, the tip first senses an attractive force that decreases the resonance frequency. The negative frequency shift,  $\Delta f$ , varies rapidly with the minimum tip distance, especially a few angstroms away from the surface. When  $\Delta f$  is used for distance control, contrasts down to the atomic scale can be achieved in ultrahigh vacuum.

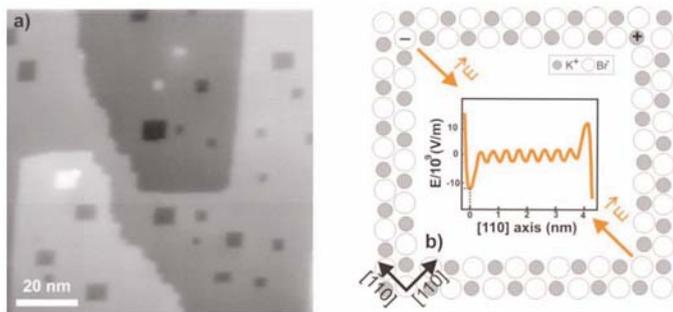
This non-destructive imaging technique, led to several studies where atomic rows [8], steps, or vacancies on flat surfaces [9] could be obtained via the tip-sample interaction as distance control. Apart from the imaging capabilities, force microscopy

experiments can also quantify forces involved in the manipulation of molecules [10]. Some successful attempts to utilize nc-AFM for these purposes have been made; well-controlled lateral manipulations of single atoms even at room temperature become possible [11].

For the first time Nony *et al.* were able to resolve single organic molecules on an insulating sample by nc-AFM [5]. The high mobility of the organic molecules on insulating surfaces at room temperature makes their imaging very difficult [12]. Therefore, an essential condition to obtain molecular arrangements on such surfaces is to lower the mobility of the molecules. One solution was to change the morphology of the ionic crystals by electron irradiation. Square and rectangular pits of nanometer size and of monolayer depth were formed [13].

### Pits formation

Irradiation of alkali halide crystals leads to the production of defects in a subsurface region of the crystal. Subsequent diffusion and interaction of these defects with the surface results in desorption processes at the surface [13]. In the literature formation of nanopits is reported on different ionic crystals (KBr, NaCl...). The desorption process takes place layer-by-layer and the efficiency of the process is influenced by the surface topography.

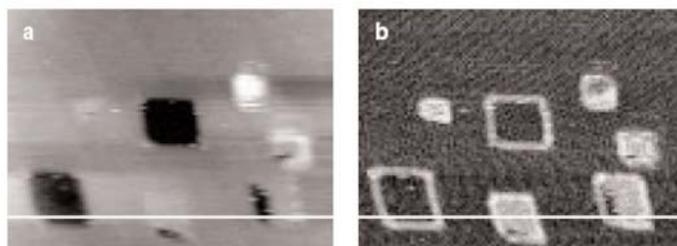


**Figure. 1** a) Pits produced by electron bombardment on KBr. b) Electrostatic field inside the pit along the [110] direction. The field was calculated by summing up the Coulomb contributions of  $100 \times 100 \times 100$  alternating electrical charges and subtracting the contribution of a  $10 \times 10 \times 10$  squared monolayer of ions.

On KBr (001), straight-edged pits can be created by exposing the surface to an electron beam of 1 keV for a short time. The pits are square or rectangular and one monolayer (i.e., 0.33 nm) deep (Fig 1a). The keV energy of the electrons arriving on the surface is transferred to valence-hole-conduction-electron pair and lattice vibration. This leads to the formation of defects like F centers when an electron is trapped in a halogen vacancy and, H center resulted from an interstitial halogen atom. Thermally activated motions of the defects carries energy to the surface of the crystal and provoke the emission of halogen atoms and the neutralization of the surface alkali atoms [14]. One mono-atomic pit created by electron bombardment and the electrostatic field inside the pit are depicted in fig 1b. The electrostatic field presents rapid variation at the corner sides and weaker modulations in the middle of the pit.

### Choosing the right molecule

The first attempt to exploit the increased interaction of molecules with the topographically modified KBr was the evaporation of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecules [15] without spacer legs. Fig. 2 shows a KBr surface with pits after evaporating a sub-monolayer of PTCDA. Some pits were partially or totally filled with molecules, but the resolution of single molecules could not be achieved [12].



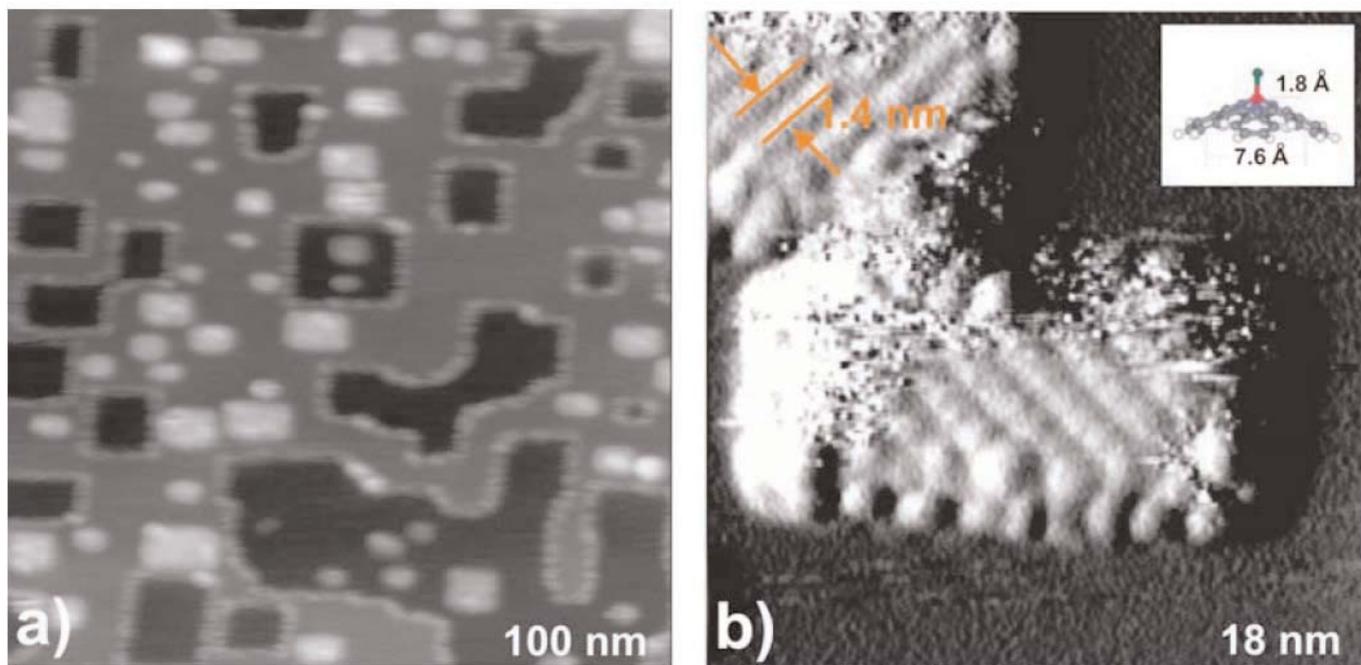
**Figure. 2** KBr(001) surface with electron irradiation-induced rectangular pits, covered with one-tenth of a monolayer of PTCDA molecules. a) Topography signal recorded by nc-AFM (frame edge 132 nm x 98 nm). b) Damping signal.

The turning point in achieving molecular resolution for molecules evaporated on insulating materials was the evaporation of the sub-phthalocyanine (SubPc), into the pits produced in a KBr sample. The three fold symmetry SubPc molecule has a strong dipole moment of 4.8 Debye pointing away from the protruding electronegative Cl atom and the electrostatically fitted effective charge on Cl was estimated to be  $-0.4 e$ .

Fig. 3 summarizes the results of this experiment. Frame (a) shows the surface after the pit formation and the evaporation of the molecules. Only smaller pits (below 15 nm) are filled with molecules. Single molecules are clearly visible in frame (b). They are organized in rows tilted  $\pm 45^\circ$  with respect to crystallographic axes. The distance between adjacent rows is 1.4 nm, and the distance between two consecutive molecules in a row is 1.0 nm. The apparent height of the rows is about 0.6 nm with respect to the surrounding KBr(001) terrace or equivalently 0.9 nm with respect to the bottom of the pit. The molecules are well ordered in the center of each pit, but rather mismatched structures occur along their edges. A blurred bright area in Fig. 3b can be attributed to mobile molecules and a few protruding molecules on top of the organized layer.

The attraction of the considerable charge of the Cl atom to the negatively charged corner of the pit, where the Cl atom gets surrounded by three  $K^+$  ions is very strong. Consequently, those corners can act as efficient nucleation centers for molecules such as SubPc. Van der Waals attraction favors also the adsorption of the SubPc molecules to the bottom of the pit via two of the "feet" and their trapping at the right corner. Intermolecular forces based

on dipole-dipole interaction are much weaker but nevertheless, they count for the relative orientation of molecules in adjacent rows. The total trapping interaction leads to an energetic barrier of about 0.15 eV ( $\sim 6k_B T$ ), preventing thus, the diffusion of a single molecule at room temperature.



**Figure 3** a) The molecules decorate steps and fill pits of width smaller than 15 nm. No molecules are observed on the KBr terraces. Molecular self-assembled structures are revealed within two pits. b) Frame size 18 nm. Molecular resolution reveals that the structures are tilted  $\pm 45^\circ$  with respect to the pit edges. The inset image is a sketch of the SubPc molecule.

Keeping in mind the main goals of this research, namely integrating a calculation unit in a molecule, the next step would be to study the trapping of various molecules, to produce "molecular wires" with "wisely" positioned polar groups on different nanostructured ionic substrates. A further goal is to achieve intramolecular resolution. Further connection of the molecules immobilized on insulators to metallic wires will represent a step forward to a viable molecular structure.

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## Part 2 - Molecular molds

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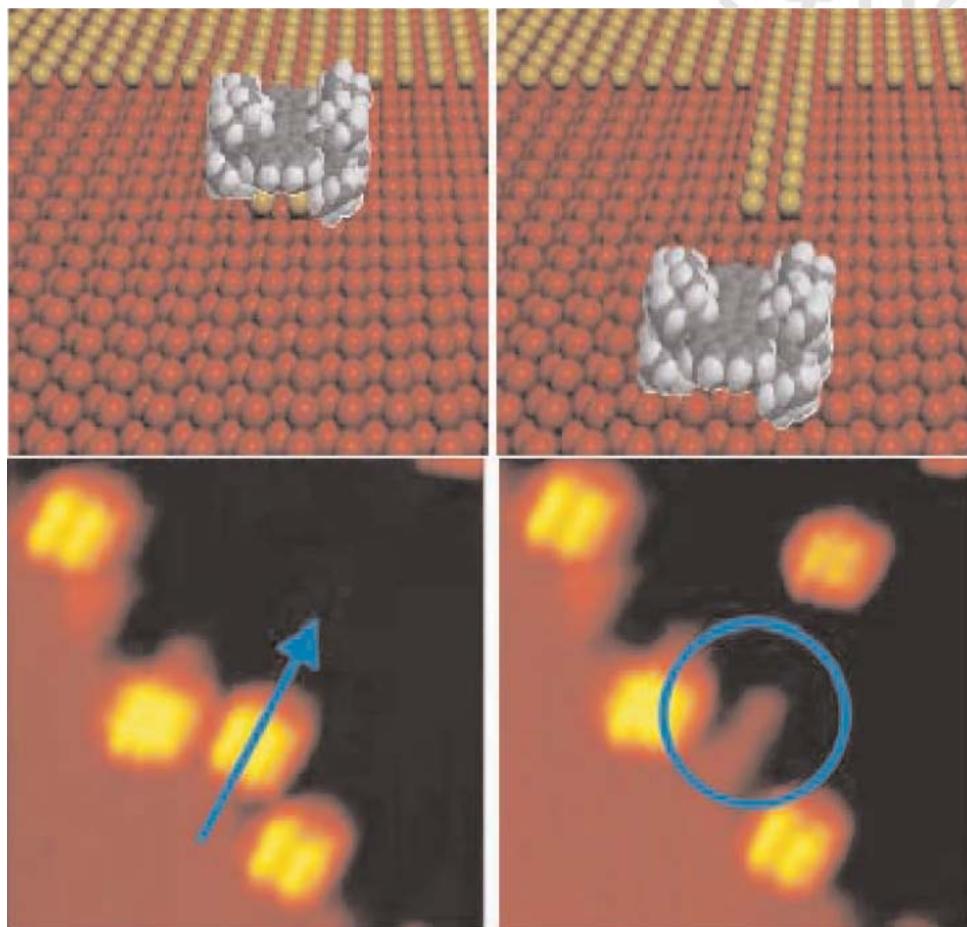
The idea in molecular molding is to use the interaction between an organic molecule and metal atoms to form well-defined metallic nanostructures on surfaces. The principle was demonstrated by Rosei et al [1] who used a C<sub>90</sub>H<sub>98</sub> organic molecule known as the Lander to synthesize metallic nanostructures on a Cu surface. As shown in the figure, Lander molecules consist of an aromatic board equipped with moieties that act as legs, lifting the board away from the surface. When Lander molecules were deposited on a Cu(110) single crystal surface at room temperature they diffused to step edges where they adsorbed. Upon cooling the surface to temperatures in the range 100-200 K it was possible to use the tip of a Scanning Tunneling Microscope to gently manipulate the adsorbed molecules away from the step edges, revealing a well-defined nanostructure of 0.75x1.85 nm<sup>2</sup> dimensions. The nanostructure consists of two adjacent rows of Cu atoms protruding from the step edge. At room temperature, there is a high mobility of step edge atoms on the Cu surface. The formation of the observed nanostructure involves the trapping and stabilisation of such thermally activated atoms by the Lander molecules. Since the space underneath the molecular board favourably matches the dimension of the double-row nanostructures, the low-coordinated atoms of these metallic protrusions are stabilized by interaction with the pi-system of the aromatic board. In this way the shape of the organic molecule is effectively used as a mold that is replicated in the resulting metallic nanostructure. Molecular molding effects have also been demonstrated for isolated metal structures underneath molecules adsorbed at terraces [2] and for larger molecules [3], and in an elegant recent experiment, Gross et al used an organic molecule in combination with STM manipulation to sequentially scoop up 5 metal atoms adsorbed on a surface, thereby forming a metallic nanocluster [4].

Within unit 3 of the "Pico-Inside" project, we will explore the use of molecular molding to provide nanoscale contacting between molecules and metal electrodes and to synthesize metallic nanowires on surfaces. Using derivatives of the

original Lander molecule equipped with functional groups that provide directional and specific molecule-molecule interaction, we hope to be able to synthesize unidirectional molecular structures that can subsequently act as larger-scale molds for the self-organization of one-dimensional metallic nanowires formed in the space underneath the molecular structures. A particularly interesting challenge will be to perform such experiments on non-metallic substrates (oxides or insulating thin films) where the grown metal wires and metal-molecule interconnects will be more or less electrically isolated from the substrate. Presumably this will involve modification to the leg moieties of the Lander molecules in order to optimize their diffusional properties for these substrates.

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**Figure. 1** Molecular molding of atomic wires. Adapted from [1].

### Part 3- Metallic Nanostructures Assembled on InSb(001) Surface by Submonolayer Deposition of Gold

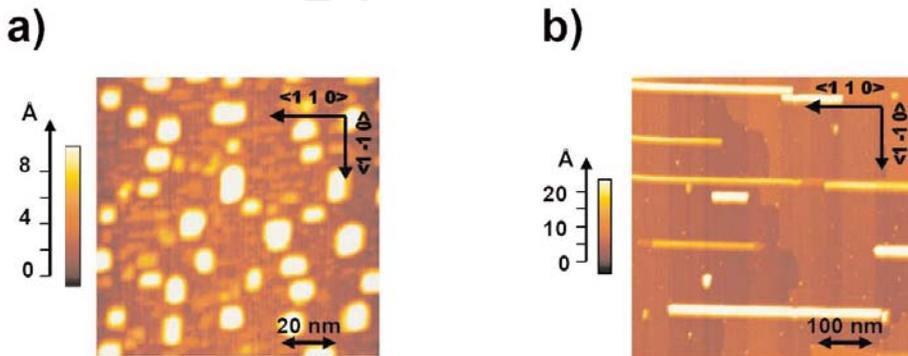
M. Goryl, F. Krok, J.J. Kolodziej, P. Piatkowski and M. Szymanski

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Fabrication of atomic scale conductive interconnects to a single molecule on one side and to nanoscopic atomically oriented metallic pads on the other side, is vital for successful communication between nano- and micro- environment of the electronic circuit. Suitable solutions for such a task might be obtained by thermally-assisted assembling processes occurring at atomically ordered surfaces of AIII-BV semiconductors. In particular, gold seems to be a promising material for manufacturing of micrometer-long conductive nanowires aligned along the surface reconstruction rows of In-terminated (001)  $c(8 \times 2)$  face of InSb.

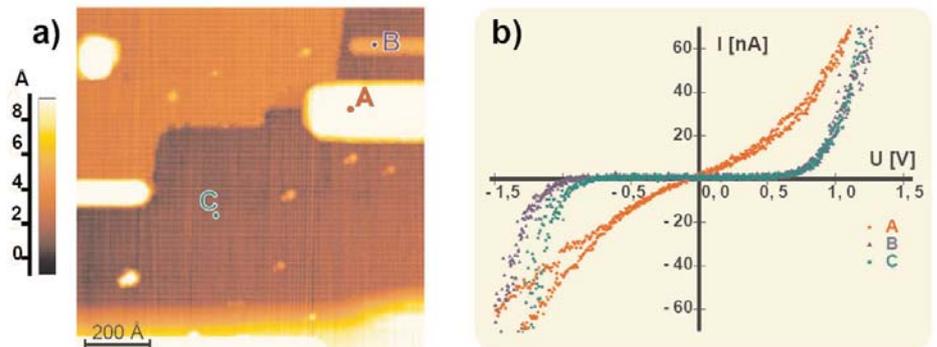
atomic composition. In particular, the deposition on the substrate kept at 300 K, results in formation of rectangular islands with edges oriented along  $\langle 011 \rangle$  and  $\langle -1-10 \rangle$  directions (see Fig. 1a). The average island edge length is of 15 nm.

Increasing of the substrate temperature up to 600K during deposition results in formation of narrow, long structures (nanowires) with a length up to 800 nm (see Fig. 1b). The nanowires are created along atomic troughs of the reconstructed InSb (001) surface ( $\langle -110 \rangle$  directions). High resolution KPFM and STS measurements indicated that nanowires of different heights could have different chemical composition and electronic structure. The example of such analysis is shown in Fig. 2. The  $c(8 \times 2)$  reconstruction troughs of In terminated InSb (001) surface are clearly visible at the STM image (Fig. 2 a) and the elevated wire-like features (denoted A and B) are perfectly oriented along the direction of the troughs. The tunneling current,  $I$ , measured at various points of the sample (A, B, and C) as a function of the tip-sample voltage,  $U$ , indicates different electronic properties of the fully developed wires with respect to the sample. For heights of the wires larger than 2 ML (point A) a metallic character can be deduced from the  $I(U)$  dependence displayed in Fig. 2 b. 1-2 ML high wires (point B) have essentially the same  $I(U)$  dependence as the substrate itself (point C).



**Figure. 1** Nanostructures created by Au evaporation ( $<1\text{ML}>$ ) on InSb (001) surface at various temperatures. a) The substrate kept at 300 K. The average island dimensions are: length 50-100 Å, width 50-100 Å, and height 2-8 Å. b) The substrate kept at 600 K. The average wire dimensions are: length 3000-8000 Å, width 100-50 Å, and height 8-12 Å. Reproduced from M. Goryl et al., *Microelectronic Engineering*, 2005.

Dynamic Force Microscopy (DFM), Kelvin Probe Force Microscopy (KPFM) and Scanning Tunneling Microscopy/Spectroscopy (STM/STS) have been used to study epitaxial nanostructures formed as a result of 0,1- 1 ML deposition of gold on clean  $c(8 \times 2)$  InSb(001) surface. It has been found that gold atoms could disrupt the interatomic bounds on the substrate, causing significant change of the InSb (001) topography and assembling of epitaxial nanostructures with composition and atomic structure strongly dependent on the substrate temperature during evaporation. Subsequent annealing of the system could cause further modification of its structure and



**Figure. 2** Scanning tunneling spectroscopy characterization of the epitaxial nanostructures assembled for Au/InSb(001) system at 600K. a) High resolution STM image of the sample with atomically flat terraces (orange and brown color) and wires of different heights (bright lines). b) Current versus voltage,  $I(U)$ , dependence for various areas of the system.

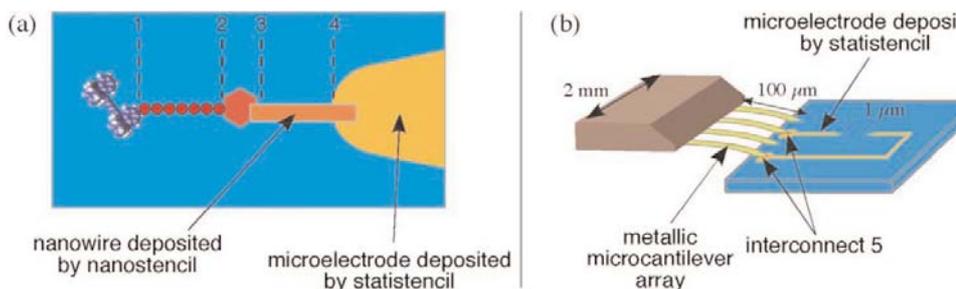
## Part 4 - Nano level to macro level interconnects through static and nanostencil techniques

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### 1-General description of the micro cleanroom for Pico-Inside

The aim of this part is to obtain an electrical contact of low resistance between a thin metallic pad 10 to 100 nm wide and



**Figure. 1** In the GNS group of Toulouse, the interconnects 3 and 4 are made by nanostencil with the micro cleanroom (a), and the interconnect 5 consists of a metallic microcantilever array contacting pads at the end of microelectrodes deposited by the static stencil process.

a macroscopic wire. One possibility is to add each interconnect (3 to 5) by different techniques: the micro clean room developed in the Nanoscience Team of the CEMES institute at Toulouse is based on this solution. Indeed the interconnect 3 is obtained by dynamic nanostencil [1], the interconnect 4 by static stencil, and the last one by microcantilever array as shown schematically on the figure 1. The two last steps 4 and 5 have been already tested in air using e-beam lithography nanowires ending by  $2 \times 2 \mu\text{m}^2$  pads which are contacted with a metallic microcantilever array [2].

The first step is the growth of microelectrodes on the substrate by the static stencil process which is evaporation through a thin membrane bored by the desired pattern. Then the interconnects 3 and 4 between the end of one microelectrode and a thin metallic island are made by depositing a small wire with the nanostencil process which consists to use a drilled cantilever as a shadow mask to write on the surface [3]. And the last interconnect 5 is done by positioning the extremities of metallic microcantilevers array (microcomb) on pads at the end of the microelectrodes.

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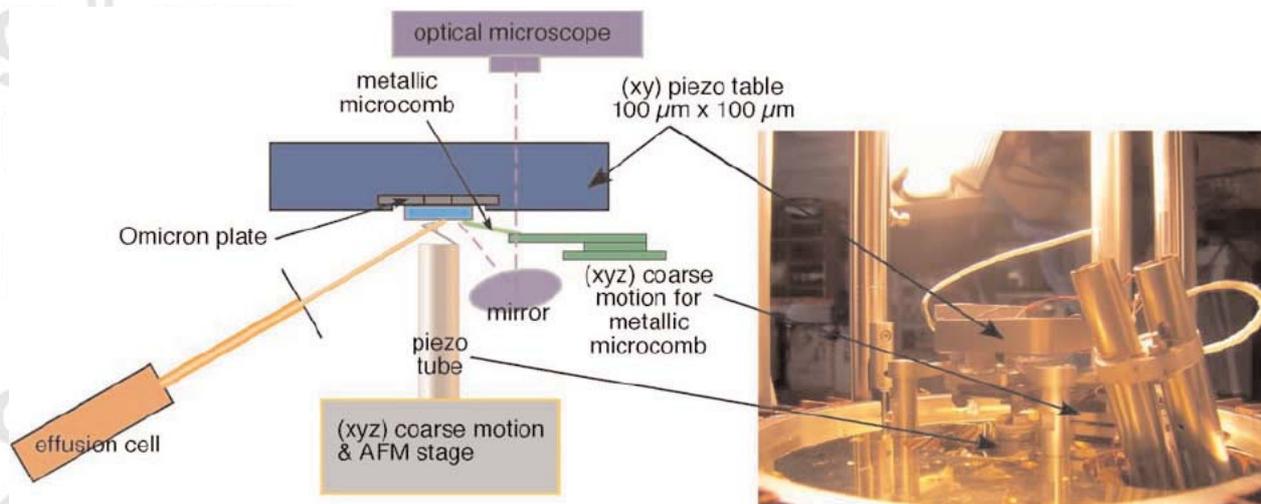
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**Figure 2** The micro cleanroom developed in the GNS group is based on a VT AFM/STM Omicron head which has been modified: the Omicron plate is now placed on a (XY) piezo table allowing fine motion on a (100 μm x 100 μm) area, an (XYZ) table allows the positioning of the microcomb, and the scene is seen through an optical microscope.

To do successfully all these steps, one needs to 'see' at different scale. For the last interconnect, the microcomb should be positioned at a micrometer scale, so a direct vision of the scene by the way of an optical microscope is sufficient. This optical microscope is also useful to approach the cantilever close to the microelectrodes array. However to find the area between electrodes, it is necessary to see at sub-micrometer scale but on a wide range of several tens of micrometers.

The UHV micro cleanroom developed in the GNS group of Toulouse has all these functionalities. As presented on the figure 2, it is a commercial VT AFM/STM Omicron head which has been modified.

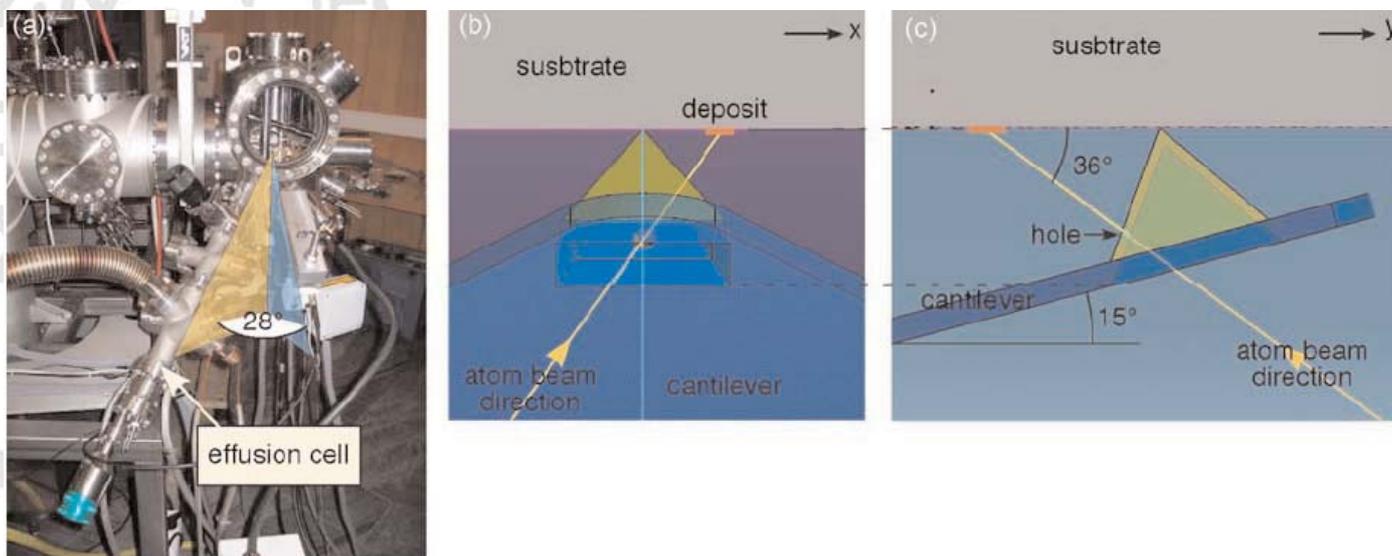
The first modification was to add a flexural-hinge guided (XY) table (100 μm x 100 μm with a repeatability of a few nanometers) which carries the Omicron sample plate. With this table, it is possible to do wide scale AFM/STM images, greater than those obtained with the normal Omicron piezo tube which supports the tip or the cantilever. And the repeatability of a few nm allows a "blind" (ie without AFM

imaging) positioning of the cantilever on the surface. Combined with an effusion cell highly collimated on the cantilever, it allows the growth of nanowires (nanostencil process). The positioning of the microcomb is realized by an (XYZ) piezo table under an optical microscope.

## 2-Technical description of the nanostencil stage

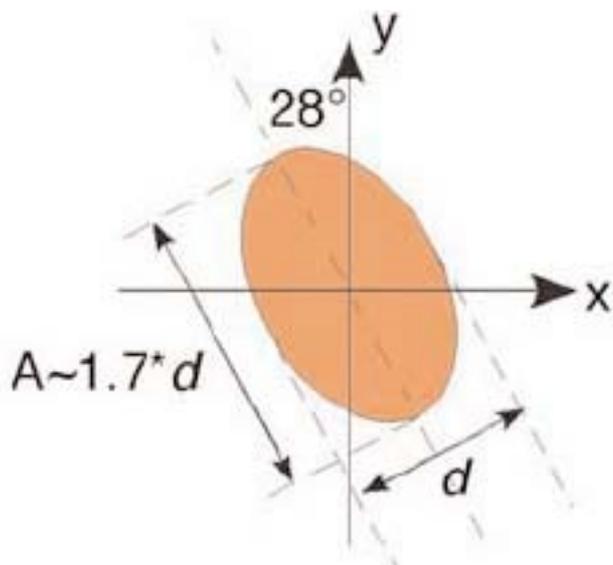
The quality of the nanostencil process depends strongly on the geometrical position of the metal source, the drilled cantilever and the surface. Figure 3 presents our configuration.

The effusion cell is mounted directly on the VT AFM/STM UHV chamber: the geometry of the flange defines two angles for the atom beam direction. The first one is between the two vertical planes passing through the atom beam and the y direction of scan and is equal to 28°. The second one is defined by projection on the vertical plane passing through the y direction and is equal to 36°. This



**Figure 3** (a) an effusion cell is mounted on the VT AFM/STM ; (b) and (c) plane view of the cantilever tip on the surface along the y axis and x axis of scan respectively.

geometrical configuration is reproduced when fabricating the drilled cantilever by FIB. Indeed the holes of the desired figures are drilled with a focused ion beam oriented in the same direction than the atom beam of the effusion cell. The image of a circular hole made on the cantilever tip will be an ellipse on the surface sample at  $28^\circ$  from the y scan axis as shown on figure 4.



**Figure 4** The image of a circular hole made by FIB on the cantilever tip will be an ellipse on the surface sample.

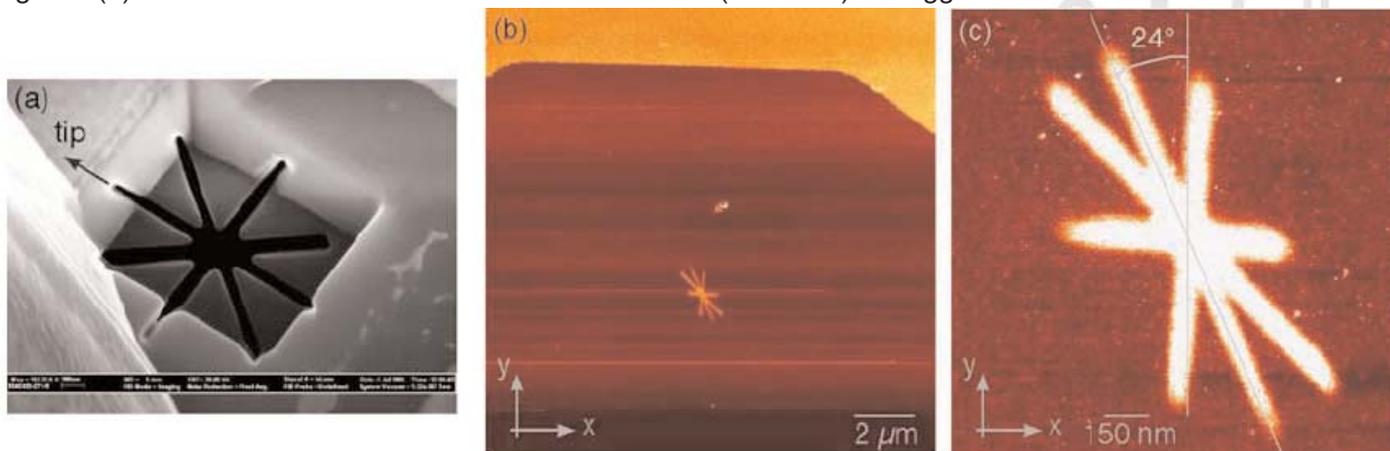
### 3-Some results obtained by the nanostencil process

To observe the distortion induced by the position of the effusion cell, an experiment was done with a cross drilled on the cantilever tip as presented on figure 5(a). To decrease the clogging effect during metal evaporation, the first thing done by FIB is to thin the side of the cantilever tip until a thickness of around 100 nm. This leads to the formation of a box where the desired pattern is drilled. Here we choose a cross with eight lines having between them a similar angle of  $45^\circ$ . After deposition of 4 nm of Titanium on a silicon substrate, we evaporated 50 nm of silver through this drilled cantilever. Our (XY) sample table allows us to obtain wide scale STM images of the deposition as presented on figure 5(b).

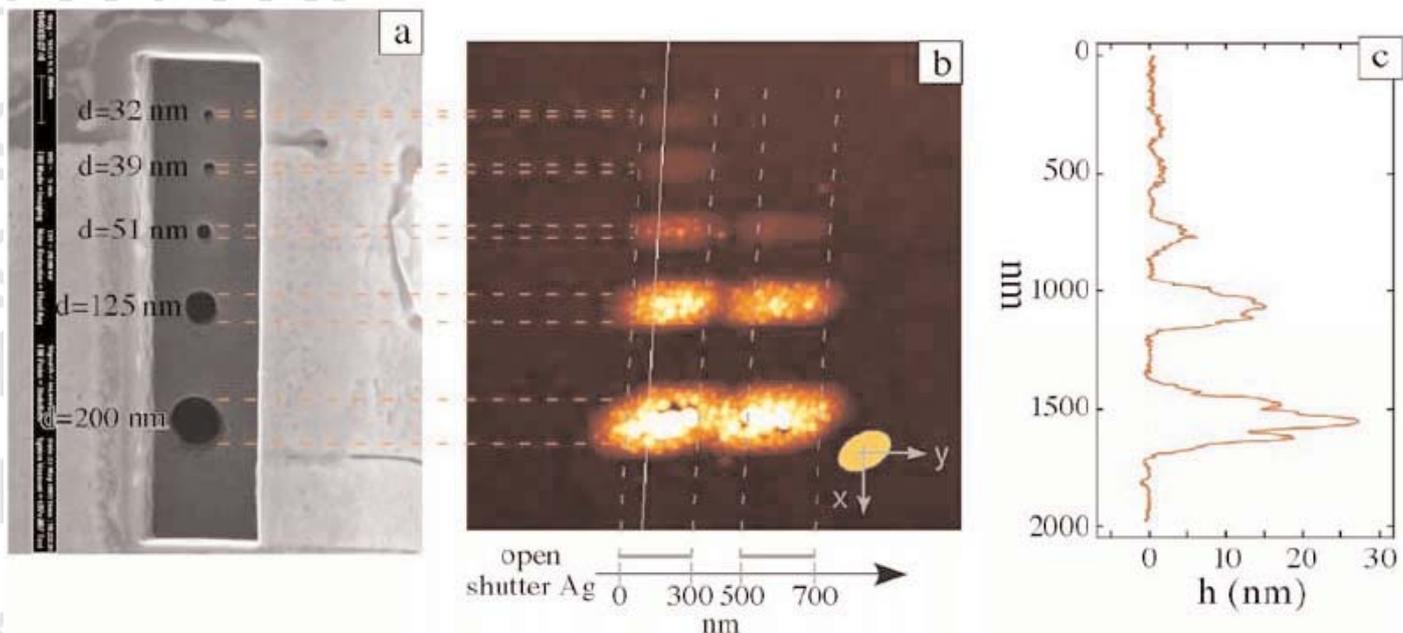
The ability to do wide scale STM image allowed us to find rapidly the small cross: we can see on this wide scale STM image the shadow of the cantilever, and the silver cross deposited through the drilled pattern. A closer view obtained also by scanning with the (XY) table allows us to determine precisely the distortion induced by our geometrical configuration. For example we can measure the angle between the y scan direction and the line passing through the end of the cantilever tip. As this line should be in a vertical plane parallel to the y scan direction, we should obtain  $28^\circ$  after deposition. We measure only  $24^\circ$ , the difference is probably due to the misorientation of the cantilever during the gluing on the holder. Such a misorientation is observed on the wide scale STM image (see fig 5(b)) and adds  $2^\circ$  to the measured angle, which gives a value of  $26^\circ$  closer to the  $28^\circ$  expected.

The nanostencil process allows us to deposit a desired pattern directly on a surface without using an etching process. To successfully contact a molecule we need to draw a thin line between a metallic pad and a micro-electrode. This means that we will evaporate through a hole drilled in a cantilever tip while moving in the same time the substrate to connect the two objects. However the atoms of the beam stick also on the cantilever and after a while the deposit formed on the edge of the hole will clog it. This well known phenomenon [4] is the main disadvantage of the nanostencil process. To study it we drilled a cantilever tip with five holes of increasing diameter from 32 nm to 200 nm as presented on figure 6(a).

We used this drilled cantilever to draw two lines of silver of 300 nm width, and separated by a gap of 200 nm. The silver flux is equal to  $48 \text{ \AA/mn}$  and the sample is moving along the y axis with a speed of 20 nm/mn. The shutter of the silver cell was open and closed in order to obtain the described pattern. The AFM image presented on figure 6(b) shows clearly large differences depending on the diameter of the holes. For the two small holes (32 and 39 nm), only the first line is drawn: after the two holes are clogged. The third hole ( $\phi=51 \text{ nm}$ ) is clogged at the end of the second line and



**Figure 5** (a) SEM image of the cross drilled by FIB on one side of a cantilever tip ;(b) wide scale STM image ( $15 \mu\text{m} \times 15 \mu\text{m}$ ) obtained by moving the sample with the (XY) table ; (c)  $1.5 \mu\text{m} \times 1.5 \mu\text{m}$  STM image showing the silver cross deposited.



**Figure 6** (a) 5 holes of increasing diameter drilled on a cantilever tip; (b) AFM image after deposition of silver ( $48 \text{ \AA}/\text{mn}$ ) while moving the substrate at  $20 \text{ nm}/\text{mn}$ ; (c) cross section along the white line.

the two bigger ones are not clogged after the deposit of 120 nm of silver. A careful analysis of the pattern obtained with the smaller holes gives a thickness of clogging equal to three times the diameter of the holes. Another effect observed on the AFM image is the ellipsoidal shape of the lines due to the geometrical configuration of our system.

**Computing inside a Single Molecule using Atomic Scale Technologies (Pico-Inside)** is one of the new Integrated Projects funded within the IST-FET programme (proactive initiative: <http://www.cordis.lu/ist/fet/nid.htm>).

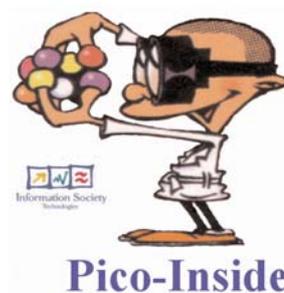
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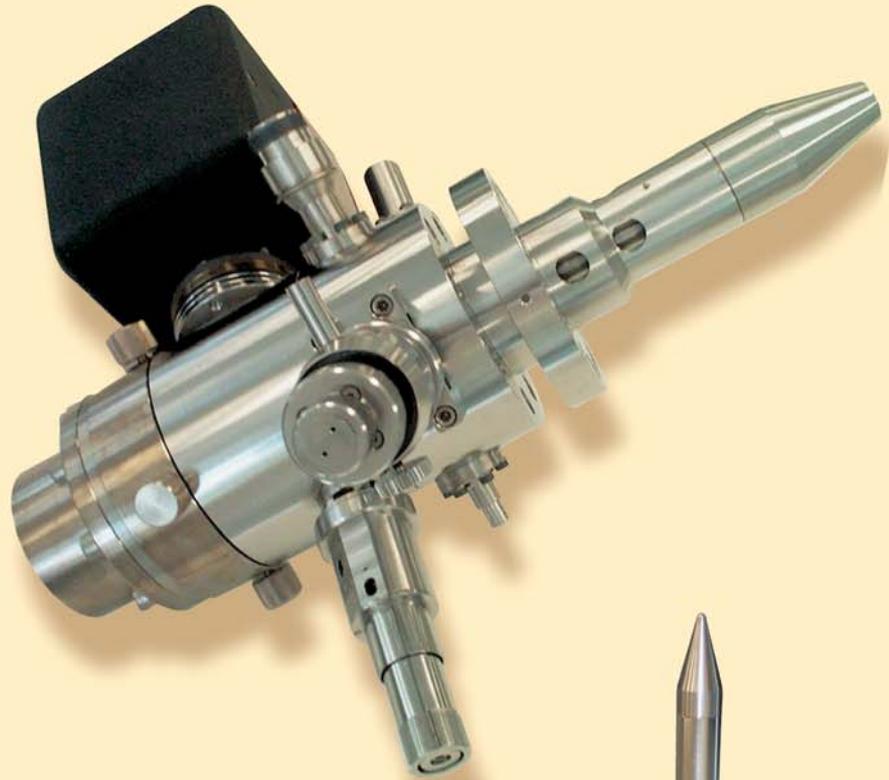


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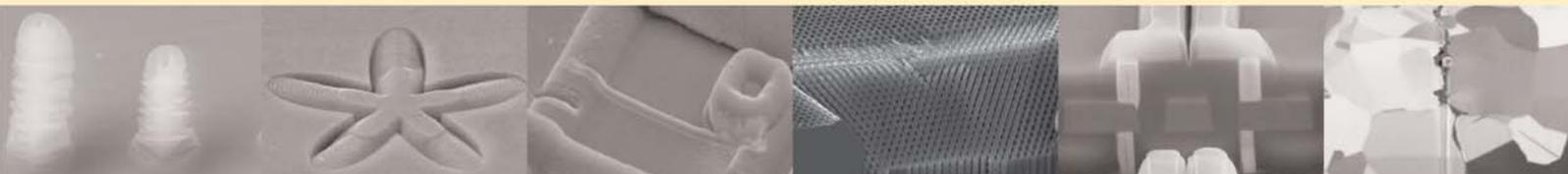
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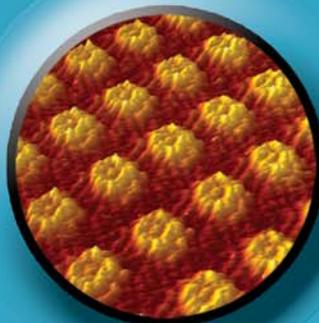
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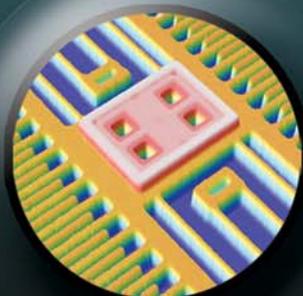
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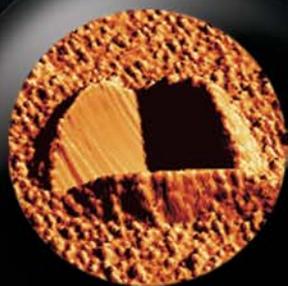
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