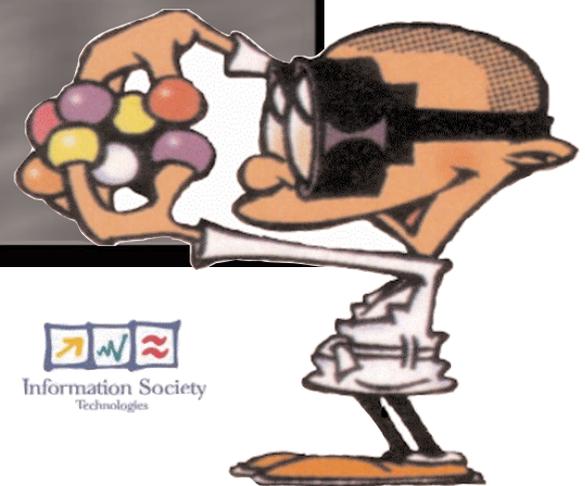
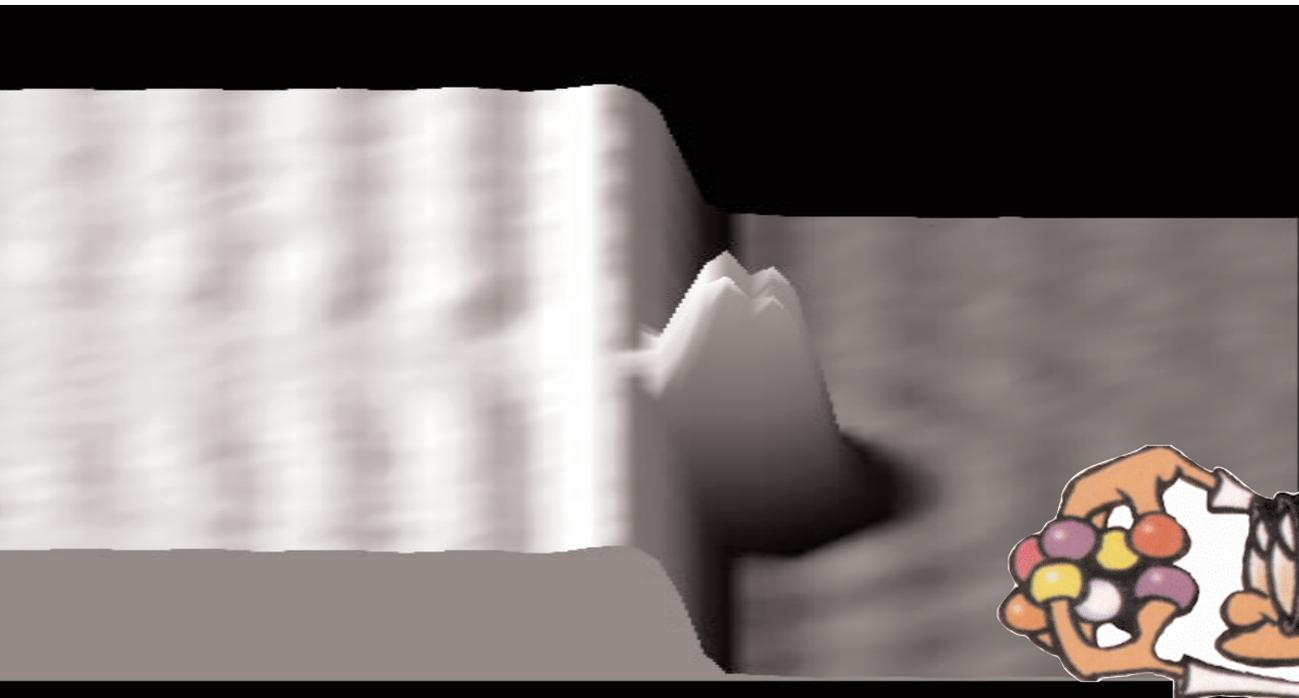




Charge Transport in DNA



Pico-Inside

Hybrid and Mono Molecular Electronics

CNTs Attached to AFM Microcantilevers and STM Tips

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Dear Readers:

Welcome to the second issue of the E-NANO Newsletter that three-monthly provides the latest news, research articles, reports and resources from the Nanotechnology world.

Creating an Atomic Scale Technology is now a necessity for any uni-molecular device and machine in molecular electronics, molecular mechanics, molecular transducers and for laboratory scale experiments on one molecule. In the IST priority 2 of Framework Programme 6 (Emerging Nanoelectronics FET proactive initiative), the Pico-Inside consortium will explore Atomic Scale Technology with the final goal of integrating a complex logic gate inside a single molecule. The E-NANO newsletter will three-monthly publish relevant information and latest results about the Pico-Inside (IST/FET/NANO) project, raising therefore awareness of scientists in this emerging research area.

In this issue, we publish a review article prepared by Prof. Christian Joachim (CEMES/CNRS - GNS, France) on the current status of "Molecular Electronics" and a list of the partners involved in the Integrated Project, detailing their activities and core competences.

In addition, two research articles provide insights in "Charge Transport in DNA" and "CNTs attached to AFM Microcantilevers and STM Tips". These two studies are particularly important due respectively to their possible applications in future (bio)electronics or DNA-based chips and in Scanning Probe Microscopy.

We invite readers to send us their scientific contributions either as articles, reviews or publication highlights.

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

Dr. Antonio Correia (Editor)
Phantoms Foundation

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Issue n°04: March 15, 2006

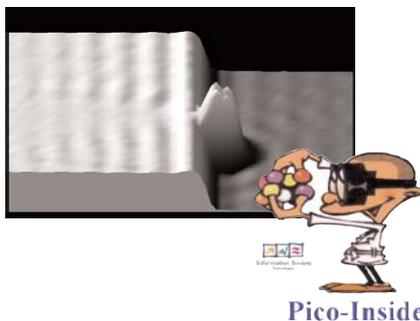
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Cover Picture:

Interconnecting a molecular wire supported by 4 legs to a mono-atomic step edge on Cu(111). LT UHV-STM image of the molecule at contact. (Ref: F. Moresco et al., *Phys. Rev. Lett.*, **91**, 036601 (2003))

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Charge Transport in DNA

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Abstract: The Charge transport in desoxyribonucleic acid (DNA) is being intensively investigated in view of its biological implications in damage and repair, protein bonding, and envisioned integration in future (bio)electronics or DNA-based chips. Notwithstanding, despite sustained efforts to unveil the nature and range of charge transfer in these biomolecules, present knowledge lacks stable foundations. Here we discuss basics of charge transport in the quantum coherent regime (unistep tunnelling), and shows that some concepts of electronic conduction need to be revisited for DNA.

Keywords: DNA, charge transport, nanoelectronics, coherent tunnelling.

1. Introduction

The double-helix structure of DNA is made from two weakly hydrogen-bonded strands, each of which, consisting in a sequence of four nucleotides (A-adenine, T-thymine, C-cytosine, G-guanine) that strictly follows the Watson-Crick complementarities law (i.e. interstrand pairs only appear as AT or CG). Charge transport is believed to be conveyed through the highest occupied molecular orbitals of the guanine base (G-HOMO), given its smaller ionization potential.

In the recent years, two kinds of experiments have provided valuable information on charge transfer in DNA. First, fluorescence experiments have relied on the use of intercalated metallic complexes acting as donor and acceptor to photoinduce and follow charge migration along small DNA fragments [1,2]. Such experiments have pointed towards an efficient transfer over unprecedented length scale for biomolecules. Other experiments have focused on contacting DNA with conducting electrodes, and performing mesoscopic conductance measurements under various physical conditions. Presently available results lack consistency since all kinds of transport regimes have been proposed, from metallic-like, superconducting, semi-conducting or strongly insulating behaviours. Transport mechanism might be purely hole transport, or polaronic-based.

2. Theoretical model for charge transfer

We have recently performed a theoretical study on several kinds of both artificial or genomic DNA. To discuss basic transport mechanisms we have elaborated on a modelling of hole transport through the guanine bases, described within an effective 1D tight binding Hamiltonian,

$$H = \sum_n -t_{\text{DNA}} \cos(\theta_{n,n+1})(c_n^\dagger c_{n+1} + \text{h.c.}) + \varepsilon_n c_n^\dagger c_n$$

c_n^\dagger (c_n) is the operator corresponding to charge creation (annihilation) at site n , t_{DNA} gives the amplitude of π - π coupling between nearest neighbours orbitals, ε_n the hole site energies and $\cos(\theta_{n,n+1})$ is temperature dependent and describes the lowering of coupling between base pairs due to thermal fluctuations [3].

In order to evaluate the conductivity of the system, we use the Landauer formulation of electron transmission, and we compute the energy-dependent transmission coefficient $T(E)$. Our modelling is such that the full energy dependence of T is necessary to discuss the charge transfer properties, although the DNA chain is connected to metallic leads and the electrode Fermi levels are lined up to the G-HOMO. In the Landauer formalism used here, one considers an electronic wavepacket of wave vector k and energy E which is injected from a metallic contact (see Fig.1) inside a DNA sequence. The coefficients R and T give the amplitudes which are respectively reflected by the DNA sequence and transmitted to another one or to the other metallic contact. Current conservation implies $R+T=1$. The inverse transmission rate R/T is related to the dimensionless resistance (ρ), and for weak transmission, the DNA resistivity is proportional to $[(1-T_{\text{av}})/T_{\text{av}}] S_{\text{DNA}}/L_{\text{DNA}}$ taking T_{av} an average of the transmission coefficient for energies close to the HOMO-G ionisation energy, $S_{\text{DNA}}=3 \cdot 10^{-18} \text{ m}^2$ the average DNA cross section, and L_{DNA} the sequence length [3].

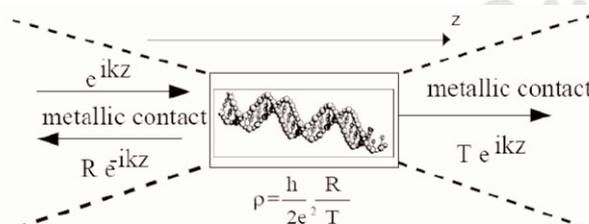


Figure 1: Representation of the transmission throughout a DNA sequence connected to two metallic contacts.

3. Charge transfer in periodic PolyG-PolyC sequences

We have considered synthetic Poly(dG)-Poly(dC) sequences consisting of G and C bases alternated on each strand and sequences extracted from the biological λ -bacteriophage or from the Human Chromosome 22 DNA. The transmission coefficient was studied for finite sequence from 20 nm up to 200 nm long.

As expected Poly(dG)-Poly(dC) sequences were found to follow a "semiconducting-like" regime mainly due to a transmission gap stemming from the two spectral bands (see Fig. 1). The transmission is equal to one at resonant states, whose number is proportional to the number of nucleotide inside the DNA sequence. The bandwidth of the transmission bands is proportional to the parameter t_{DNA} , which is here taken as $t_{\text{DNA}}=0.4$, to reproduce ab-initio results.

The temperature is found to reduce coherent charge transfer, but a theoretical calculation for the DNA resistivity (following the Landauer formalism) gives good agreement with some experimental estimates.

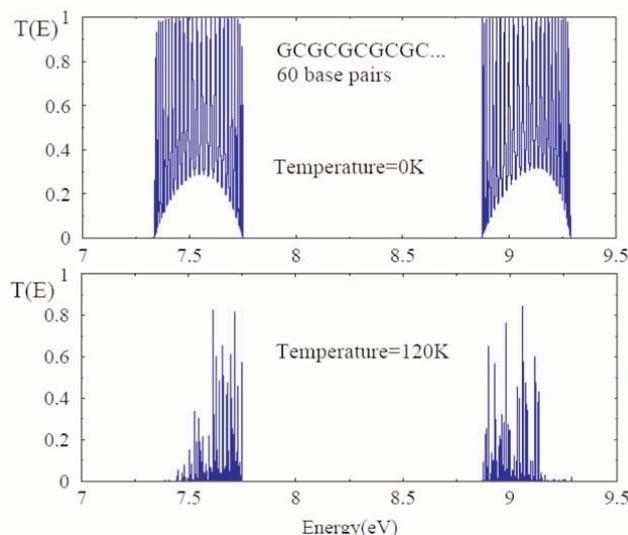
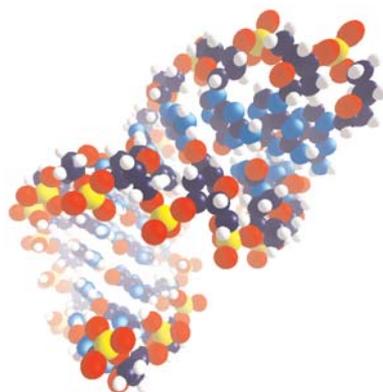


Figure 2: Left : Theoretical transmission coefficients for a periodic Poly(dG)-Poly(dC) sequences with 60 base pairs at two temperatures. Right: Picture of a 10 base pairs Poly(dG)-Poly(dC).

4. Charge transfer in aperiodic λ -bacteriophage sequences

Differently, λ -bacteriophage or Chromosome 22-based sequences is found to exhibit much more resistance to charge transport [3]. Actually, each specific {A,T,C,G}-based sequence follows a complex order which lacks periodicity, although encompassing long range correlations. In our modelling of hole transport through the G-HOMO, any other A, T or C nucleotide acts as a potential barrier that reduces coherent tunnelling, so that larger aperiodic chains exhibit strong backscattering efficiency irrespective of the energy of the injected charges [3]. This phenomenon is illustrated in Fig. 3 for λ -bacteriophage-based sequences with increasing number of base pairs.

The nature and contribution to charge transfer of long range correlations that display complex patterns in different genomic chains have also been the subject of a full study. It is found that if compared with random sequences with uncorrelated distribution of nucleotides, charge transfer in Chromosome 22-based sequences turns out to be much more efficient [4].

In the genomic sequences, it is not possible to estimate any resistivity since resistance increases considerably with sequence length. Thermal fluctuations that reduce π - π coupling strength between intrastrand neighbouring nucleotides also strongly disfavour charge transport. From our calculations, it appears that strong insulating behaviours are expected for length above ~ 10 nm in genomic sequences, and that periodic synthetic sequences may sustain long range transport over 20 nm at small temperatures.

5. Contact-dependent electrical currents

The role of contacts deserves a particular attention. In many measurements, DNA contact with metal electrodes was

achieved by laying down the molecules directly on the electrodes. In this case, it is rather difficult to prove that the DNA molecule is in direct contact with the electrodes. Even so, the weak physical adhesion between DNA and metal may produce an insulating contact. Recent transport experiments have shown that deliberate between DNA and metal electrodes is a prerequisite for achieving reproducible conductivity results [5]. As a suitable representative example, we have considered the properties of a periodic

polyGACT tetranucleotide chain, connected to metallic leads at both ends by means of an effective tight-binding Hamiltonian. Interference effects between the DNA molecular bands and the electronic structure of the leads at the metal-DNA interface give rise to the presence of a set of resonant states in the system. These states are determined by the resonance condition, $\tau = \sqrt{t^* t_m}$, where τ measures the DNA-metal coupling strength, t and t_m are the hopping terms between adjacent nucleotides and neighbour atoms in the metal, respectively. The current intensity of the obtained I(V) curves increases by an order of magnitude when the DNA-metal junction is arranged in the resonance setup as compared to the values obtained for non-resonant conditions, hence illustrating the relevance of contact effects on current characteristics [6].

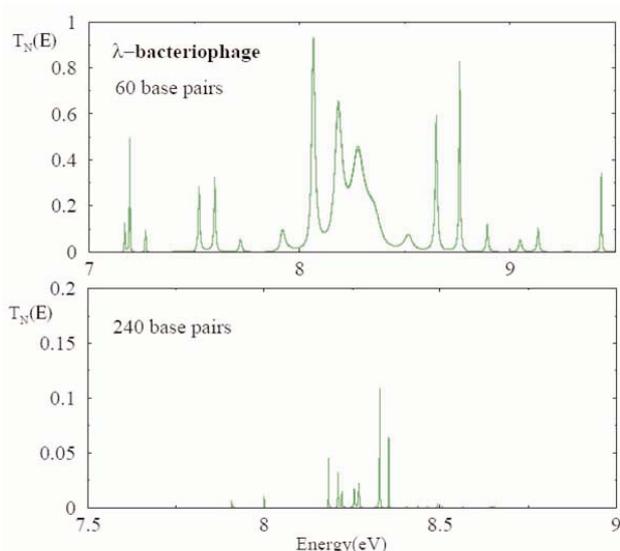


Figure 3. Theoretical transmission coefficients for λ -bacteriophage-based sequences with increasing number of base pairs.

Finally on Fig.4, we show the results for the computed electrical currents through some small DNA sequences in the tunnelling regime. We use platinum as metallic contacts and adjust the corresponding energetics of our electrodes to account for the mismatch between the metallic work function and the G-HOMO. The results show a clear negative differential resistance that is usual in tunnelling heterostructures, but our modelling allow to elaborate on some fundamental features of charge transport. Indeed, it is clearly seen that larger current density are driven through the DNA for the sequences richer in Guanine base. Also, increasing the length of the sequence yields enhancement of tunnelling barrier depth and width, which result in strong damping of transmitted current intensity. From our calculations, it turns out that pure G-periodic sequences, can at most deliver currents in the nA regime, for sequences up to 20nm. In contrast, random sequences for similar length can only deliver current intensity in the pA regime.

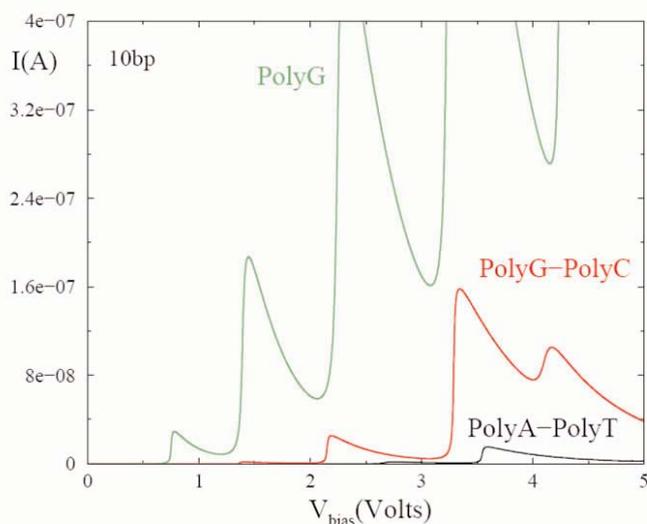


Figure 4. Tunneling currents in the coherent transport regime for different synthetic sequences with ten base pairs.

6. Thermopower of DNA based molecular junctions

The experimental study of thermoelectric voltage over guanine molecules adsorbed on a graphite substrate using a STM tip [7], opened novel perspectives in the quest for thermoelectric devices based on molecular electronics engineering. In fact, due to the extreme sensitivity of thermopower to finer details in the electronic structure one can think of tailoring the Fermi level position in order to optimize the thermoelectric performance of a given molecular arrangement. Such a possibility has spurred theoretical studies regarding the possible use of suitable organic molecules to design novel thermoelectric devices. Although the experimental thermopower values reported to date are too low (about $+20 \mu\text{VK}^{-1}$) to be of technological interest, it is reasonable to expect that the thermoelectric response may be improved by a proper choice of the molecular junction materials. On the basis of the vast knowledge gained from bioengineering research during the last decade, we have performed a systematic study on

the thermoelectric properties of DNA based short molecular arrangements connected to either guanine [8] or graphite leads [9]. From these studies we conclude that conductance and thermopower transport curves are quite similar for both monomers and dimers, irrespective of the chemical nature of their bases, and that the main dimerization effects are an appreciable decrease in the conductance (upper inset Fig.5), accompanied by a slightly increase in the thermopower. In comparison, the trimers exhibit quite remarkable transport properties characterized by a significant enhancement of both electrical conductance and thermoelectric power due to the presence of relevant resonance effects, as it illustrated in Fig.5.

In this sense, by comparing the thermopower curves corresponding to different types of trimers we have recently shown that a characteristic thermoelectric signature can be used to identify the XXY type codons from XXX homonucleotide ones [10]. Since the coding properties of DNA introns are closely related to codon triplet associations these results may enclose some biological relevance well deserving a more detailed study by means of more realistic modelling of both the electronic structure of nucleotides and the codon-lead bonding geometry [11].

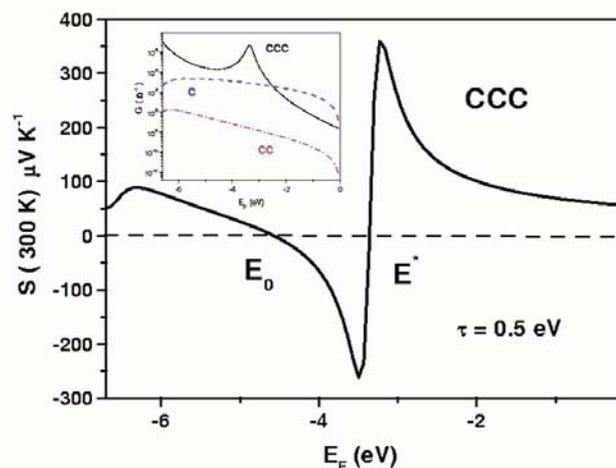


Figure 5. Room temperature dependence of the Seebeck coefficient (main frame) and Landauer conductance (inset) as a function of the Fermi level energy for C (dashed curve), CC (dot-dashed curve) and CCC trimer nucleobases (solid curve).

6. Conclusion

To summarize, we have presented some charge transport modelling and basic results concerning artificial and biological DNA. The charge transfer was shown to be critically dependent on the sequence nature and length of base pairs as well as thermal fluctuations.

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LITHO 2006

Ultimate Lithography and Nanofabrication for Electronics and Life Science
LITHO2006 - Marseille (France): June 26-30, 2006

Since early seventies, microelectronic industry has been the motor of advanced research in the field of micro and nanofabrication in order to shrink down the dimensions of the components to increase the integration rate of ICs. Today's optical lithography allows to reach feature size as small as 100 nm, and it is now expected in the ITRS (International Technology Roadmap for Semiconductors) that the 50 nm node will be reached in 2009. It is thought that optical lithography can be pushed down to roughly 30 nm. However, for further integration, New Generation Lithography (NGL) principles and tools must be designed. From the point of view of components, alternative elementary device must be imagined to replace FET, to scale down below 15 nm.

Besides electronics, Micro and Nano miniaturisation advances (breakthroughs) have now found applications in the field of life science, and scientists from biology, chemical, physical and medical communities propose currently new devices for function recognition (nano biochip), or to ensure artificially a function in human body (micro-capillaries and micro-valves...) or to reproduce artificially in-vivo environments (biomimetics surfaces)

The general purpose of this workshop is to gather researchers interested in the design and fabrication of nano-devices and micro-devices for electronics and life science. The association of researchers working in theory, design/modelling, on miniaturisation (top-down, bottom-up and coupling of both processes) and biology will be an opportunity for fruitful discussions.

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Area of Expertise

Design, fabrication and characterization of (bio)molecular constructs integrated in a technical environment by microsystem technology for applications in bioanalytics, nanoelectronics and nanophotonics

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- Chemical and biochemical/molecular biology laboratories

Dr. Wolfgang Fritzsche

Wolfgang Fritzsche is head of the Biotechnical Microsystems Department at the IPHT. He obtained his Ph.D. in the field of Physical Chemistry in 1994 from the University Göttingen, conducting the experimental work of biomolecular AFM at the Max-Planck-Institute for Biophysical Chemistry. He did his PostDoc in biological AFM and nanotechnology with Eric Henderson at Iowa State University. In 1996, he joined the IPHT, where he established the molecular nanotechnology group.

Biotechnical Microsystem Dep. Overview

The IPHT is a state-funded research institution employing over 200 researchers. Applying state-of-the-art micro- and nanostructure technology as well as specific thin-film technologies and related materials research the IPHT addresses subject areas such as superconductive and magnetic materials and systems, magnetoelectronics, optical fibers, micro-optical modules, and fiber optic sensor systems, microanalytical and biotechnical microsystems, thermosensors or laser diagnostics and laser chemistry. IPHT's main objective is to systematically apply the results of their research in applications in high technology fields such as communication and information technology, biotechnology, metrology and sensorics, process monitoring, non-destructive testing, and power and transporting engineering.

The Biotechnological Microsystems Department is engaged in development and realization of miniaturized modules for detection, characterization and manipulation of cells, molecular ensembles and individual molecules. The aim is the application in (bio)chemistry and molecular

biotechnology, in medical diagnostics and pharmacy. The combination of methods from microsystem technology and nanobiotechnology enables the integration of (bio)molecular systems in a technological setting. Physical/chemical techniques for microstructuring of glass or silicon are applied, complemented by molecular biological methods and techniques for surface modification.

Selected Research Highlights in Nanotechnology

Precise positioning of individual DNA structures

The ability to precisely position (bio)molecules onto microstructured substrates is a core technology critical to the long-term goal of molecular nanotechnology: The integration of molecular units in technical devices. Therefore, parallel processes have to be established, to facilitate in a first step large-scale scientific investigations with statistically significant numbers and later on technically relevant integration densities.

DNA molecules were aligned by a receding meniscus generated by a drying droplet. This phenomenon was overlaid by a micro-structured surface that forced the molecules to line up. The result was immobilized DNA following the electrode structures and spanning gaps. This self-assembly process presents a further step towards highly parallel processes for the precise positioning of molecular structures on chip surfaces.

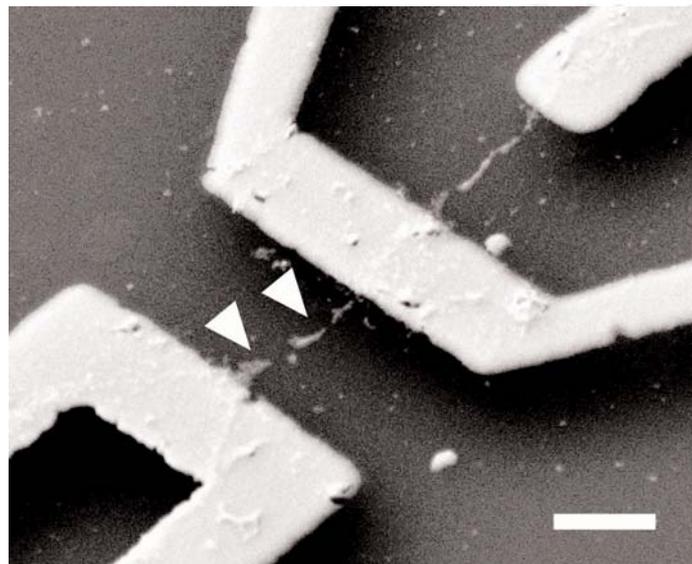


Fig. 1: Scanning electron micrograph of an individual DNA structure (arrowheads) spanning a microelectrode gap. The DNA is labeled with metal nanoparticles. Scale bar 1 μm .

Metallization & Electrical Measurements on the Single-Molecule Level

These structures were used for a nanoelectronic demonstrator. Therefore, metal nanoparticles were specifically deposited along these individual DNA-structures that were positioned in the electrode gaps (cf. figure). Such nanoscale-separated metal islands are known for interesting (e.g. single electron) effects. The experiments yielded an inhomogeneous coverage of the template DNA with metal particles, resulting in stretches of naked DNA structures of 200-500 nm length. Because the DNA structures were integrated in the microelectrode array, electrical

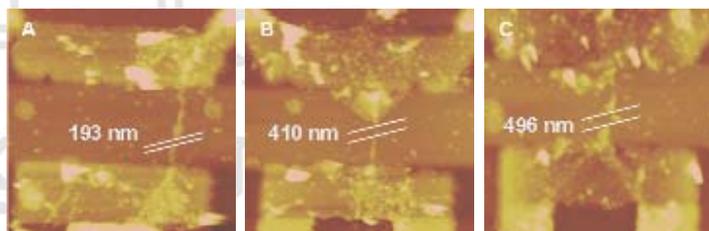
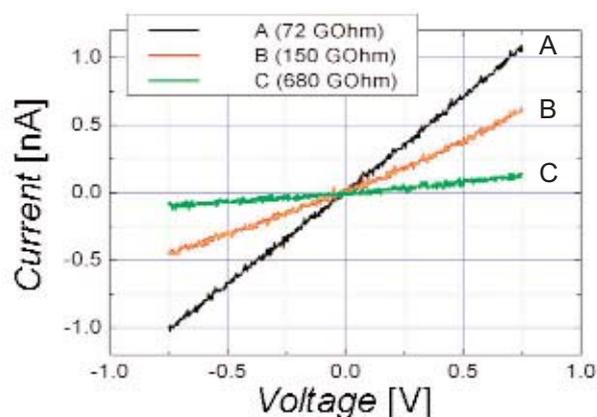


Fig. 2: Conductivity measurement on individual DNA structures (positioned in two-electrode gaps) after metallization with nanoparticles. AFM images (top) of 3 structures with different discontinuity in the metallic chain, and the respective conductivities (right)



wiring was easily accomplished. Low temperature measurements were conducted and yielded Ohmic behavior with high resistances in the GOhm range. However, the resistance correlated with the length of the uncovered DNA stretches. The successful measurement – and especially the ease of electrical access to the molecular structure – demonstrated the suitability of this novel approach.

Ordered assembly of nanoparticles by dielectrophoresis

The integration of molecular structures into microscopic electrode arrays was achieved by dielectrophoresis of gold nanoparticles in electrode gaps. Using microelectrodes realized by photolithography, the generation of pearl chain arrangements of nanoparticles in structures accessible for standard technologies was demonstrated. In order to preserve the individual particle structures in the final nanowire arrangement, several strategies were investigated. An electrical characterization of the pearl chains yielded an Ohmic behavior for this nanowire structure. The destructive effect of increased current on these structures was studied at the ultramicroscopic level. The results demonstrate the application of potential-induced self-assembly of nanostructures into photolithographic pre-structured microelectrode arrangements as another technical contribution to nanotechnology.

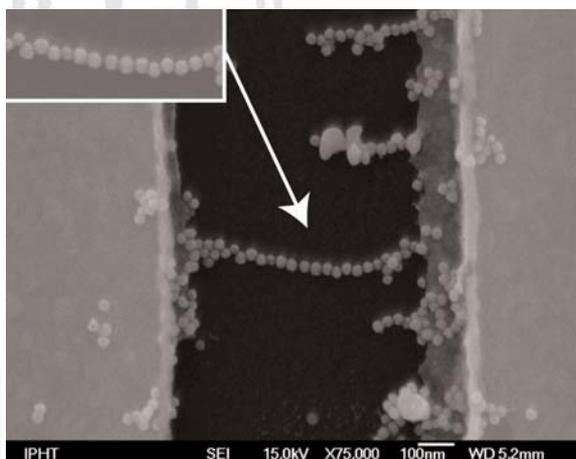


Fig.3: Pearl chain formation of 30 nm gold nanoparticles in a 1 μm microelectrode gap generated by dielectrophoresis

Optics with subwavelength apertures and nanoparticles

Apertures with subwavelength size are of high interest both for the elucidation of nano-optical effects and for

potential application in high (single molecule) sensitivity bioanalytics. Experiments were conducted with arrays of nanoapertures (hole diameter 150 nm, period 1 μm) in metal films fabricated by e-beam lithography. Selected holes were filled with metal nanoparticles, and the array was characterized by optical and ultramicroscopic methods. Aim of the experiments is the correlation of the optical signal with the nanostructure created by this process in order to identify the parameters for significant signal enhancement.

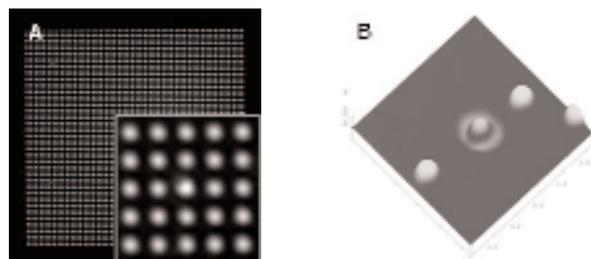


Fig. 4: Subwavelength nanoapertures fabricated in thin metal films. A: Optical micrograph of an aperture array (inset: zoom). B: One aperture (center) filled with a 30 nm nanoparticle, three other particles are also visible. AFM image.

Selected Recent Publications

- [1] G. MAUBACH, D. BORN, A. CSAKI AND W. FRITZSCHE: *Parallel Fabrication of DNA-Aligned Metal Nanostructures in Microelectrode Gaps by a Self-Organization Process*. **Small** 1 (2005), 619-624
- [2] R. KRETSCHMER AND W. FRITZSCHE: *Pearl Chain Formation Of Nanoparticles In Microelectrode Gaps By Dielectrophoresis*. **Langmuir** 20(2004), 11797-11801
- [3] G. MAUBACH AND W. FRITZSCHE: *Precise positioning of individual DNA structures in electrode gaps by self-organization onto guiding microstructures*. **Nano Letters** 4 (2004), 607-611
- [4] A. CSAKI, P. KAPLANEK, R. MÖLLER AND W. FRITZSCHE: *Single particle sensitivity in the optical detection of individual DNA-conjugated nanoparticle after metal enhancement*. **Nanotechnology** 14 (2003), 1262-1268.
- [5] G. MAUBACH, A. CSAKI, R. SEIDEL, M. MERTIG, W. POMPE, D. BORN AND W. FRITZSCHE: *Controlled positioning of a DNA molecule in an electrode setup based on self-assembly and microstructuring*. **Nanotechnology** 14 (2003), 546-550.
- [6] M. URBAN, R. MÖLLER AND W. FRITZSCHE: *A paralleled read-out system for an electrical DNA-hybridization assay based on a microstructured electrode array*. **Review of Scientific Instruments** 74 (2003), 1077-1081.
- [7] A. CSAKI, G. MAUBACH, D. BORN, J. REICHERT AND W. FRITZSCHE: *DNA-based Molecular Nanotechnology (Review)*. **Single Molecule** 3(2002),275-280.

TNT2006

Trends in NanoTechnology

04 - 08 September, 2006 Grenoble (France)

MINATEC and Trends in Nanotechnology Conference series will join forces to organise 2006 event in Grenoble (France)

In response to the growing awareness of the importance of nanotechnology, many workshops, symposia, and conferences are being organised worldwide to discuss the latest advances and future tendencies of this field. Among those, the "**Trends in Nanotechnology**" conference series has become, undoubtedly, a key meeting in Europe.

This high-level scientific meeting series aims, therefore, to present a broad range of current research in Nanoscience and Nanotechnology as well as related policies (European Commission, etc.) or other kind of initiatives (iNANO, IEEE, GDR-E, etc.). **TNT** events have demonstrated that they are particularly effective in transmitting information and establishing contacts among workers in this field. Graduate students fortunate to attend such events quickly learn the importance of interdisciplinary skills, thereby becoming more effective in their future research.

During the **TNT2005** edition, the conference attracted around 370 scientists worldwide and featured ~70 talks, ranging from 15 minutes to 30 minutes. Approximately 250 posters were presented in two sessions. 11 companies also exhibited the latest advances in instrumentation, bibliography, etc.

One of the main objectives of the "**Trends in Nanotechnology**" conference is to provide a platform where young researchers can present their latest works and also interact with high-level scientists. For this purpose, 76 grants (travel bursaries) were available in 2005. In addition 28 prizes (around 8000 Euros) to best student posters were awarded. More than 60 senior scientists were involved in the selection process. Grants and awards were funded by the **TNT** Organisation in collaboration with an increasing number of Research Institutions and Industrials involved in Nanotechnology.

TNT2006 is being launched following the overwhelming success of earlier Nanotechnology Conferences. The **TNT2006** edition will be organised out of Spain for the first time - Grenoble (France) - to emphasise the importance at the European level of the launch of the Centre of Innovation in Micro and Nanotechnology, MINATEC. This centre, to be inaugurated in June 2006, came into existence at the instigation of CEA-LETI Grenoble and Institut National Polytechnique Grenoble and its ambition is to become Europe's top centre for innovation and expertise in micro & nanotechnology. **TNT2006 "Trends in Nanotechnology"** (04-08 September, 2006) will be held in the brand new congress facilities of the Micro & Nanotechnology House within the MINATEC complex.

The **TNT2006** structure will keep the fundamental features of the previous editions, providing a unique opportunity for broad interaction. **TNT2006** will be organised by the following institutions: Phantoms Foundation, Universidad de Oviedo, Universidad Autónoma de Madrid, Consejo Superior de Investigaciones Científicas, Universidad Carlos III de Madrid, Universidad Complutense de Madrid, Donostia International Physics Center, NIMS, University of Purdue, Georgia Tech, CEA-LETI-DRFMC and MINATEC.

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For more info, please visit:
<http://www.tnt2006.org>

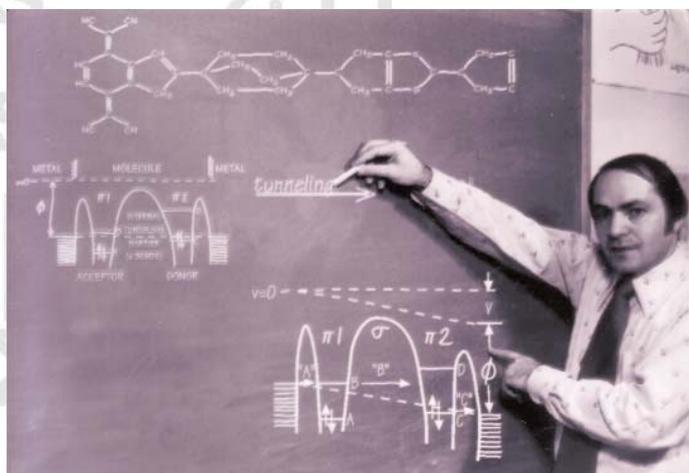
Trends in NanoTechnology

Hybrid and Mono Molecular Electronics

Background before starting the Pico-Inside IST FET European Integrated Project

Christian Joachim (Pico-Inside Coordinator)
CEMES-CNRS (France)

The 1974 seminal Aviram-Ratner paper had created a bridge between electronic circuits for computers and molecules. Ten years before, the relation between cybernetic and biomacromolecules was used by J. Monod in explaining the genetic machinery. The bridge between conducting materials and macromolecules was indicated by StGyorgi 30 years before. We have to appreciate the insight of A. Aviram and M. Ratner in their way to obtain a rectifier with a minimum number of atoms and 2 electrodes. Molecular Electronics was born from the idea that a single molecule will perform the same way a solid state device does with the advantage of its size. 30 years later, Molecular Electronics matures because of the invention of new tools to access electronically to a single molecule (and always the same) during the measurement. This had created an explosion of sub-field in Molecular Electronics from plastic electronics to quantum computing in a single molecule.



At the origin of molecular electronics: Ari Aviram and its molecular rectifier in the 70's

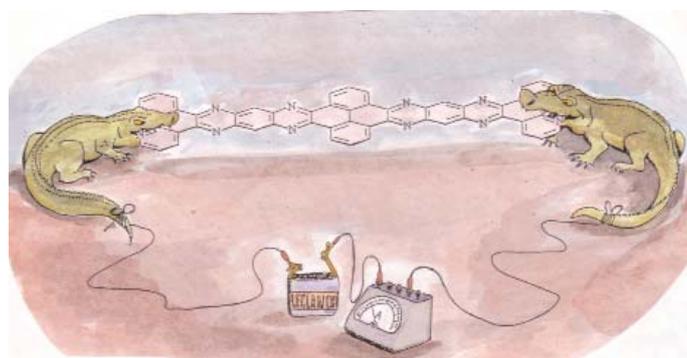
Following up the development of each Molecular Electronics sub-field, the initial concept of A. Aviram and M. Ratner can be pushed at the limits by asking a simple question: What is the minimum number of atoms required to embody a computer? Of course, the same question arises for mechanics machines, for transducer devices and also for communication machineries. But we will limit our analysis to computers. This question calls for a new approach designated by "monumentalization" and opposed to the miniaturization approach of the micro-electronics industry. With miniaturization, the game is clearly to keep an industry growing with production plan and products. Physics, material sciences and technologies follow. With monumentalization, the game is first to built up

epistemological machines at the nanoscale not for sale but for the sake of understanding where are the physical, chemistry and technological limits of a machine like a computer. This is an up limit and not a down limit.

There are many possibilities to embody a computer with molecule(s). (1) take benefit of the quantum answer of a molecule prepared in a non-stationary state to perform a computation. (2) force a molecule to have the spatial shape of a circuit. (3) attribute a particular electronic function to a molecule and interconnect each function (each molecule) with metallic wires. (4) attribute a particular electronic function to a macromolecule and interconnect them too. (5) instead of one molecule per electronic function, fabricate a small film or crystal of such molecules and interconnect each device to shape the electronic circuit. (6) Create a crystal or a plastic and print the electronic circuit on this material as an equivalent to solid state micro-electronics.

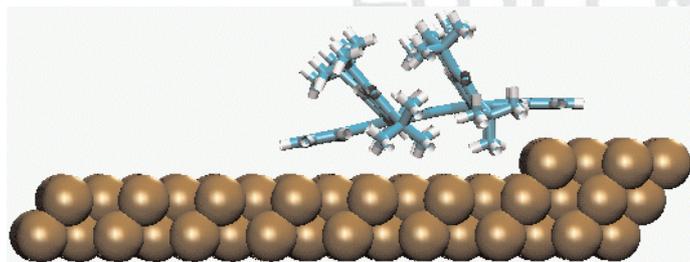
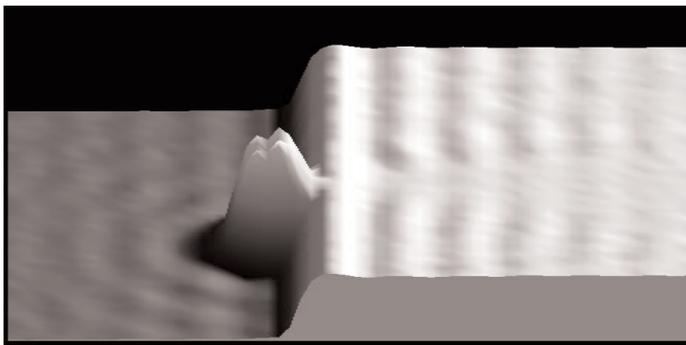
All those possibilities have their advantages in term of technology, material science and performances. We will restrict our description to (1), (2) and (3) which are in directly lineage with the Aviram-Ratner molecular rectifier. Macromolecular electronics (4) with for example carbon nanotubes or semi-conductor nanowires are leading to fantastic devices. But they are too close to the actual solid-state nano-electronics transistor technology to be a valid candidate for exploring monumentalization. The new 2005 integrated project NODE of the European Commission was selected to explore this branch of technology. The 2005 PICO-INSIDE integrated project launched in parallel to NODE under the Emerging Nanoelectronics priority of the IST-FET program will start from (1). It will explore how monumentalization can lead not only to a simple uni-molecular device embarked on a molecule but to a possible large complex computing machine embodies in a single molecule.

An atomic scale technology



At the origin of the alligator clip in molecular electronics: the artistic view of the interconnection problem painted by C. Coudret from CEMES-CNRS in the 90's

At the laboratory scale and common to (1), (2) and (3), there is an urgent technological problem to be solved in Pico-Inside before asking for complexes architectures and production of molecular chips: how to interconnect a molecule to metallic electrodes? A related problem is the



Interconnecting a molecular wire supported by 4 legs to a mono-atomic step edge on Cu(111). Left, LT UHV-STM image of the molecule at contact. Right: determined conformation of this Lander molecule from the experimental left image. (ref: F. Moresco et al., Phys. Rev. Lett., 91, 036601 (2003).

cleanness and precision of the connections. The rush in fabricating co-planar metallic electrode with a separation below 10 nm starts in the early 90's culminating with the nanofabrication of 2 nm junctions 10 years later in the BUN IST-FET project of the fifth framework. This was obtained by pushing e-beam nanolithography to the limit while in the mid 90's alternative solutions like the breaking of a metallic wire or the electro-migration techniques started to be explored.

But connecting a molecule to $N = 2$ or more metallic electrodes means creating an electronic interaction between parts of the molecule and the end surface of the metal electrodes. Therefore, from a surface science point of view, any change of the detail atomic ordering at the surface-end of the electrodes or any change in the adsorption site of the molecule in interaction with the metal will modify the orbital mixing between the metal surface and the molecule. Then, the conductance of the device will change. This is the explanation of so many different results published in the 90's and at the beginning of this century on planar metal-molecule-metal junctions and why, in the best case, statistical analysis of such experiments are needed. Clearly, the solutions for molecular interconnects explored in the 90's were not adapted to an ultra clean demand. In the mid 90's, this point of view was enforced by the first use of UHV-STM to image and contact a single atom and a single molecule in a very reproducible way. As a consequence both the atomic organization of the electrodes and the adsorption site must be mastered with a precision better than 0.05 nm. There is no technology ready yet to achieve such a precision. In PICO-INSIDE, one goal is to explore the possible developments of a new technology called "Atom based technology" for laboratory electrical experiments on a molecule. Ingredients of such a technology are known.

First, the atomic structure and ordering of the surface end of the contact metallic wire must be known. This forbid the use of any resist lithography technique and even of the break junction technology for $N = 2$. For this "pico to nano" interconnection step, an atomic scale technology is not existing in the actual clean rooms and the new nanostencil technique may not be clean enough. In PICO-INSIDE, one solution will be the growth of mesa ultra flat metallic nanocluster. Furthermore, certain well designed molecules can manipulate surface metallic atoms by themselves and will be used to assemble very short atomic wires.

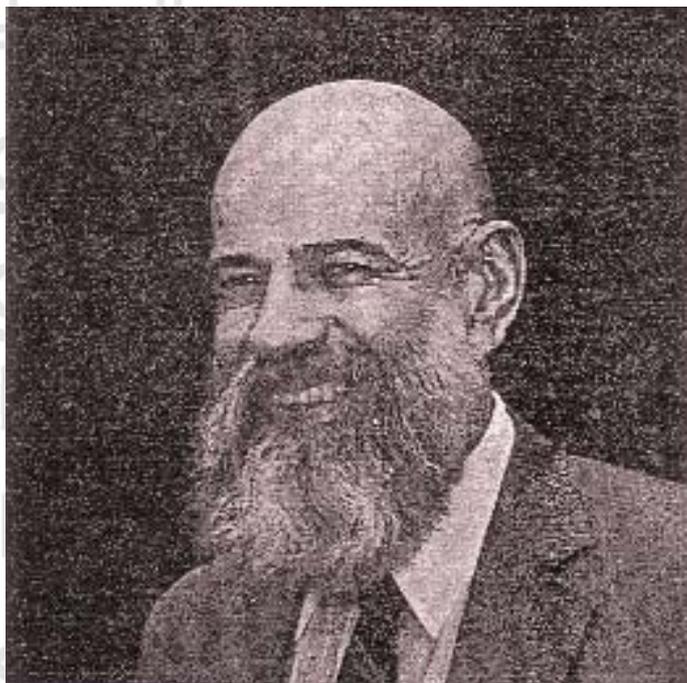
Second, an imaging technique is required to determine the atomic ordering at the interconnections. Scanning tunneling microscope in the UHV (UHV-STM) is very capable of such a characterization for semi-conductor surface and the non-contact Atomic force microscope for plain insulator. An intermediate step is the use of an ultra thin insulating layer on metal. The ultra low feedback loop tunneling current set-up of certain low temperature UHV STM will help in understanding surface science at the atomic scale on insulating surface with a mixture of metallic cluster and organic molecules adsorbates.

Third, after this first atomic scale fabrication, the wiring fabrication technique for the "nano to meso" interconnection step must also be ultra clean. Again, this forbids the use of resist-like nanolithography. This points out the nanostencil technique with a mastering of lateral diffusion through the stencil to limit the spreading of metal atom around.

Fourth, similar to the millipede technology, the "meso to micron scale" interconnection step will be deported on a second surface independent of the active atomic scale precision one. This second floor of interconnect open the possibility to use standard nano and micro-lithography technique and to ultra-clean the device before performing the interconnection step. Relative positioning between the "ground" atomic floor and micro-technology floor is a very interesting technology to be developed in Pico-Inside.

Digital logic in a molecule without circuits

Integrating a full electronic circuit inside a single conjugated molecule with the goal to reduce the fabrication costs and increase reliability was first proposed by F.L. Carter in the 80's. Similarly to the "tyrannies of numbers" met in the 50's by those attempting to wire thousand of electronic devices together, F.L. Carter foresees at the end of the seventies that it will not be possible to wire together millions of discrete molecular devices to assemble a molecular circuit. Then, he proposed to shape the conjugate molecule like an electronic circuit. In our days, there are at least 2 possibilities to embody a logic function inside a molecule: (1) the use of intramolecular quantum time-dependent processes occurring when a molecule is prepared in a non-stationary state (with or without a structuration of the molecule in qubits) and (2) to force the molecule to have the shape of a standard electronic circuit as proposed by F.L. Carter.



Going away from Hybrid molecular electronics: F.L. Carter in the 80's and its mono-molecular analogue to a Nand gate

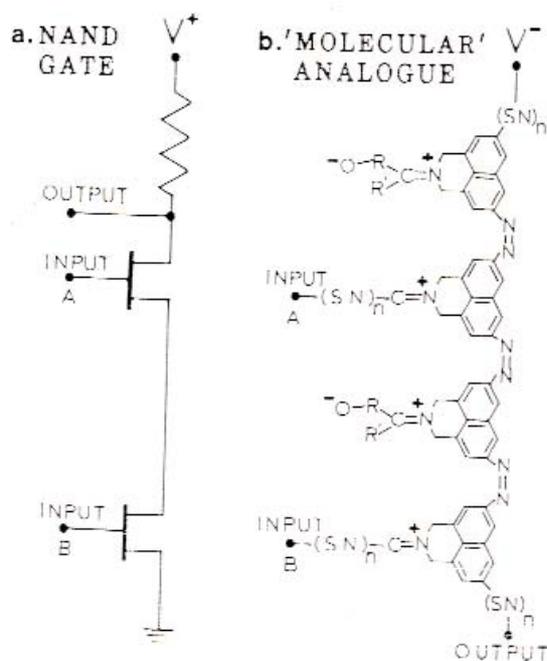
For (1), the goal is to prepare the molecule in a non-stationary state and to optimize the molecular chemical composition in such a way that during the quantum time dependent evolution of this non-stationary state, the quantum trajectory of the molecule in its state space reaches well specified target states according to the initial preparation or to specific conformations of the molecule. This distinction between different initial preparations points out different kind of quantum computing. When the datum defines the initial quantum state, the molecule is structured in qubits and one recover the initial 1984 proposal of R.P. Feynman. When the data are input on the molecule by changing for example the conformation of some small lateral groups, a quantum Hamiltonian computing is implemented. In both cases, the very difficult part of an experimental implementation is the fast intramolecular decoherence of the initial state because of the numerous quantum states weakly coupled to the ones in charge of performing the computation inside the molecule. On the top of that, intramolecular relaxations occur. In such a situation, one has to be fast enough to measure the result or to refresh the initial non-stationary state a lot of time to stabilize the result. This is the quantum Hamiltonian computing (QHC) scheme which is under study in PICO-INSIDE following the fifth framework IST project CHIC (Consortium for Hamiltonian Intramolecular Computing). Spontaneously, a tunnel junction is preparing billions of electron transfer events per second between the electrodes. The data are input on the molecule by changing the conformation of well positioned lateral group around a conjugated board. AND, OR, XOR, NAND and fi Adder molecules have already been optimized and are ready to be tested experimentally according to the above discussion on progresses of an Atom based technology. One advantage of QHC over a qubit like quantum computer approach is that only one molecule is active and the statistic is provided by the quantum measurement performed natively by the tunnel

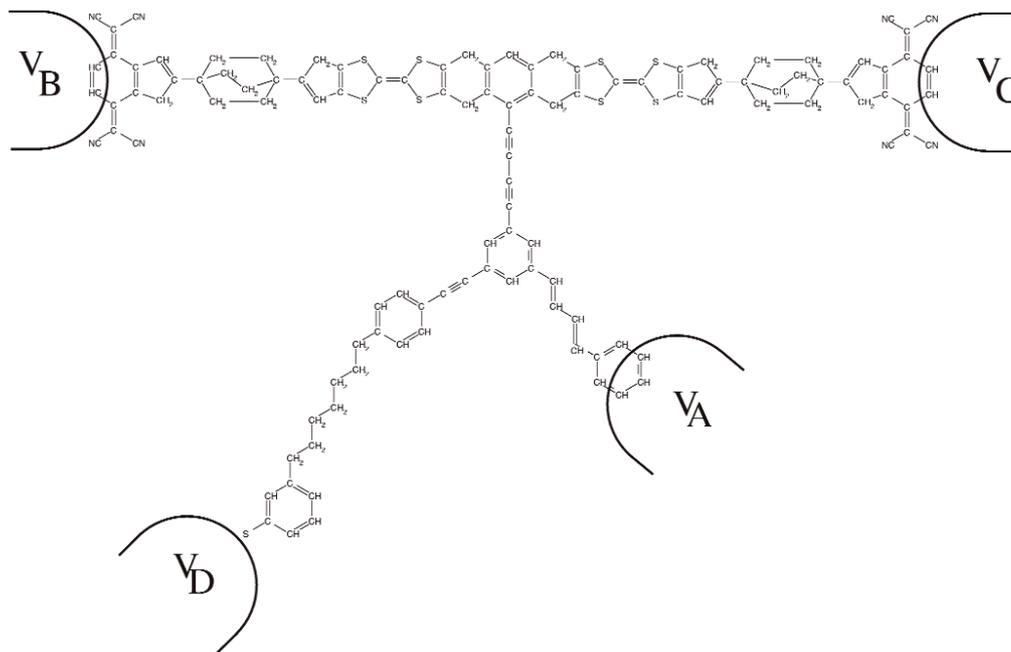
junction. For an NMR like qubit molecular quantum computer approach, the statistic is dependent on the number of active molecules present in solution.

For (2), the molecule must have the real shape of an electrical circuit with all the node and meshes required integrated in a single molecule. In this case, specific intramolecular circuit law are needed because they are different from the standard Kirchhoff node and mesh laws. In the past, a few monumental molecules have been proposed integrating mainly molecular rectifiers groups along the intramolecular circuit. None have been designed according to the specific intramolecular circuit laws. Following those laws, OR-molecules and an AND-molecules have been designed in the BUN IST-FET project. The architecture problem we are facing in Pico-Inside is the native decay of the electronic transparence of a molecular wire group as soon as it is elongated. Tunnel current intensity of the order of a femto-ampere had been calculated for the AND-molecule interconnected between $N = 4$ electrodes. This open a large field of research on how to optimize the architecture of an intramolecular circuit to compensate this secular property. One has to invent chemical groups able to compensate this phenomenon providing some kind of intramolecular gain. At present, all the intramolecular circuits more complicated than the AND-molecule lead to impracticable tunnel current intensity well below the atto-ampere when calculated using the N-ESQC routine developed in BUN.

Molecular board and molecular equipments

The molecular boards supporting the logic function are essentially poly-aromatic like molecules. For (1), qubits separation can be triggered from inside the molecule. For (1), the QHC approach is requiring a full poly-aromaticity to beneficiate from a very fast computation time and to use





A mono-molecular AND gate integrating 2 Aviram Ratner molecular rectifiers groups and a few molecular wire groups to form an intramolecular circuit. The logic response of the molecule was optimized using the N-ESQC code (Ref: S. Ami and All, *Chem. Phys. Lett.*, 367, 662 (2003))

the different symmetry of π molecular levels to play with intramolecular time interferences. For (2), some saturated bonds are required for circuit design purpose to compensate for the exponential decay of the electron transfer rate with an increase of the length of the wire groups required along the intramolecular circuit.

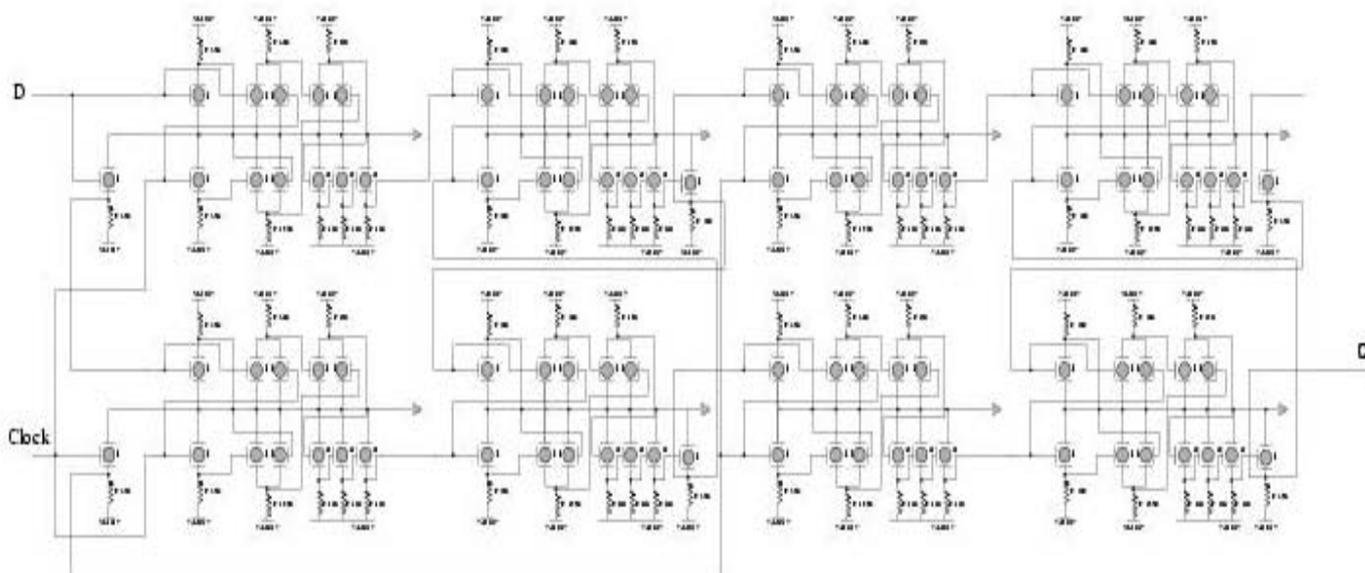
Molecular equipments are the chemical groups required to port the molecular board in a given environment, to protect the digital logic function embarked on the board and to ease user-molecule nano-communication. Molecular legs are very popular on a metal surface to separate the conjugated board from the surface. But other separating groups may be needed on insulating surfaces. Input/output groups can be specific end groups to increase the electronic interaction between a molecular wire and a metallic pads or rotating group to define the logic digital input mechanically. The Pico-Inside chemists will have the heavy task to synthesize those multi-functional and large molecule with the constrain that up to now, only sublimation techniques are suitable to launch and land the molecules on the surface. This deposition technique is very destructive, a real design challenge.

Molecular devices

Substituting each of the solid state devices integrated on the surface of a semi-conductor by a molecule is the hybrid molecular approach (3) mentioned above, in direct lineage with the Aviram-Ratner 1974 seminal paper. Adding one grid electrode to a single molecule properly interconnected between 2 metallic electrodes may lead to a transistor like behavior. There are many possible parameters to be controlled to obtain a molecular device presenting a power gain: the electronic coupling between the molecule and the source-drain electrodes, the homo-lumo

gap of the molecule or the position of the energy level of the molecule relative to the electrode Fermi level. Shifting a few molecular levels by a lateral electric field applied via the grid electrode had long been advocated. But the range of electric field where a power gain can show up is not yet accessible experimentally: the electric field required is so large for the molecule design up to now that the breakdown limit of the metal-molecule-metal junction is reached before gain. Of course, a lot of 3 electrodes structure with a molecule in the nanojunction have been proposed and experimented. But their transconductance is so low that no gain will result while loading the device with an external resistor. A variant of this set-up is to perform an electrochemical experiment where the molecular levels are controlled relative to a reference electrode using an electrolyte. Here, the grid is no more on scale with the molecule.

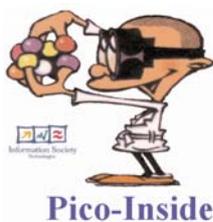
One solution to this problem was to control the closure of the homo-lumo gap of a molecule positioned between the source and the drain of a tunnel junction by a mechanical deformation. The original experiment was performed in 1997 on a single C60 molecule trapped in the tunneling junction of an STM. A small deformation of the C60 cage provides a large variation of the metal-C60-metal junction conductance leading to power gain. This was a proof of concept that a single molecule-device can provide gain by using the intrinsic electronic property of a single molecule. For C60, the 5 fold degeneracy of its Homo and 3-fold of its lumo are creating a nice destructive interference effect whose matching is cancelled by a compression of the molecule by the tip. This is a perfect example of a pure intramolecular electron transfer quantum phenomenon converted in a measurable tunnel current by the interaction of the molecule with the electrodes. A full planar version of this device had been proposed and its performance simulated in BUN. A full electrical circuit was established and included in a SPICE circuit simulator to evaluate the performances of a complete ALU up to 1000 C60 transistors. Aside from the real difficulties to find a technology to fabricate such a molecular circuit, the gain in miniaturization is not exceptional since each C60 transistor need a minimum separation distance of a few ten of nanometer for the Kirchhoff electrical circuit node and mesh laws to be applicable. In comparison to the gigantic progress of solid state nano-electronics, the future progress margin of hybrid molecular electronics is not very clear. This is the explanation why Pico-Inside was organized remaining away from this Hybrid approach.



A full D latch hybrid molecular electronic circuit using 94 single molecule C60 transistors in a co-planar configuration whose time-dependant response had been simulated using SPICE (R. Staddler and All., *Nanotechnology*, 12, 350 (2001)).

Starting Pico-Inside

Pico-Inside is a 3 years integrated project whose partnership is explained below. The Pico-Insiders have all decided to explore the monumentalization of a calculating unit up to the limits imposed by physics, chemistry and technology. Atomic scale technology is a very challenging path to be explored. But architecture, surface science (both experimental and theoretical) and chemistry figure also on the agenda. Pico-Insiders have to determine if a single unique molecule can compute and communicate its results to the macroscopic level.



Further reading

- BUN IST-FET final Report:
<http://www.phantomsnet.net/Enano/euprojectreports.php>
- CHIC IST-FET Project:
<http://www.cemes.fr/chic/>
- Pico-Inside IST-FET project:
<http://www.picoinside.org>
- C.JOACHIM, J. K. GIMZEWSKI AND A. AVIRAM, *Nature*,408, 541 (2000)
- Molecular Electronics, **Special issue of the Proceeding National Academy of Science, USA, 102 n°25, June 21 (2005)**

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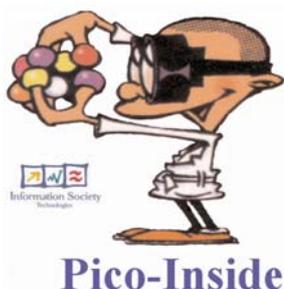


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Pico-Inside: Summary, Objectives and Partners

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

Below are detailed a summary of the project objectives (more info available at <http://www.picoinside.org>) and a list of the partners involved.



In 3 years, Pico-inside will develop:

- (1) the architecture,
- (2) the atomic scale technology and
- (3) the chemistry to explore and quantify intramolecular resources for integrating much more than a single logic gate inside a single molecule.

Five very recent breakthroughs are fully exploited by Pico-Insiders.

- (1) The theoretical demonstration that intramolecular quantum evolution based on the nonstationary mixing of large molecule quantum states can perform digital operations.
- (2) The new intramolecular mesh and node circuit rules for large molecules whose internal chemical structure is similar to a standard electronic circuit architecture.
- (3) The experimental demonstration that the electronic contact between a single molecular wire and its contacting atomic pad requires 0.05 nm precision.
- (4) The atomic resolution now obtained by a non-contact UHV-AFM on insulating surfaces and by low temperature UHV-STM on insulator on metal systems.
- (5) the progresses of organic chemists to design and synthesise large multi-functional molecules adapted to surface performances at the atomic scale.

Pico-Inside integrates the necessary groups to explore new architecture concepts with Fujitsu Europe. LT-UHV-STM and NC-UHV AFM offer a complete and true access to the atomic scale for interconnects with Omicron. This includes nano-stencil contact experiments, the necessary chemistry labs task force and the required theoretical group to support the architecture, the molecular design and the analysis of Pico-Inside nanoscale experiments. This integration is completed by a true will to create and diffuse original roadmaps to a large community around Pico-Inside towards mono-molecular computing and atomic scale technologies.

Pico-Inside Partners:

- P1.1** Centre d'Elaboration des Matériaux et d'Etudes structurales - CEMES/CNRS (France)
P1.2 Laboratoire de Physique Théorique de la Matière Condensée / CNRS (France)
P1.3 Laboratoire de Photophysique Moléculaire / CNRS (France)
P2 Fujitsu Europe (France)
P3 Frei Universität Berlin (Germany)
P4 Jagiellonian University (Poland)
P5 Universität Osnabrück (Germany)
P6 Aarhus Universitet (Denmark)
P7 Universität Basel (Switzerland)
P8 Omicron GmbH (Germany)
P9 Institute of Organic Chemistry and Biochemistry (Czech Rep.)
P10 Institute of Chemical Research of Catalonia - ICIQ (Spain)
P11 King's College London (UK)
P12 University College London - UCL (UK)
P13 Phantoms Foundation (Spain)

P1.1

Research group / Company:

GNS-CEMES/CNRS

Contact Person & E-mail:

joachim@cemes.fr, gourdon@cemes.fr,
gauthier@cemes.fr

Nano Activities:

Design and synthesis of uni-molecular machines, intramolecular logic gates
ESQC STM image interpretation, intramolecular circuit theory, UHV Nanostencil

Pico Activities:

LT-UHV-STM, 5 pm noise
Contact conductance optimisation with a precision better than 0.05 nm

Core Competences:

Molecular design and synthesis, UHV-STM, NC-AFM
Nanostencil

Equipment:

2 UHV-STM, LT-UHV STM, NC-AFM

WEB site:

<http://www.cemes.fr/GNS/>

P1.2

Research group / Company:

Laboratoire de physique théorique de la matière condensée, Université Pierre et Marie Curie et CNRS Paris, France

Contact Person & E-mail:

Rémy Mosseri, mosseri@ccr.jussieu.fr

Core Competences:

Theory: solid state physics - quantum information

Equipment:

Computers

WEB site:

<http://www.lptl.jussieu.fr/>

P1.3

Research group / Company:

Molecular nanoscience group, Laboratoire de Photophysique Moléculaire (Orsay), France

Contact person:

Dr. G erald Dujardin, Gerald.dujardin@ppm.u-psud.fr

Pico activities:

Local electronic excitation of single molecules and nanocrystals by using STM, conducting AFM and combined laser+STM. Electronic control of dynamics and luminescence of individual molecules and nanocrystals.

Picometer-scale electronic control of molecular dynamics inside a single molecule

M. Lastapis, M. Martin, D. Riedel, L. Hellner, G. Comtet, G. Dujardin Science 308, 1000 (2005)

Core competences:

STM, AFM and Laser+STM manipulations of individual molecules and nanocrystals. Atomic-scale studies on wide band gap semiconductor surfaces. Molecular nano-machines, movement and luminescence.

Equipment:

UHV room temperature STM, UHV variable temperature STM, UHV low temperature (5K) STM, laser+STM, air AFM.

Web site:

<http://voyager.ppm.u-psud.fr/nanophysics/nanophysics.html>

P02

Research group / Company:

Fujitsu Systems Europe, France

Contact Person & E-mail:

Pierre Lagier - pierre.lagier@fujitsu.fr

Jean Latour - jean.latour@fujitsu.fr

Nano Activities:

Image synthesis, architecture

Pico Activities:

Architectures for mono-molecular electronics

Chemistry

Core Competences:

computer science, physics

Equipment:

Computers

WEB site:

<http://www.fujitsu.com>

P03

Research group / Company:

Institut fuer Experimentalphysik, Freie Universitaet Berlin

Contact Person & E-mail:

Francesca Moresco, francesca.moresco@physik.fu-berlin.de

Pico Activities:

Manipulation of single molecule on metal surfaces.

Contacting single molecules between nanoelectrodes.

Core Competences:

Low Temperature STM, manipulation of atoms and molecules

Equipment:

Scanning Tunneling Microscopes working at 5K

WEB site:

<http://www.physik.fu-berlin.de/~ag-rieder/LT-STM2>

P04

Research group/Company:

Centre for Nanometer-scale Science and Advanced Materials (NANOSAM) at the Institute of Physics, Jagiellonian University, Krakow, Poland

Contact Person & E-mail:

Prof. Marek Szymonski, ufszymon@cyf-kr.edu.pl

PicoInside activities:

UHV-STM on semiconducting surfaces; UHV-NC AFM on semiconducting and bulk insulator surfaces; Metallurgy of nanoscopic mesa pads

Core Competences:

Preparation and investigation of surfaces of III-V semiconductors and ionic insulators, preparation of insulator/metal thin films/nanostructures on semiconductors, NC-AFM, ion/electron induced desorption/sputtering

Equipment:

UHV STM/NCAFM, UHV LT-STM, AES, LEED, XPS, SNMS, QMS, multi-technique surface analysis and MBE systems, ambient AFM/STM microscopes

Web site:

<http://www.if.uj.edu.pl/NANOSAM/>

P05

Research group / Company:

NanoScience / Universit at Osnabr uck

Contact Person & E-mail:

Michael Reichling, reichling@uos.de

Nano Activities:

Imaging and manipulation of molecular assemblies and ultra-thin films

Pico Activities:

Characterization and manipulation of internal molecular structures and conformation

Characterization of the bonding of molecules to substrates and contacts

Core Competences:

Atomic resolution force microscopy

Imaging and manipulation of insulating surfaces and nanostructures

Imaging and manipulation of molecules and ultra-thin films

Equipment:

Ultra-high vacuum force microscopes operated at Room temperature, variable temperature and cryogenic temperature

WEB site:

<http://reichling.physik.uos.de/>

P06

Research group / Company:

SPM group, Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Denmark

Contact Person & E-mail:

Flemming Besenbacher, fbe@inano.dk

Nano Activities:

Development of High resolution Scanning Probe Microscopes.

SPM studies of molecular adsorption and self-assembly, heterogenous catalysis and metal growth.

Development of biosensors and biocompatible implants.

Pico Activities:

Studies of organic molecules on surfaces with Scanning Tunneling Microscopy under Ultra-high vacuum conditions

Core Competences:

Development of Scanning Tunneling Microscopes; Surface Science; Nucleation and Growth of metallic and molecular nanostructures at surfaces; Heterogeneous catalysis; Bio-molecular adsorption; Biosensors; biocompatibility.

Equipment:

8 UHV setups equipped with variable temperature STM/AFMs and auxiliary techniques.

4 Liquid phase afm/stm's.

QCM and SPR set-ups.

WEB site:

<http://www.inano.dk> and www.phys.au.dk/camp

P07**Research group / Company:**

UHV-AFM (Ernst Meyer group) Universitaet Basel

Contact Person & E-mail:

Prof. Ernst Meyer Ernst.Meyer@unibas.ch

Pico Activities:

Unit 3: Atomic scale technology (E. Meyer)

Equipment:

UHV- AFM

WEB site:

<http://monet.physik.unibas.ch/gue/uhvafm/>

P08**Research group/Company:**

Omicron NanoTechnology GmbH

Contact Person & E-mail:

Dr. Albrecht Feltz, a.feltz@omicron.de

Nano Activities:

Development of analytical instruments for Nano Technology

Development of Scanning Probe Microscopes

Development of 4 point Nano Probers

Development of sensors and detectors

Pico Activities:

Development of AFM sensing technology for low temperature AFM and nano structuring

Development of instrument control software for nano structuring and atomic/molecular manipulation

Core Competences:

Team with high experience and skills in Scanning Probe Microscopes

Instrument design for ultimate resolution

Ultra high vacuum technology

Capabilities for multi technique integrations thin film growth, e-beam lithography, focussed ion beam,

Electron spectroscopy, scanning auger microscopy, scanning probe microscopy, nano probing

Instruments for characterisation of nanostructures and devices

Equipment:

Scanning probe microscopes in UHV

SEM in UHV

Instrument and system manufacturing

WEB site:

<http://www.omicron.de>

www.phantomsnet.net

P09**Research group / Company:**

Group of Organic Synthesis / Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic

Contact Person & E-mail:

Dr. Irena G. Stara, stara@uochb.cas.cz

Core Competences:

Organic synthesis of complex aromatic systems

Equipment:

Laboratory equipment and analytical instruments for organic synthesis

WEB site:

<http://www.uochb.cas.cz/~organic/>

P10**Research group / Company:**

Institute of Chemical Research of Catalonia (ICIQ)

Contact Person & E-mail:

Antonio M. Echavarren, aechavarren@icq.es

Nano Activities:

Design and synthesis of large polyarenes

Pico Activities:

Synthesis of functionalized polycyclic aromatic and heteroaromatic hydrocarbons

Core Competences:

Organic and organometallic synthesis and structural characterization

Equipment:

High field NMR, mass spectrometry, X-ray crystallography

WEB site:

http://www.iciq.es/english/grups_eng/echevarren/entrada.htm

P11**Research group / Company:**

King's College London, Physics Department

Contact Person & E-mail:

Lev Kantorovich, lev.kantorovitch@kcl.ac.uk

Nano Activities:

Theory of AFM atomic scale imaging, both topography and dissipation

Manipulation of C60 on Si(001) surface

Ab initio modelling of molecules on crystal surfaces

Pico Activities:

Ab initio modelling of molecules on crystal surfaces

Core Competences:

Ab initio modelling including DFT methods; AFM theory; non-equilibrium statistical mechanics; theory of defects in solids and on surfaces; embedding methods

Equipment:

2 Beowulf clusters with Dolphin connections: 8 and 16 dual nodes

WEB site:

http://www.kcl.ac.uk/kis/schools/phys_eng/physics/people/lev.html

P12

Research group / Company:

London Centre for Nanotechnology, University College London

Contact Person & E-mail:

Professor Alexander Shluger, a.shluger@ucl.ac.uk

Nano Activities:

Modelling of defect structure and defect processes in gate oxide materials for nano-CMOS devices; modelling of contrast formation in Atomic Force Microscopy on insulating surfaces; theoretical studies of the mechanisms of manipulation of nano-structures (clusters and molecules) at insulating surfaces; modelling of adsorption and diffusion of molecular species at insulating surfaces; mechanisms of photo-induced processes in nano-clusters.

Pico Activities:

Adsorption, structure, diffusion and manipulation of prototype molecules for molecular electronic devices at insulating substrates; effect of current and charging on the structure, stability and diffusion of adsorbed molecules.

Core competences:

Development and application of computational methods for theoretical modelling of atomic and electronic processes in the bulk and at surfaces of insulators.

Equipment:

Computers

WEB site:

<http://www.cmmmp.ucl.ac.uk/>

P13

Research group / Company:

Phantoms Foundation

Contact Person & E-mail:

Dr. Antonio Correia, antonio@phantomsnet.net

Core Competences:

Nanoelectronics

Team with high experience and skills in project management and scientific conference organisation

WEB site:

<http://www.phantomsnet.net>

For more information about Pico-Inside Project, please visit the related web site at: <http://www.picoinside.org>

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MONA EU funded project to coordinate optics and nanotechnology research [03-10-2005]

A new IST project has been launched that will contribute to the coordination of research in photonics and nanotechnologies

Nanophotonics & Nano-Optoelectronics

MINATEC and Trends in Nanotechnology Conference series will join forces to organise 2006 event in Grenoble (France) [28-09-2005]

TNT2006 (www.tnt2006.org) is being launched following the overwhelming success of earlier Nanotechnology Conferences. The TNT2006 edition will be organised out of Spain for the first time - Grenoble (France) - to emphasise the importance at the European level of the launch of the Centre of Innovation in Micro and Nanotechnology, MINATEC.

Nanoelectronics, Nanobiotechnology, Scientific Policy

CEA initiates the first French nanobiotech cluster in Grenoble [28-09-2005]

CEA announces the creation of the first French nanobiotechnology cluster. The official launch was made on September 9th with the signature of a real estate operation dedicated to host new equipments and research teams in Grenoble close to the Minatec facilities.

Nanobiotechnology

Detailed plans for implementing the Seventh Framework Programme (FP7) [22-09-2005]

On 21 September 2005 the European Commission approved its detailed plans for implementing the Seventh Framework Programme (FP7). Provisional versions of the Specific Programmes - the four pillars of Cooperation, Ideas, People and Capacities, as well as research under Euratom and by the JRC under Euratom and EC treaties - are now available.

Scientific Policy

Measuring Nanotube's Conductivity [06-09-2005]

Hongjie Dai and his colleagues at Stanford have made the first electrical measurements of currents flowing under high voltage (high bias) through single-walled carbon nanotubes suspended like miniature power lines.

Nanotubes

Launch of the European Technology Platform on NanoMedicine [06-09-2005]

NanoMedicine is defined as the application of Nanotechnology to Health. It exploits the improved and often novel physical, chemical, and biological properties of materials at the nanometric scale. NanoMedicine has potential impact on the prevention, early and reliable diagnosis and treatment of diseases.

Nanomedicine, Scientific Policy

Intel Drives Moore's Law Forward With 65 Nanometer Process Technology [30-08-2005]

A significant milestone in developing next-generation chip manufacturing technology has been achieved by Intel Corporation. The company has built fully functional 70-megabit static random access memory (SRAM) chips with more than half a billion transistors using the world's most advanced 65 nanometer (nm) process technology.

Nanoelectronics, Nanofabrication

Boosting Europe's semiconductor research [18-08-2005]

Though Europe's top semiconductor research centres are separated by hundreds of miles they could unite in a vast, distributed R&D network thanks to the work of a EU-funded project.

Nanosensors & Nanodevices, Scientific Policy

EU funded projects resulting from the Emerging Nanoelectronics Call [14-08-2005]

The FET "Nano" 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.

Nanoelectronics, Molecular Electronics, Scientific Policy

Contacting single molecules [11-08-2005]

The field of molecular electronics has so far developed relatively slowly. But now researchers at the Weizmann Institute of Science (Israel) have come up with a method for contacting single molecules more reliably.

Molecular Electronics

Templates yield nano branches [10-08-2005]

Researchers from Rensselaer Polytechnic Institute have devised a way to make highly branched nanostructures from many different types of materials.

Molecular Electronics, Nanotubes, Nanofabrication

Carbon nanotubes sort themselves out [09-08-2005]

Researchers have come up with a technique that could sort carbon nanotubes according to their length. Applying a shear stress to a suspension of multiwalled carbon nanotubes caused shorter tubes to move towards the walls while longer tubes headed for the middle of the container.

Nanotubes

Nanolithography Impact [04-08-2005]

Nanolithography offers an economical, high-resolution alternative to EUV and next-generation lithography.

Nanofabrication, Nanolithography, Nanoimprint

(November 2005)**NanoSolutions 2005**

8-10 November 2005

Köln, Germany

<http://www.nanosolutions-cologne.com>**2nd International Symposium on Nanotechnology in Construction**

13-16 November 2005

Bilbao, Bizkaia, Spain

<http://www.mmsconferencing.com/nanoc/>**Veeco UK Scanning Probe Microscopy Conference and User Meeting**

22-23 November 2005

Oxford, Oxfordshire, United Kingdom

<http://www.veeco-europe.com/others.news.users-meetings.102.cescreen>**BioNanoMAT: Bioinspired Nanomaterials for Medicine and Technologies**

23-24 November 2005

Marl, Germany

<http://events.dechema.de/bionanomat.html>**(December 2005)****International Symposium on Molecular Electronics**

05-06 December 2005

Tsukuba, Japan

<http://www.nanoworld.jp/mole/index.php>**Micro and Nanotechnology 2005 (MNT 05)**

12-14 December 2005

London, United Kingdom

<http://www.iom3.org/events/mnt2005.htm>**Towards Molecular Electronics: 5th International Conference on Advanced Materials and Nanotechnology**

12-17 December 2005

Srem, Poland

<http://main2.amu.edu.pl/~tme/>**European Nano Systems 2005**

14-16 December 2005

Paris, France

<http://tima.imag.fr/conferences/ENS/>**Second Meeting on Molecular Electronic Elec mol'05**

19-21 December, 2005

Grenoble Joseph Fourier University (France)

<http://www.elecmol.org/>**(January 2006)****NanoSingapore 2006: IEEE Conference on Emerging Technologies – Nanoelectronics**

10-13 January, 2006

Singapore

<http://www.ieeecet.org/>

Post-doctoral Position: "Functional Polymers within Organic and Biomolecular Electronics"

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More information on the announced position could be given by professor Olle Inganäs, e-mail: ois@ifm.liu.se, tel. no. +46 13 28 12 31. The union representative is Per Larsson (SACO), e-mail perla@ikp.liu.se, tel. no. +46 708 28 11 02.

The application should be sent to Linköpings universitet, IFM, Ingmarie Åkesson, SE-581 83 Linköping, Sweden.

10 PhD Positions: "CHEMTRONICS - Chemistry and Nanoelectronics"

This training project for 10 PhD students during 3 years, in the frame of the MINATEC innovation center (Grenoble, France), will allow a better coupling both between chemistry and nanoelectronics and between scientific and technological research. It will favour a multicultural approach so that experts, researchers, engineers and students can run or take part to multidisciplinary projects, which are crucial for the future of nanoelectronics.

To get additional information, please send a mail to : helene.ulmer@cea.fr. To apply, please send a CV, a letter of motivation, two letters of recommendation, a copy of the last diploma, and a list of publications.

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Department of Engineering Materials, University of Sheffield

Fully funded PhD project studentships are available for immediate application, inclusive of overseas candidates, with any start date between now and 1st Jan 2006.

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Please send your CV and statement of interests plus name of at least 2 referees to

Dr G Moebus, g.moebus@sheffield.ac.uk,

Dept of Engineering Materials, University of Sheffield, Sheffield S1 3JD, UK.

The Sheffield University prospectus can be found on <http://www.sheffield.ac.uk/apply/research.html>

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The applicants should have a PhD in chemistry, chemical physics, materials science, or experimental condensed-matter physics.

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Dr. Dario Pisignano

National Nanotechnology Laboratory CNR- INFM - Universita' di Lecce

c/o Palazzine Garrisi; via Arnesano - I-73100 Lecce (Italy)

Phone +39 0832298146

FAX +39 0832298238

E-mail dario.pisignano@unile.it

CNTs Attached to AFM microcantilevers and STM Tips

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W. Lafayette IN 47907 (USA)

Abstract. Carbon nanotubes attached to STM and AFM tips are considered advantageous for applications in scanning probe microscopy for several reasons; they have a small apex radius, a large length to diameter aspect ratio, a well defined atomic configuration and significant bending flexibility. This article is a short summary of the work we have performed to learn more about the advantages and limitations that these novel scanning probes might offer.

Keywords: Carbon Nanotubes, AFM, STM, SPM, field emission

Introduction

The use of sharp tips to probe locally the properties of substrates has received increased attention since the invention of the Scanning Tunnelling Microscope (STM) and Atomic Force Microscope (AFM). The search for better probe tips to enhance information from scanning probe instruments is ongoing and well-established standards to assess more accurately probe performance are clearly needed. While most conventional probe tips are chemically etched or lithographically fabricated, carbon nanotubes (CNTs) attached to either STM or AFM tips are an important new class of probes. In addition to their small apex radius, the large length to diameter ratio of CNTs provides a unique advantage that more conventional scanning probes do not possess. Not surprisingly, attempts to exploit the unique geometric properties of CNTs have led to many studies of their properties. In what follows, we briefly summarize a number of studies conducted during the past five years to investigate what advantages, if any, that probes made from CNTs might offer.

In order to perform a variety of different experiments, simple techniques to attach multi-walled CNTs (MWCNTs) to STM and AFM tips are required. Our focus has been largely on multi-walled nanotubes because their multiple concentric shells offer a number of inherent advantages over single-walled CNTs (SWNTs). While learning how to manipulate and position CNTs for transport measurements,[1,2,3] we have developed a variety of techniques using nanomanipulators and dark field microscopy to select and attach MWCNTs to field emission, AFM, and STM tips. By applying a bias voltage between a MWCNT and a nearby substrate during the manipulation process, the length of a MWCNT can be trimmed to a desired length. In other studies, CNTs have been grown on AFM tips either by the deposition of post-synthetic CNTs

through dielectrophoresis[4] or by the growth of low density, individually separated MWCNTs by chemical vapour deposition [5]. Subsequent SEM and TEM studies have been typically used to more precisely measure the length and diameter of the probe tips prepared.

In what follows, we summarize a few of the salient results obtained from these studies of CNT probes in such diverse areas as electron emission, tapping mode dynamics, novel sensing applications, and AFM imaging artefacts. We make no attempt to survey or critique the existing literature, since this information can be found in the relevant publications. While a rapid and reliable manufacturing process has not yet been developed, the prototypical studies undertaken so far indicate a number of novel and unexpected properties directly attributed to the CNT tips.

1. Electron Emission from CNTs

Perhaps the most obvious advantage of conducting CNTs is the enhancement of the electric field at the apex of the CNT due to the large length to diameter ratio. The implications of this geometrical shape factor for electron field emission are significant and imply that small applied voltages will produce large electric fields at the apex of a protruding CNT. It is therefore not surprising that a number of studies of the electron emission characteristics of CNTs have been performed.

Studies were conducted to measure the electron energy distribution of electrons emitted from rope of SWNTs attached to a tungsten tip.[6] By measuring the distribution of emitted electrons as a function of energy, information about density-of-state features inherent in the emitting tip can be obtained. In addition, time-tested theories predicting the shape of the emitted distribution of electrons in terms of the field strength and work function of the emitting surface are already available in the literature.

In our work, a standard probe-hole technique was employed in which the entrance to an electron energy analyzer was situated behind a small probe hole in a fluorescent screen. By viewing the emitted field emission pattern on the fluorescent screen, it was possible to steer electrons from the CNT through the probe hole for energy-resolved analysis. The CNTs under study were simply attached to W tips using the vdW force of attraction. Confirmation that electron emission from the sharp apex of the CNT tip was achieved by the significant field emission current obtained at low applied voltages (approximately a factor of 30 lower than required to obtain emission from a sharp, thermally annealed W tip). Subsequent TEM studies conducted after the electron emission experiments showed that the emitting CNT was a rope of CNTs having an outer diameter of ~17 nm.

As shown in Figure 1, the measured energy distribution could be well explained by a free electron model, with two small features evident at well-defined energies below E_F . Further studies using field-ion microscopy (FIM) to image the emitting atoms at the end of the CNT were also performed.

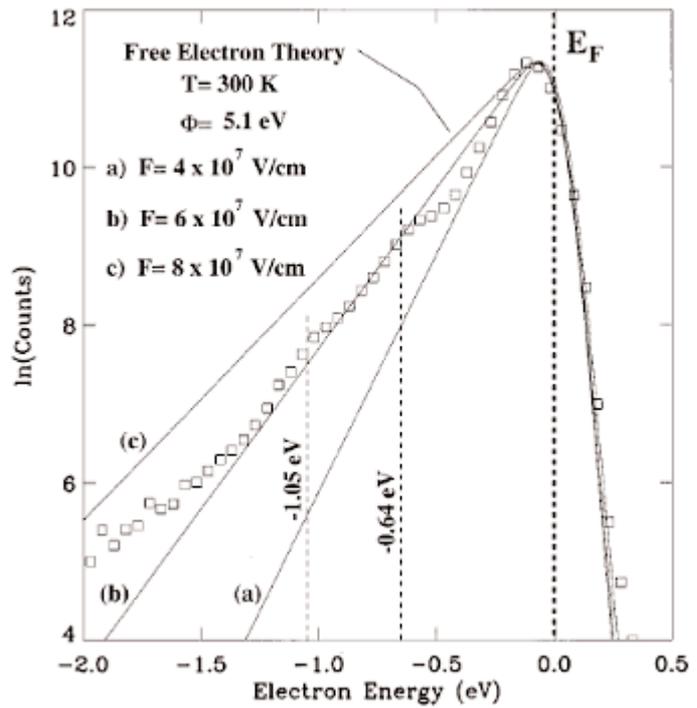
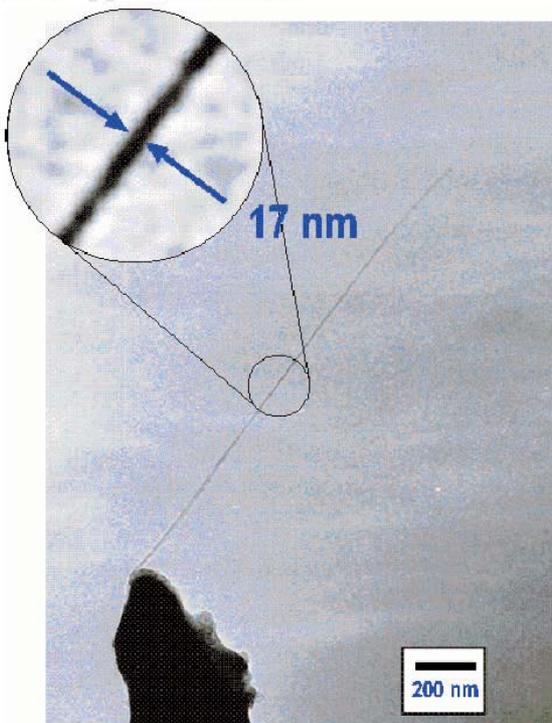


Figure 1: [a] A TEM photo of a rope of single wall carbon nanotubes attached to a tip. [b] The measured field emission total energy distribution (at room temperature) from the end of the carbon nanotube tip with respect to the Fermi energy. The solid line is a fit using a free electron theory. From Ref. [6].

2. CNTs attached to AFM tips – characterizing dynamical behaviour in Scanning Probe Microscope applications

A special configuration of an AFM system was assembled to investigate the static force vs. distance curve from a long (~7.5 mm long, 10 nm diameter) MWCNT attached to an AFM tip. The results of the experiment showed evidence that both buckling and slipping of the MWCNT play important roles in describing the tip-substrate interaction.[7,8] The results of a particularly informative experiment are plotted in Figure 2 which shows how the force on a cantilever varies as the CNT tip-substrate separation distance is systematically varied.

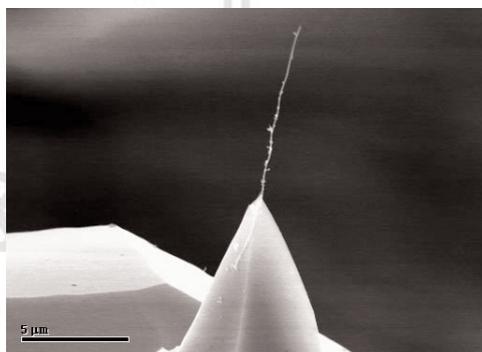
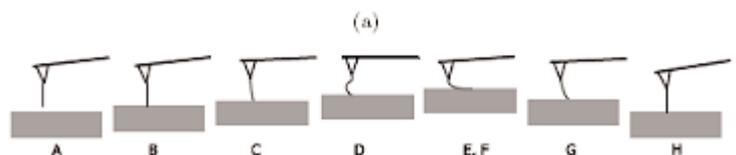
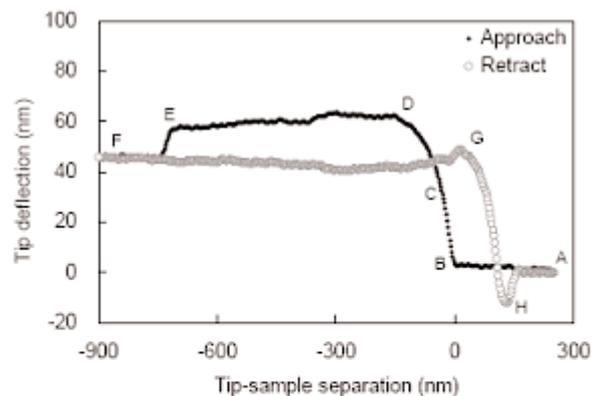


Figure 2: [a] A SEM photo of an AFM tip with a multiwalled carbon nanotube attached. The nanotube is ~7.5 mm long. [b] The resulting force vs. distance behavior measured for the carbon nanotube shown in [a]. The data reveal two significant features. The feature marked D is interpreted as a buckling of the nanotube. The feature marked E is interpreted as slipping of the nanotube across the substrate after ~800 nm of deflection. From Ref. [7].

As the CNT tip approaches the substrate (from A to F), the cantilever shows a snap into contact at B followed by a linear deflection from point B to C as the CNT pushes against the substrate. From point C the cantilever exhibits a highly non-linear deflection with increasing z displacement, indicating the onset of a buckling of the MWCNT tip. The nearly constant cantilever deflection beyond point D indicates that the deformation is directed into MWCNT buckling rather than producing additional cantilever deflection. Beyond Point E (after ~800 nm of deflection), there is a sudden decrease in deflection, suggesting that the MWCNT has slipped on the HOPG substrate.

As the tip is retracted (F→G→H→A), the high adhesive forces between the bent MWCNT sidewall and



the substrate ensures that the cantilever deflection remains nearly constant from F to G. From G to H the static force distance curve is similar to that during approach from B to D, albeit in the reverse order. Due to thermal drifts in the z position, the data between B to D and G to H do not exactly coincide. This static force vs. distance data were repeated several times with similar qualitative and quantitative results.

We have shown that the static force distance curve described here influences directly the dynamic behaviour in Tapping Mode AFM using this tip [7,8]. In particular we have demonstrated using theoretical models and careful experiments that the co-existence of attractive and repulsive regime imaging is strongly correlated to the buckling properties of the CNT tip. Because the buckling properties of CNT's are strongly influenced by their lengths, we are in the process of systematically investigating the effects of CNT length on the dynamic response of the CNT AFM probes.

3. CNTs attached to AFM Cantilevers – Novel Sensors

In an effort to harness the high mass sensitivity inherent in carbon nanotube resonators, we have investigated experimentally and analytically the unusual coupled vibration characteristics of MWCNTs suspended from flexible microcantilevers (CNT “whiskered” cantilever sensors). The advantage of this approach is that by monitoring the different vibrational resonances of the microcantilever, it is

possible to gain information about the vibrational properties of the attached CNT. We have found that the addition of a gauge mass to the free end of the CNT changes dramatically the coupled vibration characteristics of the system and unexpectedly *increases* some of the cantilever resonance frequencies.[9] This non-intuitive behavior is shown to arise as a natural consequence of curve veering in coupled eigenvalue problems, and impacts directly the possibility of small mass detection using such whiskered cantilever sensors.

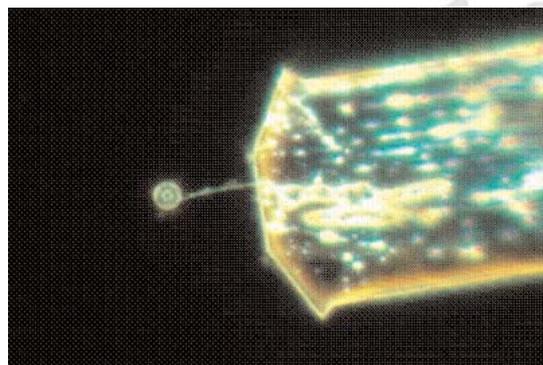


Figure 3: A MWCNT nanotube attached to an AFM microcantilever. By studying the motion of the microcantilever, information about the dynamics of the nanotube can be inferred. As an example, a particle (mass ~10 pg) has been intentionally added to the end of the nanotube to learn more about the vibrational dynamics of the nanotube itself. From Ref. [9]

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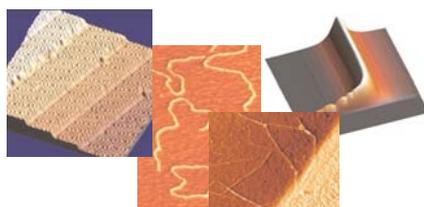
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e-mail: nanotec@nanotec.es

The CNT whiskered cantilevers employed in this study were fabricated in a number of steps. First mats of MWCNT's were grown using a chemical vapor deposition method. Next the MWCNT's were harvested using sticky carbon tape from a carbonaceous mat. Long (10-12mm), protruding MWCNT'S were then targeted using a darkfield optical microscope. Using micropositioners, the chosen MWCNT was first transferred onto a freshly etched W tip. Finally, using the micropositioners, the MWCNT was then transferred to the free end of a chosen microcantilever, using a very small amount of SEM adhesive tape to aid in the transfer and adhesion of the MWCNT to the microcantilever. In what follows, the CNT whiskered cantilevers prepared in this way are referred to as simply sensors.

To investigate the mass sensitivity of the sensor resonances, borosilicate glass microspheres were chosen as gauge masses. These gauge masses had a certified average diameter of $2\mu\text{m} \pm 0.5\mu\text{m}$, a standard deviation of $0.7\mu\text{m}$, a coefficient of variation of 35%, and a mass of ~ 10 pg (comparable to roughly the mass of ten bacteria). The first three resonances of the sensors were studied under different conditions: (i) as fabricated, (ii) after the gauge mass has been attached at the free end of the MWCNT, and (iii) after the gauge mass is removed from the MWCNT and re-attached to the free end of the microcantilever.

Our studies showed that the addition of the gauge mass directly to the end of the microcantilever caused the expected *decrease* in resonance frequency. However, the addition of the same gauge mass to the free end of the MWCNT caused a slight *increase* in the resonant frequency.

To understand this unexpected behaviour, a model of two coupled oscillators was constructed to analyze the experimental results. Through a combination of experiments and theory, it was shown that the coupled resonances of the MWCNT's attached to microcantilevers behave in unanticipated ways, especially when a large gauge mass is attached to the free end of the MWCNT. Moreover, the coupled oscillator model showed that cantilever localized resonance frequencies *increases* slightly when a gauge mass is added to the MWCNT. This unusual result is shown to arise naturally out of the physics of coupled oscillators and gives rise to a new strategy for utilizing functionalized MWCNTs as selective mass sensors.

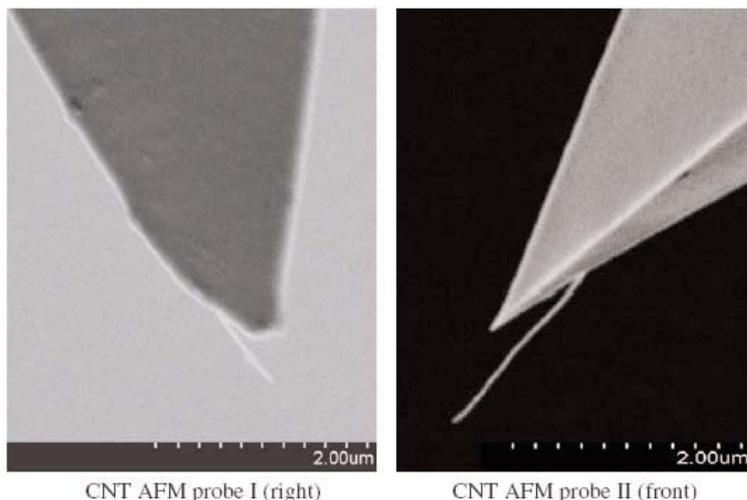


Figure 4. FESEM images of two CNT AFM tips (designated probes I and II respectively) discussed in this article. From Ref. [10].

4. CNTs Attached to AFM Tips – Imaging Artifacts

Dynamic atomic force microscopy (Dynamic AFM) with carbon nanotube tips has been suggested as an enabling tool for high precision nanometrology of critical dimension features of semiconductor surfaces. For this reason, we have investigated the performance of oscillating AFM microcantilevers with MWCNT tips interacting with high aspect ratio structures while in the attractive regime of dynamic AFM.[10] The experimental results on SiO₂ gratings and tungsten nanorods show two distinct imaging artifacts, namely the formation of divots and large ringing artifacts, that are inherent to CNT AFM probe operation. Through meticulous adjustment of operating parameters, the connection of these artifacts to CNT bending, adhesion, and stiction is described qualitatively and explained.

The experiments were performed using a scanning probe microscope operating in amplitude-modulation feedback for attractive mode imaging. Several MWCNT AFM probes have been tested. The CNT sources for the probes were obtained from either deposition of post-synthetic carbon nanotubes through dielectrophoresis or growth of low density, individually separated MWCNTs on a Pt wire through chemical vapor deposition. The CNTs were mounted on commercial microfabricated Si cantilevers and then subsequently shortened. The results presented here were obtained with the two MWCNT AFM probes shown in Figure 4.

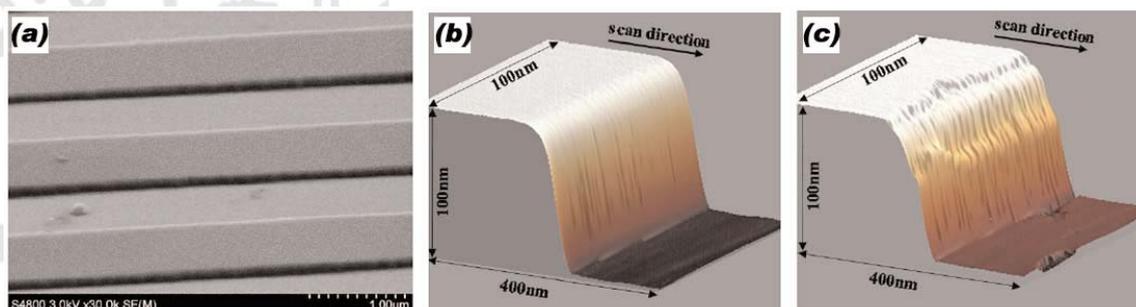


Figure 5. (a) FESEM of SiO₂ grating, (b) image taken using 91 % setpoint amplitude ratio, (c) image taken using 73 % setpoint amplitude ratio showing the onset of divot artifacts as the tip locally enters the repulsive imaging regime. From Ref. [10].

One distinctive imaging artifact is termed a “divot” artifact and arises when a CNT AFM probe operates in the attractive regime when scanning high aspect ratio features such as the SiO₂ grating shown in Figure 5(a). Figure 5 (b) and (c)

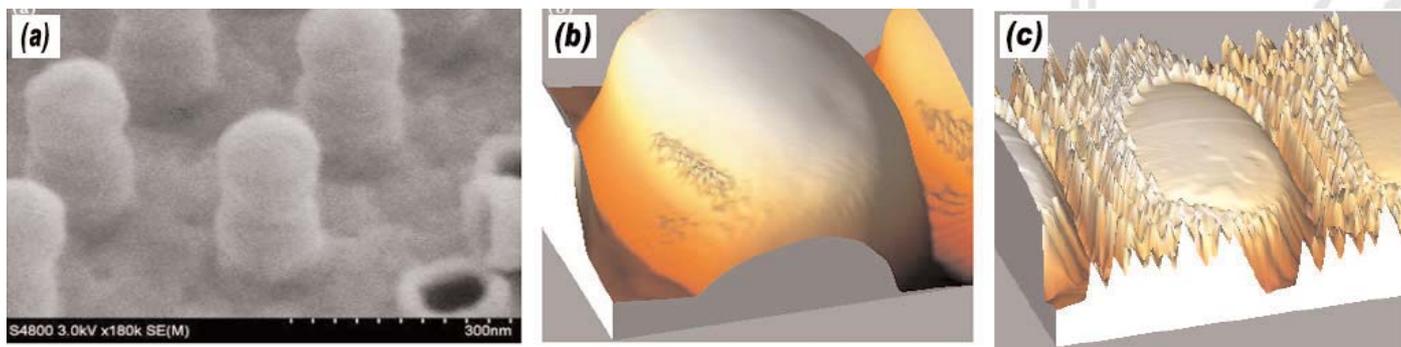


Figure 6. (a) FESEM of tungsten nanorods, (b) image taken using conventional tapping mode AFM, (c) image taken using CNT probe I showing the ringing artefacts due to CNT adhesion to the sidewalls. From Ref. [10].

show resulting AFM images of the trench wall taken under two different scanning conditions. Figure 5(c) clearly illustrates the divot artifact which is evident near the top corner of the 100 nm tall SiO₂ trench wall. Figure 5(c) is imaged with a 73% setpoint amplitude ratio. However, Figure 5 (b) is an image of the same trench wall but imaged with a 91 % setpoint amplitude ratio. Under these conditions the divot artifact has disappeared.

We have shown [10] that the divots occur at the top edge of the trench wall where the attractive tip-sample forces are the weakest. When the attractive forces are especially weak, CNT probes operating with smaller setpoint amplitude ratios in the attractive regime may suddenly switch to repulsive regime imaging. This problem is inherent to CNT tips operating in the attractive regime because of their high aspect ratios and small tip diameters, whereas conventional AFM probes have wider conical tips that maintain sufficient attractive tip-sample forces even at sharp edges.

A second imaging artifact called a “ringing” artifact was identified while scanning a tungsten post array shown by the FESEM image in Figure 6(a) and imaged with a conventional AFM probe in Figure 6(b). Each post is 300nm tall with a 100nm diameter, and is spaced in a grid with a 100nm gap between nearby posts. Figure 6(c) obtained with CNT AFM probe I shows significant ringing artifacts near most edges of the post. The underlying cause of the ringing effect has

been attributed to the bending and stiction of the CNT tip to the sidewalls of the post, and the ensuing reaction of the feedback controller to the stiction. [10]

Typically the ringing artifacts are found at small unconstrained vibration amplitudes while the divot artifacts are found at larger unconstrained vibration amplitudes. These imaging artifacts underscore the importance of understanding the nanomechanics of CNT tips to interpret high resolution dynamic AFM images using such probes.

5. CNTs Attached to STM Tips – Tunnel Gap Modulation Spectroscopy (TGMS)

We are also developing a simple method that accurately measures the natural frequency of vibration of carbon nanotubes at room temperature under ambient conditions.[11] The initial experiments are conducted using MWCNTs. The experiments demonstrate the possibility of a scannable high-frequency nanoscale oscillator (HFNO) with a promise for operation spanning the MHz-GHz range.

To implement these experiments, MWCNT's grown using a chemical vapor deposition method were attached to freshly etched W tips or cut PtIr STM tips using manipulation under dark-field microscope inspection. After selecting and attaching a carbon nanotube to an STM tip, the

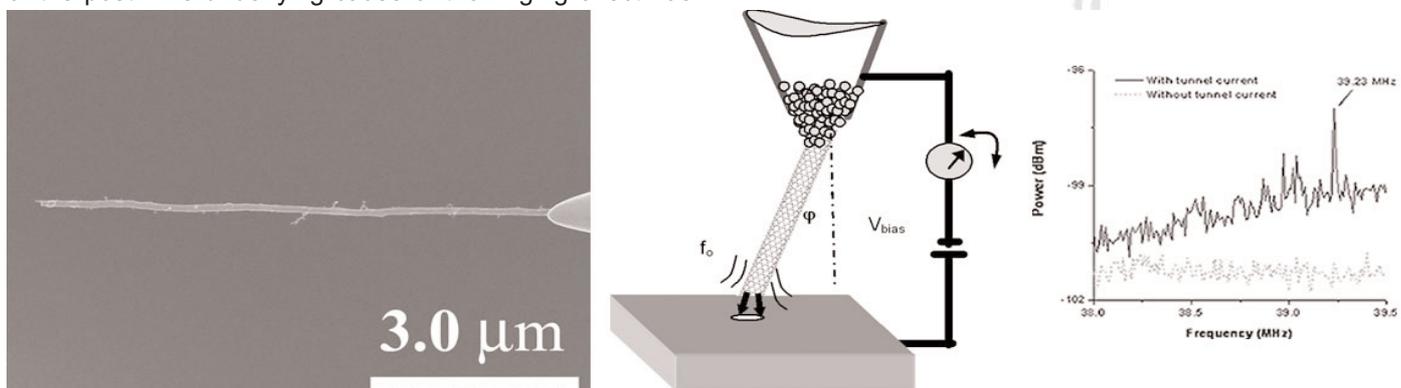


Figure 7. [a] An SEM image showing a MWCNT attached to an etched tungsten STM tip. [b] A schematic of a tunnel gap modulation spectroscopy (TGMS) experiment showing the carbon nanotube vibrating thermally on the end of an STM tip. The nanotube makes an angle f with respect to the surface normal of the substrate. The thermal vibration modulates the size of the STM tunnel gap and produces an oscillation in the tunnel current at the natural vibrational frequency of the nanotube. [c] Data showing the frequency resolved signal from the tunnel current when the tip is within tunnel range of the substrate (0.5 – 1.0 nm) and when it is withdrawn a few hundred nanometers from the substrate (out of tunnel range). From Ref. [11].

carbon nanotube/tip assembly was mounted in an STM operating under ambient conditions. The STM head was mounted on a two-stage vibration isolation system which is enclosed by a carefully constructed Faraday cage. When the apex of the MWCNT is within tunnel range of the substrate, thermal vibrations of the MWCNT at its natural resonance frequency modulate the tunnel gap to produce a small but measurable contribution in the STM tunnel current at a frequency determined by the resonant frequency of the MWCNT.

To measure the high frequency contribution of the tunnel current, the high-gain preamplifier circuit for the STM was modified to allow for amplification and extraction of the RF signal while allowing the required feedback control to operate unimpeded. This is similar to the technique used in electron spin resonance detection with STM. A commercial frequency analyzer was used to measure the spectral content from the RF amplifier. This instrument, while currently limited to frequencies lower than 40 MHz, allowed signal averaging to further improve the signal to noise ratio.

Initial experiments focused on a comparison of frequency spectra between clean PtIr tips and W tips with and without a carbon nanotube attached. Spectral data were acquired by placing the MWCNT tip in feedback mode above a freshly cleaved HOPG substrate while using the spectrum analyzer to measure the spectral content of the tunnel current. With proper attention to the setpoint conditions, we found that a reasonably stable tunnel current could be maintained for a few hours without noticeable degradation of the carbon nanotube tip. Studies showed that current instabilities (momentary jump-to-contact events) tended to be more prevalent for tunnel currents near 5 nA, presumably due to instabilities in the tunnel gap. These variations gave rise to spectral components in the kHz range, well below the MHz frequencies of interest here. For these reasons, tunnel currents near 1 nA were typically used during data acquisition in subsequent experiments.

A comparison of the spectral content of the output from the RF preamp (see Figure 7) showed clear evidence for the presence of an additional spectral peak in the MHz range when the MWCNT was in tunnelling range. Repeated spectral scans provided convincing evidence for the existence of a peak at a well-defined frequency. Parallel TEM studies to measure the dimensions of the MWCNT showed that the observed frequency peak could be reasonably explained by a simple model for a vibrating beam clamped at one end.

While these experiments are in their early stages, the presence of a clear, repeatable and identifiable signal at a well defined frequency when the MWCNT tip was in tunnel range provides convincing evidence that the observed spectral line is directly associated with the existence of a high frequency tunnel current produced at the tip of the carbon nanotube.

6. Conclusions

A variety of experiments have been briefly reviewed which illustrate the unique properties that result when a carbon nanotube is attached to either an STM or AFM tip. Both single wall and multi walled carbon nanotubes have been utilized. In most cases, the manipulation and successful attachment of the nanotube to either STM or AFM tips was achieved using a dark field microscope combined with micromanipulators, equipment commonly available in many laboratories. The experiments performed have investigated such diverse properties of carbon nanotubes as electron emission, bending, vibration and SPM imaging artifacts.

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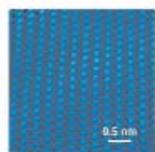
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