



# *nano*newsletter

n° 7

March 2007

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**Nanometrology at the nanoscale**

**Nanotechnology: applications and social implications**

**Molecular switches: Isomerization of single azobenzene derivatives**

**STM imaging of molecules on a thin insulating film**

**High resolution imaging of electronic and molecular structures assembled on InSb(001) c(8x2) surface with LT-STM**



The Nanoscience Cooperative Research Center **CIC nanoGUNE Consolider** invites applications for four positions as

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CIC nanoGUNE Consolider, located in San Sebastian, Basque Country (Spain), is a R&D center created recently with the mission of addressing basic and applied strategic world-class research in nanoscience and nanotechnology, fostering high-standard training and education of researchers in the field, and supporting the growth of a nanotechnology-based industry.



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# E *nano* newsletter

<b>Editorial Information</b>	<b>3</b>
<b>Research</b>	
<b>Nanometrology at the nanoscale</b>	<b>5</b>
<i>E. Prieto</i>	
<b>Nanotechnology: applications and social implications</b>	<b>8</b>
<i>A. Correia, M. Pérez, J. J. Sáenz and P. A. Serena</i>	
<b>NANO Vacancies</b>	<b>18</b>
<b>NANO Conferences</b>	<b>20</b>
<b>NANO News</b>	<b>21</b>
<b>Pico-Inside Integrated Project</b>	
<b>Molecular switches: Isomerization of single azobenzene derivatives</b>	<b>22</b>
<i>L. Grill, M. Alemani, K.-H. Rieder, F. Moresco, M. V. Peters and S. Hecht</i>	
<b>STM imaging of molecules on a thin insulating film</b>	<b>24</b>
<i>C. J. Villagomez Ojeda, S. Gauthier, A. Gourdon, S. Stojkovic and C. Joachim</i>	
<b>High resolution imaging of electronic and molecular structures assembled on InSb(001) c(8x2) surface with LT-STM</b>	<b>28</b>
<i>G. Goryl, S. Godlewski, J.J. Kolodziej and M. Szymonski</i>	

## Dear Readers:

Nanotechnology has become a rapidly growing research and development field that is cutting across many traditional boundaries. Given its multidisciplinary character, the list of potential applications is very long.

This E-Nano newsletter issue is therefore dedicated to present a review on the applications and social implications of Nanotechnology but also provide insights on the quantitative determination of dimensions (metrology) and other properties of nanostructures, crucial in R&D and also in industrial processes.

We would like to thank all the authors who contributed to this issue as well as the European Union (FET/NANO-ICT) and the Pico-Inside Integrated Project for their close collaboration.

**Dr. Antonio Correia**

**E *nano* newsletter** Editor  
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## EDITORIAL INFORMATION

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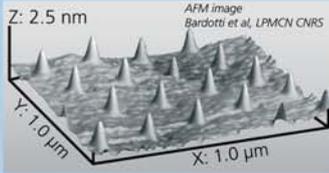
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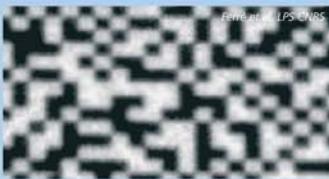
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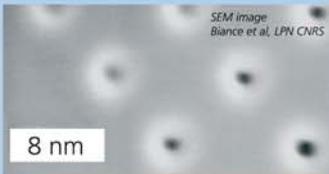
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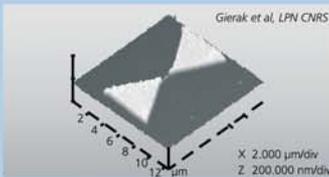
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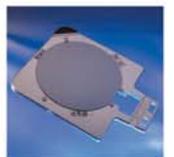
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## Metrology at the nanoscale

E. Prieto

Centro Español de Metrología (CEM), Alfar 2, Tres Cantos, 28760  
Madrid, Spain

The quantitative determination of dimensions and other properties of micro and nanostructures is crucial in R&D and also in industrial processes control. Understanding physical and chemical properties of structures at the nanoscale is in most cases directly linked to the knowledge of their critical dimensions.

SPMs are widely used for nanometre scale characterizations but quantitative measurements are only possible by using traced instruments, together with suitable calibration artefacts and right measurement procedures.

The most accurate way to perform traceable measurements with SPMs is to convert them in metrological ones by integrating 3D interferometric measurement systems. Some traceable atomic force microscopes (AFM) have been developed in last years by National Institutes of Metrology along with novel methods and standards for their calibration. Evaluating and quantifying the interaction between tip and sample, in order to differentiate features not belonging to the object under study and the design of new probes able to measure at sidewalls of nano- and micro-structures represent interesting contributions aimed to characterize accurately any kind of feature.

The idea of using coordinate measuring machines (CMMs) at the nanoscale has also expanded and CMMs have become versatile and widespread metrology tools, after improving their metrological design, minimizing ulterior corrections, and developing specific software to separate errors coming from different sources.

Most of the efforts we are observing in instrumentation, calibration and measurement methods are directly motivated by the need of fulfilling the continuously narrower manufacturing requirements as those stated, for instance, in the International Technology Roadmap for Semiconductors, where many of the figures are not reachable yet because they are depending on new measurement capabilities, not yet fully developed.

**Keywords:** nanoscale, nanostructures, critical dimensions, SPM, AFM, metrology, traceability, calibration.

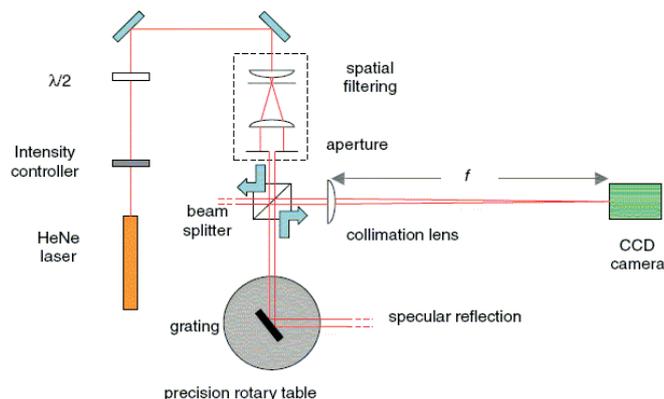
The quantitative determination of the properties of micro and nanostructures is essential in R&D and also in industrial processes control and quality assurance. Knowledge of the geometrical dimensions of structures is, in most cases, the base for understanding other physical and chemical properties [1].

As in the macro world, also at the nanometre scale all quantitative dimensional and geometrical measurements should be traceable to the definition of the metre. This means to follow an unbroken chain of comparisons with stated uncertainties (the traceability chain) in order to link the actual measurements to the highest point of the metrological pyramid, the meter, normally realized by a stabilized laser or, more recently, by femtosecond frequency combs linking the metre and the second [2].

SPMs are widely used for nanometre scale characterizations but as indicated above quantitative measurements are only possible by using traced instruments, together with suitable calibration artefacts and right measurement procedures. So, there is a real need of moving to traceable atomic force microscopes (AFM). This can be made by interferometric calibration of the scales of the AFM or by using calibrated grids as transfer standards.

One of the possible ways to calibrate grids is using a laser diffraction setup (Figure 1) composed by a precision rotary table, the sample grating mounted in Littrow configuration, a collimated spatially filtered laser source linked

to the realization of the metre and the retrorreflected diffraction order sent by a beamsplitter through a focusing lens to a CCD video camera acting as a null-position detector because its many advantages on the typical four-

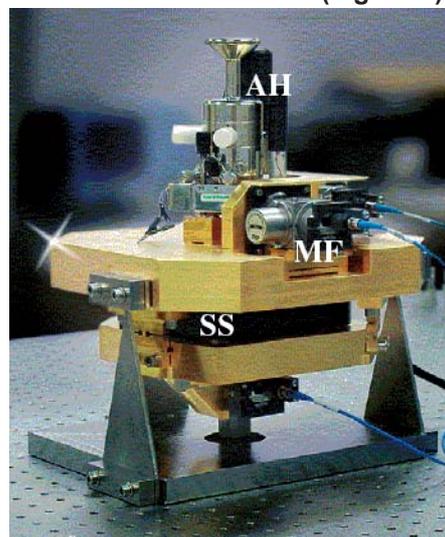


**Figure 1:** Schematic drawing of the NRC imaging diffractometer setup.

quadrant photodetectors [3].

But the most accurate way to perform traceable measurements with SPMs is to convert them in metrological ones by integrating 3D interferometric measurement systems to follow the scanner/tip position along with means to eliminate the scanner and Abbe errors [4-7].

Some traceable atomic force microscopes (AFM) have been developed by National Institutes of Metrology in the last years [8-10], along with novel methods for their calibration. Some of these 'metrological AFMs' claim to reach measurement uncertainties of 1 nm (Figure 2) [11].

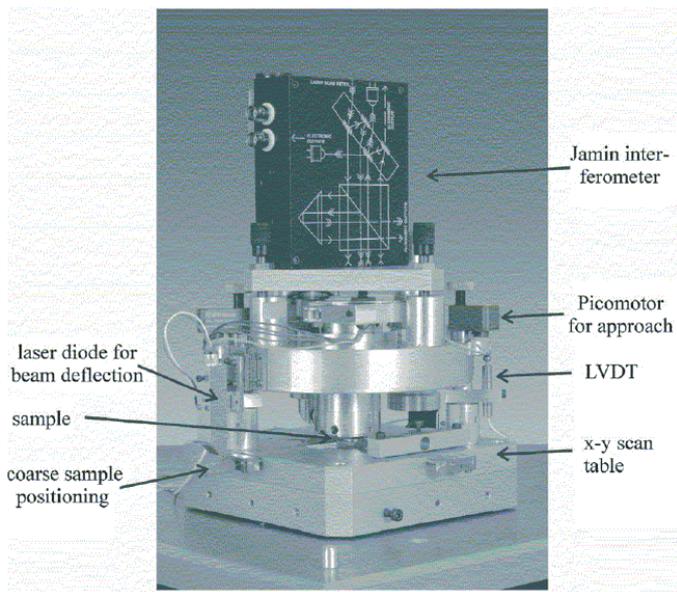


**Figure 2:** The traceable AFM developed at NMi-VSL consists of a scanning stage (SS), an invar metrology frame (MF) with a 3D laser interferometer and an AFM head (AH).

Even with these metrological instruments, it is important to evaluate and quantify the interaction between tip and sample, in order to differentiate between the features of the object and those caused by the interaction, due to affecting factors as bending and twisting of the cantilever, friction, humidity and surface forces.

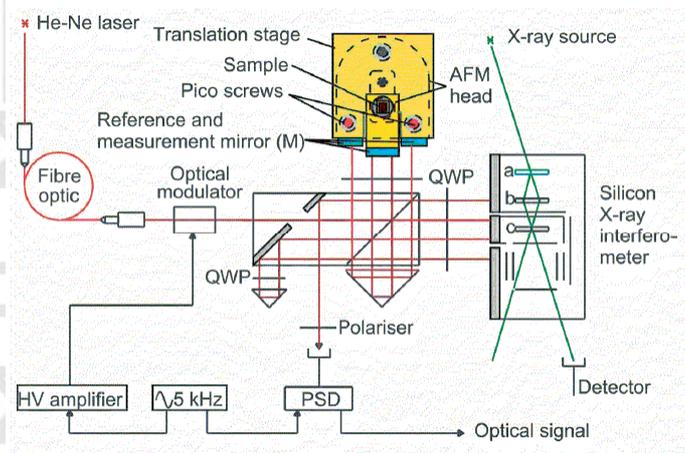
Some of these interactions have been studied with the help of a modified microscope [12] with added optical fibre and homodyne differential interferometers, able to measure the movement of the cantilever and detect residual

movements together with the vertical displacement between the cantilever holder and the sample (**Figure 3**).



**Figure 3:** Photograph of the AFM developed by NPL and PTB to study tip-sample interactions

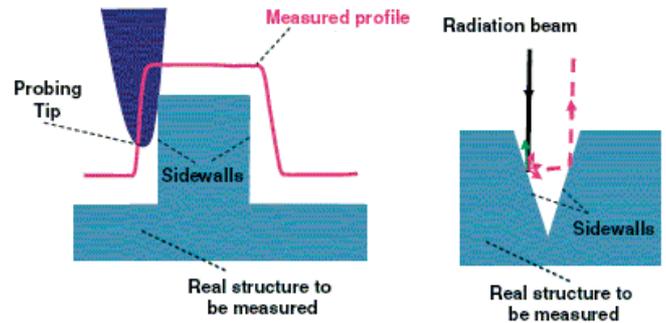
Considering the advantages of combining scanning probe microscopy with X-ray interferometry [13] such AFM has been designed so that it can also be mounted over the X-ray interferometer developed in the COXI project [14]. The X-ray interferometer would then be used as a one-dimensional translation stage for scans that require high resolution, making displacements traceable to the definition of the metre, in discrete steps of 0.192 nm, the lattice spacing of the (2 2 0) planes in silicon.



**Figure 4:** Combined optical and X-ray interferometer (COXI) Project, NPL/PTB/INRIM.

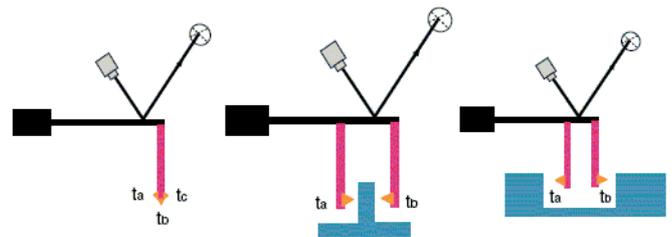
New developments also occupy on solving specific problems as nanoscale surface measurements at sidewalls. Probe tips of AFMs and stylus profilometers never come in close proximity to sidewalls, even with the sharpest and thinnest tip. Also, the radiation beams of optical or scanning electron microscopes are poorly reflected by sidewalls back to detectors and, even worse, some parts of

beams come back to detectors after being further reflected by other surfaces, as shown in **Figure 5**, leading to wrong measurement results [15].

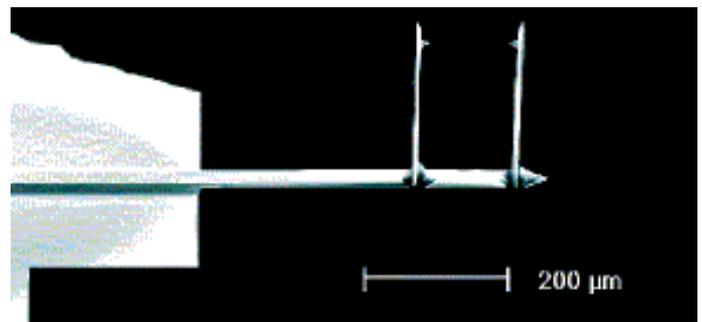


**Figure 5:** Difficulties encountered by conventional measurement techniques during sidewall profiling.

In order to solve major limitations of conventional AFM probes, novel Assembled Cantilever Probes (ACP), applicable for direct and non-destructive sidewall measurements of nano and micro-structures have been developed [15].



**Figure 6:** Schematic diagram illustrating the versatile structures of ACPs.



**Figure 7:** Micrograph of an ACP taken using a scanning electron microscope.

Another kind of instruments originated in the macro world but used now in nanometrology, because the new demands for highly accurate dimensional measurements on micro parts, are coordinate measuring machines (CMMs). These are in fact versatile and widespread metrology tools.

Various metrology institutes have developed prototype micro-probes with nanometre repeatability [16-18]. For ultraprecision measurements not only the diameter but al-

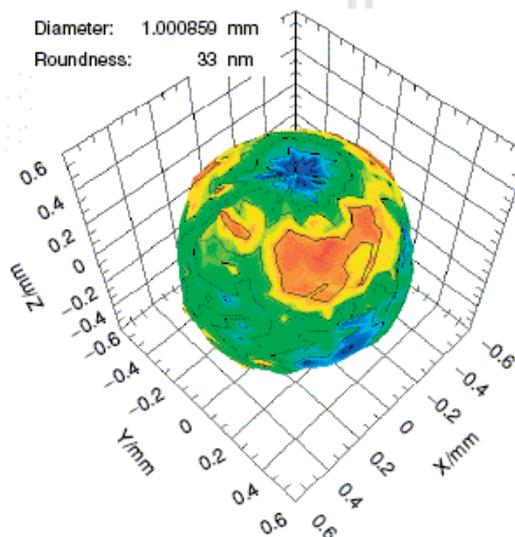
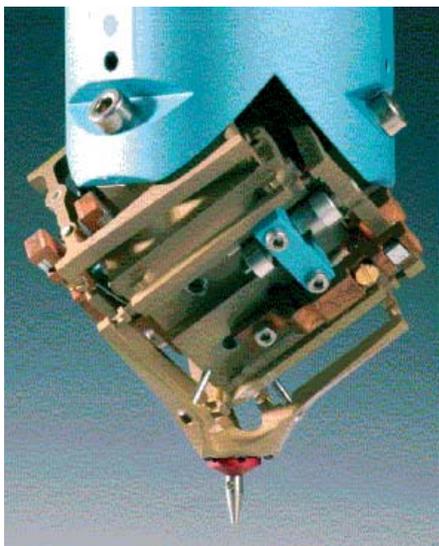


Figure 8: (a) Touch probe head of the micro CMM used at METAS (b) Deviation of Sphericity of the probe.

so the shape of the probing element is crucial. To determine roundness (in the contacting plane) and sphericity defaults, error separation techniques are applied [19].

### Conclusions

We have presented only a short sample of the very successful efforts we are observing in last years in developing instrumentation, standards, calibration and measurement methods, searching for direct traceability, error elimination and lower uncertainties at the nanoscale. Most of these efforts are directly motivated by the need of fulfilling the continuously narrower manufacturing requirements as those stated, for instance, in the International Technology Roadmap for Semiconductors, where many of the figures are not reachable yet because they are depending on new measurement capabilities, not yet fully developed.

Also in R&D the understanding of physical and chemical properties of structures at the nanoscale is in most cases directly linked to the knowledge of their critical dimensions; hence the need of their quantitative and accurate determination.

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## Nanotechnology: applications and social implications

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### 1. Introduction

Nanotechnology has become a rapidly growing research and development (R&D) field that is cutting across many traditional boundaries [1, 2]. The ability to construct nano-objects and nano-devices is expected to lead to the development of tiny but fully functional machines. Nanotechnology could affect virtually every manufactured product, energy production and storage, and a host of medical applications ranging from diagnostics to tissue and bone replacements. But nanotechnology is more than simply the next frontier in miniaturization, since the properties of materials change dramatically the farther one moves down the nanoscale, revealing an entirely new world of possibilities.

The incredibly fast rhythm of miniaturization that the microelectronic industry has maintained during the last four decades was already predicted by G. Moore 40 years ago [3]. Nevertheless, in spite of the capacity shown by the industry to overcome all sort of technological difficulties, there is a general consensus on the impossibility to maintain this fast-paced rhythm for much longer. The reasons for this predicted slowdown rely on both physical and economical factors. When silicon technology reaches its limit in feature size, there will be a desperate need for nanotechnology to keep up the technological momentum laid down by microelectronics and optoelectronics. We will abandon traditional Microelectronics to fully enter the Nanoelectronics era. However, working at the nanoscale means having the possibility of manipulating atoms and molecules at will to build devices capable of carrying out specific functions. Some of these technologies impose only limited structure control at the nanometer scale, but they are already in use, producing useful products. They are also being further developed to produce even more sophisticated products in which the structure of matter is more precisely controlled.

The control of atomic- and molecular-scale manufacturing is a need for the development of new technologies that will enable working on the nanoscale in a reliable and reproducible manner. Many of these technologies, such as SPM (Scanning Probe Microscope), are presently being outlined and improved in research laboratories and, therefore, have not yet reached their full potential. However, there is a vast knowledge on techniques that have demonstrated to have a great potential when working at the microscale. Many of these technologies can be improved to be used at the nanoscale. Right now we are in a phase of exploration where opposed visions arise on how to approach the manipulation/manufacture on the

nanoscale.

On one hand there is a more conservative vision; the so-called "top-down" approach [1, 2]. Top-down approaches seek to create nanoscale devices by using larger, externally-controlled ones to direct their assembly. This approach relies on the improvement of existing procedures to gain increasing precision in the production of the elements that form the devices. The top-down approach often uses the traditional workshop or microfabrication methods where externally-controlled tools are used to cut, mill and shape materials into the desired shape and order. An example of this way of thinking can be found on the evolution of optical lithography techniques, where each day smaller wave lengths are used, thus overcoming the numerous inconveniences (physical and economics) that arise when circuit integration is pushed towards extreme miniaturization.

A different approach consists in building larger objects from its molecular and atomic components. This approach is known as "bottom-up" [1, 2] and is closer to the perception of Nanotechnology that a chemist or a biologist would have. In contrast to top-down approaches, bottom-up methods use the chemical properties of single molecules to cause single-molecule components to automatically arrange themselves into a particular conformation. This approach is also consistent with the nanofabrication procedures based on tools designed from experience acquired with proximity microscopes (SPM).

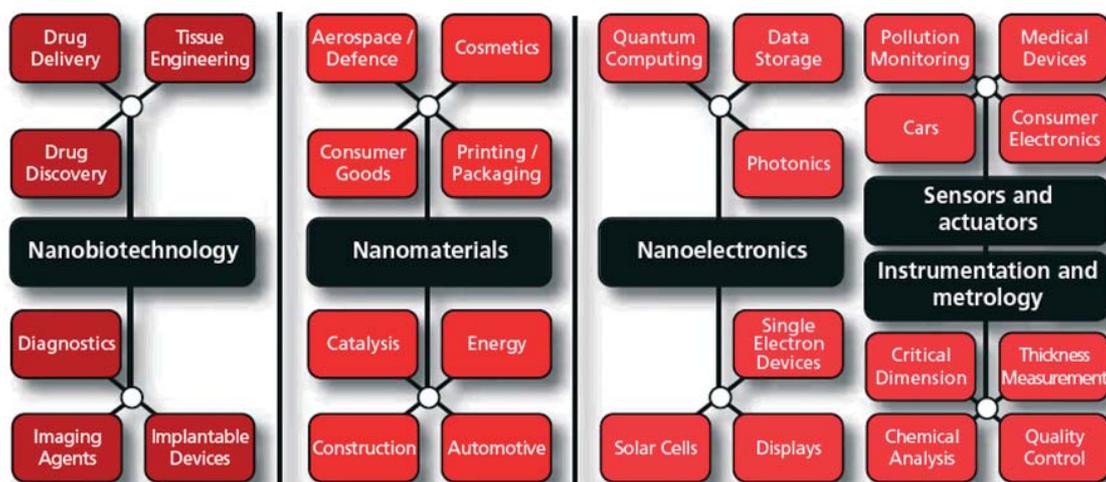
One could say that each technological problem with a well established "top-down" solution allows a plethora of possible "bottom-up" approximations. However, the appropriate design for each particular case will be determined by both industrial needs and commercial interests. It is perfectly reasonable to think that both approaches will coexist in the factories of the future, and that one or the other will be selected depending on the type of industrial process requiring optimization at the nanoscale.

### 2. Social impact of the Nanotechnology revolution

The forecast of the expected impact of a new technology is always a risky matter. Yet there seems little doubt that the very nature of nanotechnology will precipitate important changes — the only question is its timetable. In the case of Nanotechnology, the first measurable impact has perhaps been its effect on the media. In a few years everything 'nano' has gone from non-existent to being object of extensive articles and reports in scientific and non-scientific journals, as well as to be a favorite discussion topic in Internet web pages, blogs and forums.

When we speak of social implications, we are talking about the capacity of Nanotechnology to generate applications and devices that induce true changes in our daily life, our health, etc. Nanotechnology will fundamentally restructure the technologies currently used for manufacturing, medicine, defence, energy production and storage, environmental management, transportation, communication, computation and education. Given the multidisciplinary character of Nanotechnology, the list of possible applications would be very long (**Figure 1**).

- Nanotechnology will determine the design of efficient



**Figure 1:** Nanotechnology - Key Application Areas (Courtesy of Oxford Instruments (UK)) [4]

productive processes, allowing for considerable savings on strategic materials. Many of those processes will be optimized by designing catalysts (nanoparticles, nanoporous systems) that will improve the efficiency of multiple chemical processes. Besides, nanotechnological devices will improve the removal of contaminating particles found in water and air. New methods of production, with a smaller environmental impact, will be implemented, helping us to save raw materials and energy resources, and to reduce potentially harmful emissions and wastes.

-Nanoelectronics (an area of the Information Technologies) represent a strategic technology considering the wide range of possible applications. These include telecommunications, automotive, multimedia, consumer goods and medical systems.

In the semiconductor industry, Complementary Metal Oxide Semiconductor (CMOS) technology will certainly continue to have a predominant market position in the future. However, there are still a number of technological challenges which have to be tackled if CMOS downscaling is going to be pursued until feature sizes reach 10 nm around the year 2020. This miniaturisation will also offer opportunities for alternative nanodevices (molecular-based technologies [5] and nanomechanics) to be incorporated into CMOS platforms providing an increasing diversification of functions.

The revolution in this sector will maintain its momentum

thanks to the existence of tiny, cheap, sophisticated, and increasingly faster processors, memories and peripherals. This massive introduction of nanosystems dedicated to data acquisition, analysis and broadcast will fuel the revolution started by the arrival of the "digital society".

In this context we have to mention the use of carbon nanotubes as possible interconnectors between the active elements of the circuits. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Carbon nanotubes have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science (Figure 2) [6, 7].

- Nanotechnology will focus on the creation of new materials ("nanomaterials") with extremely fascinating and useful properties such as low weight, thermal isolation, electrical conductivity, surface functionality, etc. which can be exploited for a variety of structural and non-structural applications. They are exceptionally strong, hard, ductile at high temperatures, wear-resistant, erosion-resistant, corrosion-resistant, and chemically very active. Nanomaterials are also much more formable than their conventional, commercially available counterparts. These new materials will have a marked multifunctional nature. Among the nanomaterials that will be developed we can highlight those designed for energy storage, manufacture of more efficient solar cells, etc. Once more carbon nano-



**Figure 2:** Carbon nanotubes ordered over a surface using electronic lithography techniques. The image shows the official logotype of the Trends in Nanotechnology conference (TNT2004) [8] (Courtesy of Ken Teo (Cambridge University (UK)))



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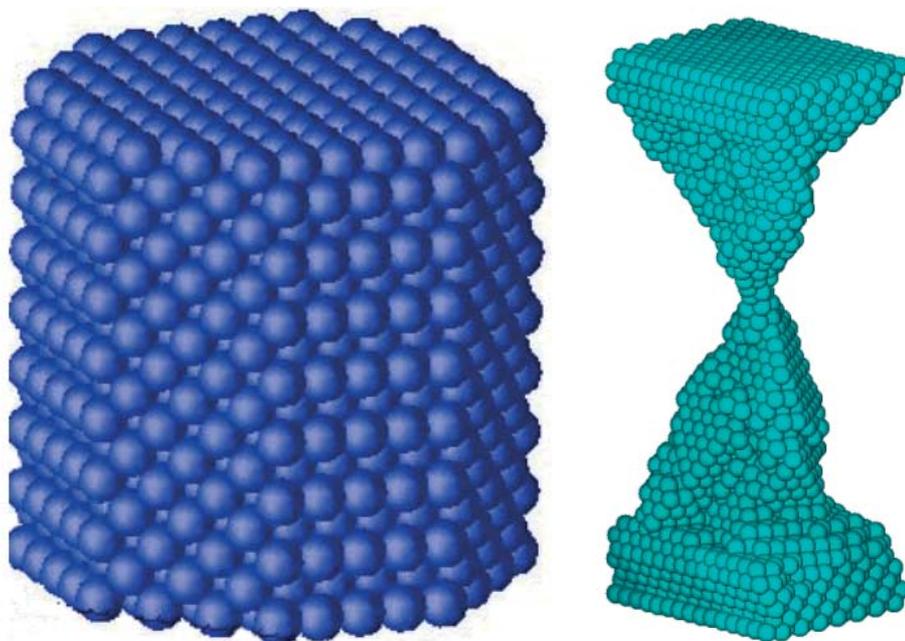


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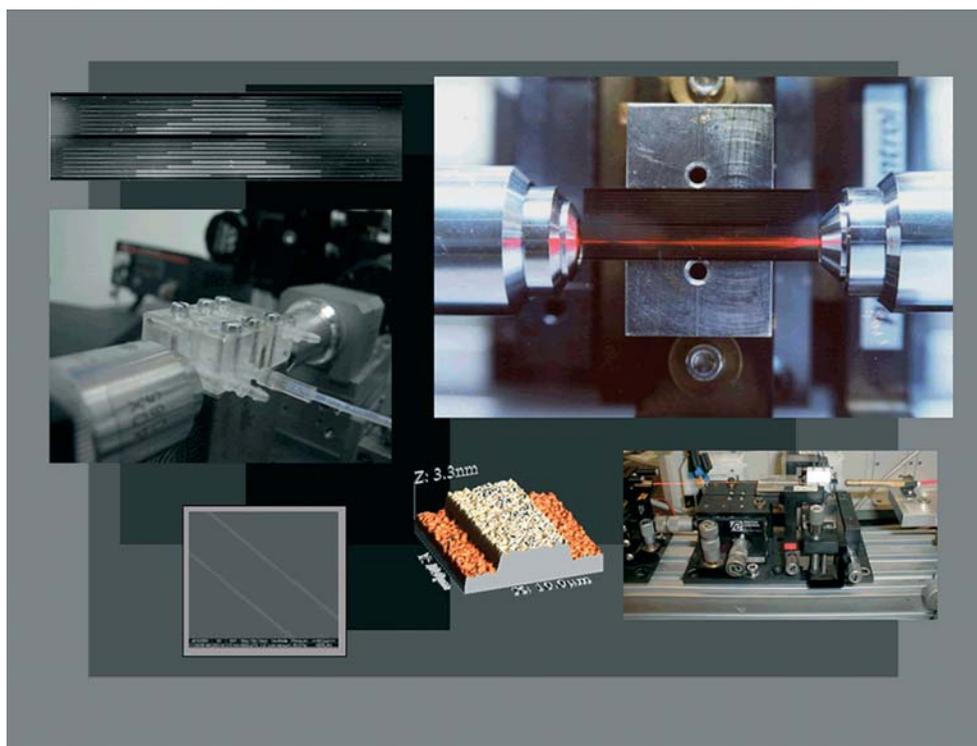
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**Figure 3:** (Left) Image of the atomic configuration of an ordered nickel nanowire exhibiting well defined magic ionic structure (Courtesy of Samuel Peláez, Consejo Superior de Investigaciones Científicas (ICMM-CSIC, Spain)). (Right) Snapshot of a Ni nanocontact during its rupture caused by stretching, obtained by Molecular Dynamics techniques (Courtesy of Pedro García-Mochales, Universidad Autónoma de Madrid (Spain))



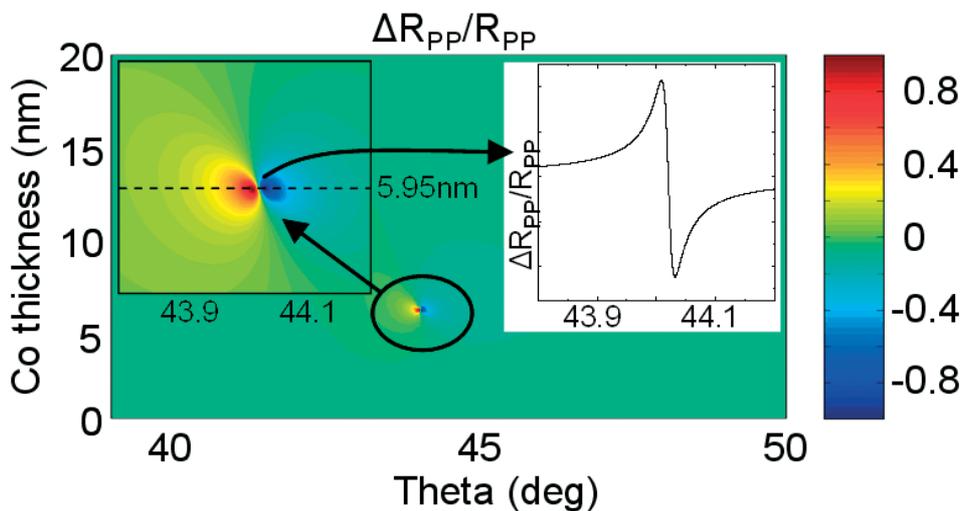
**Figure 4:** Nanophotonics biosensor based on integrated interferometers. The interferometers have a core waveguide in silicon nitride and have a channel depth of few nms in order to achieve bilateral confinement of single-mode light. The device achieves sensitivities for label-free detection of biomolecular interaction in the picomolar range (Courtesy of Laura Lechuga, Instituto de Microelectrónica de Madrid (CNM-CSIC, Spain)).

Furthermore, these lightweight vehicles would help control on fuel consumption, therefore extending the life of the scarce petroleum reserves while definitive alternatives settle down. The ability to precisely control matter at atomic and molecular level can be used not only to increase the efficiency and reduce the cost of existing energy generation and conversion systems, but also to create new energy sources. Needless to say that the modeling of nanomaterials is crucial for their study and development. In fact, researchers possess multitude of computational tools (many of them based on Quantum Physics) capable to simulate the behavior of these materials

when subjected to pressure, heat, stress, etc. (in **Figure 3** this aspect is illustrated with an example). Biomedical nanotechnology is leading to major advances in molecular diagnostics, therapeutics, molecular biology and bioengineering. In the short-term Nanotechnology will allow to develop "nanosensors" (**Figure 4**) that will be massively produced. These low-cost sensors will be incorporated into our daily life in thousands of applications. Networks of "nanosensors" will allow real-time control of the quality of waters, foods, and atmosphere. They will be able to control the environmental conditions in houses, offices and factories. Nanosensors will have a strong impact on Medicine, improving real-time diagnostic techniques thanks to the monitorization of tens of variables in a trustworthy, fast and cheap way. The new sensors will also have their application in the area of security, providing sophisticated detectors for explosives or biological threats. As previously mentioned, modeling plays a very important role in studying and developing novel nanosensors (**Figure 5, Page 12**)

tubes arise as crucial players in the development of these new nanomaterials, due to their large resistance to stress (in relation to their weight). This property made them key elements for many applications, especially in transportation technologies due to the possibility of fabricating vehicles, aircrafts, etc. lighter than the conventional models.

- Also related to Medicine a powerful trend exists to construct nanodevices capable to efficiently travel along the circulatory system, detect and attach to the focus of disease and then deliver drugs on local targets with nano or micrometric sizes without damaging surrounding areas



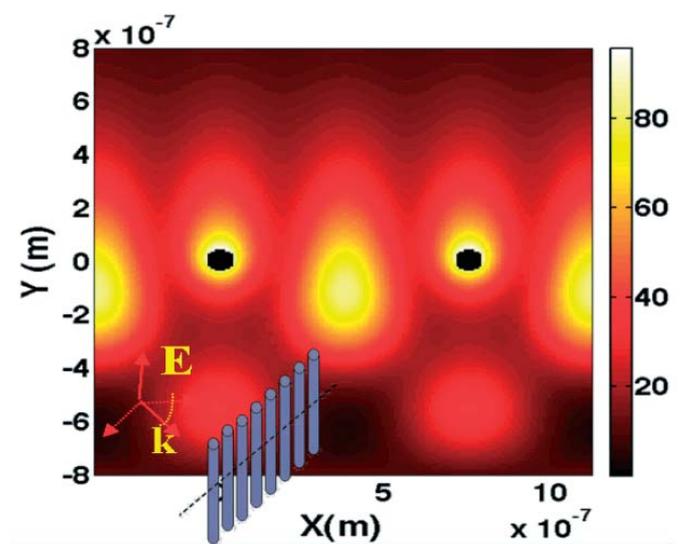
**Figure 5:** The Transverse Magneto-Optical Kerr Effect (TMOKE) is defined as  $\Delta R_{PP}/R_{PP}$  being  $\Delta R_{PP}$  defined as  $\Delta R_{PP} = R_{PP}(M_S) - R_{PP}(-M_S)$ ,  $M_S$  is the magnetization of the Co layer at saturation, and  $R_{PP}$  the reflectivity in absence of magnetic field, reflects the difference in the reflectivity of a magneto-optically active material (e.g. a ferromagnet such as Ni or Co) when the magnetization is reversed. The figure shows the TMOKE signal of a sample consisting in a trilayer Au/Co/Au where the thickness of the Cobalt layer and the incidence angle of the light are varied [9]. The signal is virtually zero but for a very small region where the surface Plasmon of the trilayer is excited. The properties of Plasmon excitation in noble metals are routinely used in Surface Plasmon Resonance (SPR) sensors and biosensors due to their good sensitivity. An evolution of the SPR sensor consist in combining the plasmonic properties of the noble metal with the magneto-optical ones of the ferromagnet (MOSPR sensor). In Ref. [10] the sensitivity of an Au/Co bilayer MOSPR sensor is reported to be three times larger than the conventional SPR. The optimized TMOKE signal shown in the figure shows a very sharp feature that allows it to be an excellent candidate for enhanced sensitivity MOSPR sensor (Courtesy of Antonio Garcia Martin, Instituto de Microelectrónica de Madrid (CNM-CSIC, Spain)).

where disease is not present. These "nanomachines" will be the product of a combination of sensors (based on hybrid nanoelectronic or biological compounds), structures where the drug will be lodged (cavities based on porous materials, systems that emulate cellular membranes, hollow nanoparticles, etc.) and a propellant (nanomotors based on examples offered by nature such as bacteria, spermatozooids, etc.). In addition, much research is going into biologically inspired functional nanodevices, such as the development of DNA/polymerase chain reaction or protein-based molecular computers, which encode information in the nucleotide sequences of DNA molecules or in the tertiary structure of proteins and carry out computations by following different biochemical reaction pathways. Another area of interest is biomimetic self-assembling molecular motors, such as the flagella of bacteria, or the mechanical forces produced by RNA polymerase during protein transcription. These molecular motors provide excellent examples of naturally occurring biological self-assembly, since they are composed of different molecular "parts" that self-assemble to produce the functional structure. These models are important targets to study and emulate in order to develop synthetic nanomotors that can interact with biology, for example. For now we have to content ourselves with the existence of "nanodispensers", although there are many expectations for Nanotechnology in the field of Medical Sciences, particularly in areas such as diagnostics, implants and prosthetics, cell and tissue engineering, and drug delivery.

- The advances in the understanding of new optical phe-

nomena on the nanometer scale ("Nano-Optics") have been especially relevant in the development of new sensor devices [11]. The initial steps of Nano-Optics can be traced back to the development of different optical counterparts of the Scanning Tunneling Microscope. The research effort in subsequent years led to the introduction of new concepts and fields like single molecule spectroscopy or plasmonics. Today the applications of Photonic Crystals and nanostructured materials with unusual optical properties are scattered across different disciplines. Tailoring the optical properties of these new materials is especially relevant for thermophoto voltaic (TPV) applications or the design of efficient light and infrared sources. On the other hand, controlling the absorption and extinction spectra of nanoparticle arrays have

drawn much attention recently for their potential applications to chemical and biological sensors as well as for surface enhanced Raman scattering (SERS) and fluorescence (Figure 6). These new sensors have their application in the area of security, providing sophisticated detectors for explosives or biological threats.



**Figure 6:** Light intensity map corresponding to a field enhancement resonance of a periodic array of rutile ( $TiO_2$ ) dielectric nanorods [12,13] (Courtesy of Marine Laroche, Silvia Albaladejo, Remi Carminati and Juan Jose Saenz).

The implications of Nanotechnology are many and they affect different aspects of the activity of human beings. Nevertheless we can highlight that many of the applications of Nanotechnology are focused on the improvement of human health, whereas others will facilitate a more sustainable economic development allowing for the optimization of resources and diminishing environmental impact.

### 3. Nanotechnology Research Funding

Nanotechnology is taking its first steps outside the laboratory, but it presents an immense potential for the manufac-

invested \$2850 million on Nanotechnology promotion, an investment even higher than that of USA. China has also recently joined this race, making millionaire investments for the creation of university-industry poles dedicated to Nanotechnology.

Europe has given a serious impulse to Nanotechnology [16] within the VI [17,18] and VII [19-21] Framework Programs (denoted as FP6 and FP7, respectively), through the creation of a thematic Area denominated "Nanotechnologies and nano-sciences, knowledge-based multifunctional materials and new production processes

**Table 1 – Estimated worldwide Nanotechnology funding (M\$ / year)<sup>1</sup>**

	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Europe	126	151	179	200	225	400	650	950 <sup>4</sup>	1050 <sup>4</sup>	-	-
Japan	120	135	157	245	465	750	810 <sup>3</sup>	875 <sup>4</sup>	950 <sup>4</sup>	-	-
USA <sup>2</sup>	116	190	255	270	422	604	862	989 <sup>4</sup>	1200 <sup>4</sup>	1351 <sup>5</sup>	1392 <sup>5</sup>
Others <sup>6</sup>	70	83	96	110	380	520	511 <sup>3</sup>	900 <sup>4</sup>	1000 <sup>4</sup>	-	-
TOTAL	432	559	687	825	1502	2274	2833	3714	4200	-	-
<sup>1</sup> Source: Ref. [24]			<sup>2</sup> Do not include regional initiatives				<sup>3</sup> Source: EU [16]				
<sup>4</sup> Source: National Science Foundation (USA)											
<sup>5</sup> Source: Ref. [25]											
<sup>6</sup> Others: Australia, Korea, Canada, Taiwan, China, Russia, Singapore, Eastern Europe.											

ture of consumer goods that, in many cases, will not be commercialized before a couple of decades. However, it is expected to bring tangible and promising results for the economy. Because the strong economic impact, nanotechnology has roused great interest among organizations, institutions and companies of the world's most developed countries.

In the period 1997-2005 worldwide investment in Nanotechnology research and development has increased approximately nine times, from \$432 million to \$4.2 billion [14]. This represents an average annual growth rate of 32%. Nanotechnology represents one of the fastest growing areas of R&D. The first set of coordinated efforts oriented to promote Nanotechnology at national scale took place in the US on 1996, when several federal agencies launched the National Nanotechnology Initiative (NNI) [15] that has invested more than \$2700 million in the 1997-2003 period to support long-term nanoscale R&D. In 2003 the US Government allocated \$43.7 billion over a four year period to Nanotechnology R&D. Current estimates indicate that the global government spend for 2006 has been \$6 billion. In addition to the federal initiative, an important effort has been carried out by the different US state governments, as well as companies (Motorola, Intel, Hewlett-Packard, IBM, etc).

Industrialized Asian countries have promoted the development of Nanotechnology from the industrial and governmental sectors, with investments similar to those of USA. Countries as Taiwan and Korea have made a great effort to keep their current privileged positions in the control of the tools and knowledge of nanotechnological nature. As an example, during the period 1997-2003 Japan has

and devices" (NMP) that counted with a budget of 1.300 million euros for the period 2003-2006 [17] or with the creation of the NID proactive initiative within the IST (Information Society Technologies) program [18]. In addition, other FP7 themes such as Health, Transport or Energy also opened funding calls directly related with Nanoscience & Nanotechnology [19]. There has been a boom of European initiatives dedicated to develop and popularize Nanotechnology, to the point of having today almost 200 national or regional networks. In the VII Framework Program Nanotechnology will maintain its stellar role, as proved by the creation of Technological Platforms with a strong industrial component to drive this technological development in areas such as Nanoelectronics (ENIAC) or Nanomedicine (NanoMED) [21].

The UE has also taken into account serious concerns on Nanotechnology, appearing in diverse forums during the last decade, in relation with its possible environmental and health effects. These non-desired drawbacks would provide a negative social perception on the development on Nanotechnology. In order to allow a coherent (rational, sustainable, non-aggressive, etc) development of Nanotechnology, the UE has promoted basic and applied research on nanoecotoxicology [22] and, simultaneously, has improved the communication and dissemination among population on the future advances that Nanotechnology will bring. In addition, UE has also promoted the generation of knowledge based on Nanotechnology emphasizing the role of this techno-scientific area as foundation for future convergence with other disciplines such as Biotechnology, Medicine,

## Research

Cognitive Science, Communications and Information Technologies, etc. [23].

### 4. Nanotechnology in Spain: a case study

In view of the absence of an institutional frame that fostered Nanotechnology R&D, it was the scientific community which led the promotion of initiatives directed to strengthen research in Nanotechnology and, at the same time, to raise the awareness of Public Administration and industry about the need to support this emergent field. Examples of these initiatives were the creation of "Nanociencia" and "NanoSpain" [26] research networks, the later, coordinated by the Phantoms Foundation and the Spanish National Research Council, and bringing together almost 1200 investigators belonging to 203 different research groups. Another initiative carried out by Spanish researchers is the organization in Spain of the Trends in Nanotechnology (TNT) conferences [8]. TNT has become an international reference in the field of Nanotechnology that annually convokes around 400 worldwide researchers who show the latest advances in this field and analyze its evolution.

These efforts to articulate the interaction among scientists who work in Nanotechnology were followed by initiatives of a more institutional character driven by Universities, local and regional governments. The Generalitat of Catalonia has probably played the most relevant role promoting Nanotechnology through its Special Action for the development of Nanoscience and Nanotechnology in Catalonia, funding scholarships for postdoctoral stays in prestigious research centers, and creating two relevant institutions: the Nanoengineering Laboratory belonging to the "Catalan Bioengineering Institute (IBEC)" [27] and the "Instituto Catalán de Nanotecnología" [28]. Following the

Catalonian initiative, several regional-driven initiatives were carried out such as the creation of the "Instituto de Nanotecnología de Aragón" (INA) [29] and the "Unidad de Nanotecnología de la Universidad de Oviedo" [30]. In some cases regional Administrations have supported other initiatives such as the creation of the "Círculo de Innovación Tecnológica en Microsistemas y Nanotecnologías de la Comunidad de Madrid" [31] or the networks "NanoGalicia" [32] and "Saretek" [33]. More recent initiatives are, for example, the creation of the "The Madrid Institute of Advanced Studies in Nanoscience (IMDEA-Nano)" funded by the Madrid regional government and the Spanish Ministry of Education and Research [34], or the joint initiative between Portugal and Spain to establish in Braga (Portugal) a new International Iberian Nanotechnology Laboratory (INL). All these facts demonstrate that Spanish Administration is making a great effort to follow the path of other European countries. In addition there is a clear approach to Nanotechnology coming from Technological Centers like TEKNIKER, INASMET, CIDE-TEC, IKERLAN, LBEIN, etc. or Science and Technology Parks associated to Universities [35]. They all know that a competitive presence in Europe implies a strong bet in this field.

All these initiatives of Spanish researchers along with the decisive influence of the tendencies observed in the European Union have driven the interest of the Public Administration to this scientific-technological field. In particular, the National Plan of R+D+I for the period 2004-2007 [36] presents Nanotechnology as a high-priority line of research, and a Strategic Action in Nanoscience and Nanotechnology was defined. Among its objectives are the improvement of shared-use infrastructures, the formation of qualified personnel and the development of a series

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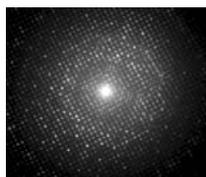
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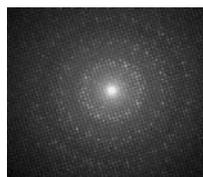
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of actions to attract the industrial sector towards the field of R+D.

On another scale, the Spanish Foundation of Science and Technology (FECyT) promoted in the period 2004-2005 a Pilot Action for the development of the Nanotechnologies [37]. Finally, it is very interesting to remark the intensive activity in Nanotechnology developed by the Spanish National Research Council (CSIC) [38] that includes the creation of several Institutes devoted to research in nanotechnology within the so called "EJE NANO" (Nano Axis) as a part of the CSIC Strategic Plan (2006-2009). More recently, the Spanish Government has established a new R&D Programme (Ingenio 2010 [39]) highly oriented towards the promotion of R&D activities with high added value to improve the excellence and competitiveness of national research teams and to increase the interconnection between public researchers and private companies, among others objectives. Within this framework, Consolider and CENIT calls allocated more than 700 M€ in 2006-2007 to reach these objectives and several CENIT Nanobiotechnology-based projects were funded. This impulse will be maintained for the next R&D National Programme, where Nanoscience and Nanotechnology will play a central role.

## 5. Conclusions

Nanoscience and Nanotechnology represent scientific-technical areas that in less than two decades have gone from being in the hands of a reduced group of researchers who glimpsed their great potential, to constitute one of the recognized pillars of the scientific advance for the next decades. The ability to manipulate the matter on atomic scale opens the possibility of designing and manufacturing new materials and devices of nanometric size. This possibility will alter the methods of manufacturing in factories, allowing for greater process optimization and automation, and therefore contributing to global sustainable development. On the other hand, the nanotechnological revolution will speed up the seemingly unstoppable expansion of the information technologies, and causing the globalization of the economy, the spreading of ideas, the access to the different sources of knowledge, the improvement of the educative systems, etc, to increase vertiginously. Finally, the irruption of the Nanotechnologies will directly affect human beings by substantially improving diagnosis and treatment of diseases, and also our capacities to interact with our surroundings.

Right now we are facing a new scientific paradigm with a multidisciplinary character, where Chemistry, Engineering, Biology, Physics, Medicine, Materials Science, and Computation converge, without this meaning that we should abandon the original perspectives. Establishing links between the scientific communities, looking for contact points and promoting the existence of multidisciplinary groups, where imaginative solutions to nanoscale problems are forged, becomes now essential.

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"Modelling for Nanotechnology" (M4nano) is a WEB-based initiative led by four Spanish Institutions: **Phantoms Foundation**, **Parque Científico de Madrid (PCM)**, **Universidad Autónoma de Madrid (UAM)** and **Universidad Complutense de Madrid** to maintain a systematic flow of information among research groups and therefore avoid that research efforts in Nanomodelling remain fragmented.

Networking is vital to any scientist and even more so for persons working in the inter-disciplinary field of Nanotechnology and in particular Nanomodelling. To fulfil this necessity, **M4nano** will provide a comprehensive guide -"who's who"- of groups working in Modelling at the nanoscale listing their accomplishments, background, infrastructures, projects and publications. In this way, **M4Nano** completes the aim of both raising awareness of scientists in Nanotechnology modelling issues and aiding them in developing beneficial collaborations and employment opportunities.

Emerging research areas such as Molecular Electronics, Biotechnology, Nanophotonics, Nanofluidics or Quantum Computing could lead in the mid-term future to possible elements of nano-based devices. Modelling behaviour of these possible nanodevices is therefore becoming more and more important and should allow to: (i) Visualise what happens inside a device (ii) Optimise the devices under study (iii) Improve understanding of device properties (physical, chemical, etc.).

**M4nano** in close collaboration with other European Research Institutions deeply involved in "modelling at the nanoscale" will develop tools such as a user's database, a forum to stimulate discussions about the future of Nanocomputing, a source of documents (courses, seminars, etc.) on modelling issues, etc. and in the mid-term future implement a computational HUB, repository of simulation codes useful for modelling and design of nanoscale electronic devices .

Information spreading will also be enhanced using mailing list alerts, press releases and flyers. Collaborations with similar initiatives such as the **NanoHub** (USA) or **Icode** ( Italy) will also be set-up.



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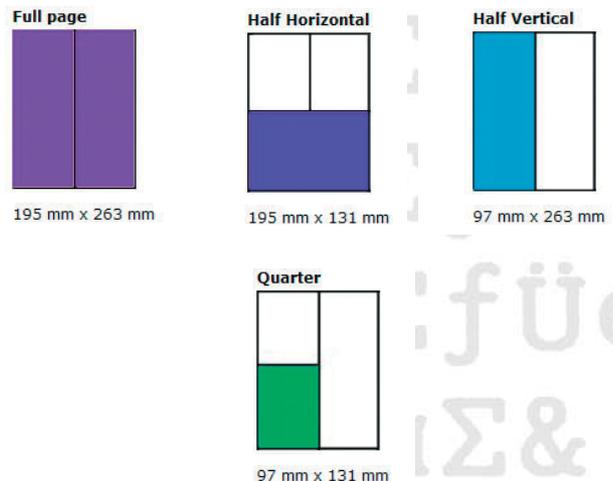
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## NANO News - <http://www.phantomsnet.net/Resources/news.php>

### ⚡ New stamping process creates metallic interconnects, nanostructures [21-02-2007]

<http://www.news.uiuc.edu/news/07/0221superionic.html>

Researchers at the University of Illinois at Urbana-Champaign have developed a simple and robust electrochemical process for the direct patterning of metallic interconnects and other nanostructures

*Keywords: Nanofabrication*

### ⚡ IMEC reports robust technology to functionalize nanoparticles for biomedical applications [21-02-2007]

<http://www.imec.be/wwwinter/mediacenter/en/Nanotech2007.shtml>

IMEC developed a generic and versatile method to synthesize stable, biocompatible magnetic nanoparticles.

*Keywords: Nanomaterials, Nanobiotechnology*

### ⚡ USA: \$1.45 billion for the National Nanotechnology Initiative [15-02-2007]

<http://ostp.gov/html/budget/2008/FY08%20NNI%20One%20Pager.pdf>

The USA President's 2008 Budget provides \$1.45 billion for the multi-agency National Nanotechnology Initiative (NNI), bringing the total investment since the NNI was established in 2001 to over \$8.3 billion and more than tripling the annual investment of the first year of the Initiative.

*Keywords: Scientific Policy*

### ⚡ Nanotube interconnects move on [15-02-2007]

<http://nanotechweb.org/articles/news/6/2/14/1>

Researchers at Intel have shown that carbon nanotube bundles could be used as interconnects in integrated circuits and possibly replace the traditionally used copper.

*Keywords: Nanoelectronics, Nanotubes*

### ⚡ First Graphene Transistors in NanoFutur Project ALEGRA [08-02-2007]

[http://www.amo.de/uploads/media/PR\\_AMO\\_Graphen\\_engl.pdf](http://www.amo.de/uploads/media/PR_AMO_Graphen_engl.pdf)

In the scope of his innovative project "ALEGRA" the AMO nanoelectronics group of Dr Max Lemme was able to manufacture top-gated transistor-like field-effect devices from layer graphene

*Keywords: Nanoelectronics*

### ⚡ Quantum dot nanowire emits light [06-02-2007]

<http://nanotechweb.org/articles/news/6/2/5/1>

Researchers in the Netherlands have made the first single quantum dot nanowire light emitting diode

*Keywords: Nanophotonics & Nano-Optoelectronics, Nanosensors & Nanodevices*

### ⚡ Latin American Nanoscientists offered EU support to visit European Nanolaboratories [01-02-2007]

<http://www.nanospain.org/files/news/NANOFORUMEULApressrelease010207.pdf>

NANOFORUMEULA invites PhD students, postdocs and senior researchers employed by a Latin American R&D organisation with prior research activities in nanotechnology to submit a proposal. Women are especially encouraged to apply.

*Keywords: Scientific Policy*

### ⚡ Focussing on Single Molecules [22-01-2007]

[http://www.phantomsnet.net/Foundation/RELATED\\_NEWS\\_PHAN.php?project=1&Noticia=442](http://www.phantomsnet.net/Foundation/RELATED_NEWS_PHAN.php?project=1&Noticia=442)

Chemists working at ETH Zurich have developed a new analytical procedure with extremely high sensitivity and precision. It allows the reliable identification of single molecules on surfaces

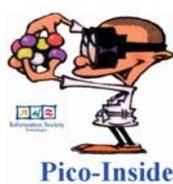
*Keywords: Nanochemistry*

### ⚡ Industrial Map of UK MNT: 2nd edition available for download [22-01-2007]

[http://mnt.globalwatchonline.com/epicentric\\_portal/site/MNT](http://mnt.globalwatchonline.com/epicentric_portal/site/MNT)

In the second edition of the "Industrial Map of the UK MNT", 643 companies have been profiled.

*Keywords: Nanotechnology Business*



## Molecular switches: Isomerization of single azobenzene derivatives

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**Keywords:** Azobenzene, Adsorption, Scanning tunneling microscopy, Single molecule chemistry

### Introduction

The investigation of single molecules has become an important and well-established research field in the last years, driven by the prospect for fundamental electronic and mechanical device miniaturization [1]. Understanding and controlling conformational changes of single molecules is very important in this regard. For this purpose, the scanning tunneling microscope (STM) at low temperature constitutes a powerful tool, as it not only allows precise sub-molecular imaging of single molecules but also permits the manipulation of atoms and molecules [2]. Recent experiments show that conformational changes within a molecule can be mechanically induced by the STM tip [3]. Molecular rotation [4, 5] and vibration [6] can be achieved by electronically exciting molecules with tunneling electrons, while diffusion [7] or desorption [8] of molecules adsorbed on surfaces are also induced by the intense electric field present between the STM tip and the sample surface. Such a field is strongly inhomogeneous and in the range of 0.2-2 V/Å, concentrated in the vicinity of the tip (i.e. in a radius of a few hundred Angstrom) [2]. Its strength can reach values required for field ionization and the desorption of an atom.

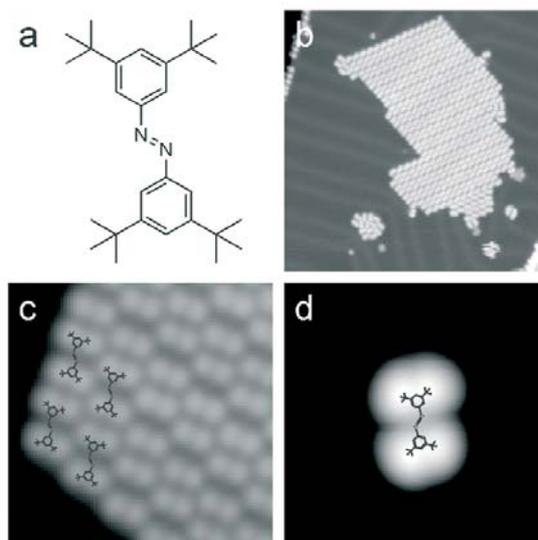
Looking for molecules suitable for application in molecular electronics, the current research interest is focusing on molecular switches [9, 10]. A molecular switch undergoes a reversible transformation between at least two distinct stable switching states, usually geometrical or valence isomers, associated with different physicochemical properties based on a change in molecular geometry and/or electronic distribution [9]. By using a Cu TBPP molecule, it has been shown how the tip of a scanning tunneling microscope can be used to trigger the switching mechanism of a single molecule [3]. Here, the interatomic forces between tip and molecule have been used for the manipulation, i.e. to rotate a single molecular leg. In this way, different conformations with characteristic junction resistances have been created in a controlled way.

The azobenzene molecule represents a very interesting example of such a molecular switch and its operating mechanism based on a trans-cis isomerization of a double

bond is conceptually related to the basic principle of vision in the human eye. In the electronic ground state, azobenzene adopts two different conformations: a nearly planar trans and a non-planar, three-dimensional cis form [11]. The reversible switching between these two isomers is well investigated in solution and in the gas phase whereby the ground state barrier for isomerization is typically overcome by photo-excitation [12-15].

### Results

The aim of the presented work is to study the possibility of using azobenzene derivatives as molecular switches, i.e. to isomerize single molecules on a metal surface in a controlled way [16]. **Figure 1a** shows the investigated molecule: 3,3',5,5'-tetra-tert-butyl-azobenzene, called TBA. It consists of an azobenzene core and four lateral tert-butyl groups that should increase the separation between surface and the azobenzene  $\pi$ -system, leading to increased surface mobility and potentially lower electronic coupling. On the other hand, the substituents do not significantly alter the electronics of the azobenzene chromophore and do not impart steric hindrance upon the isomerization process. By means of the molecular appearance in STM images, it is important to note that the four symmetrically placed legs facilitate conformational analysis, because they appear as intense lobes and thus act as markers. The molecules were synthesized by oxidative dimerization of 3,5-di-tert-butyl-aniline and exhibit the photochemical and thermal isomerization behavior typical for azobenze-



**Figure 1:** (a) TBA molecule. (b) STM image ( $40 \times 40 \text{ nm}^2$ ) of a molecular island on Au(111). The exact adsorption configuration of the molecules can be determined from the corner of an island in an enlarged STM image (c), the molecular structure is indicated. (d) shows the STM image of a single TBA molecule.

ne derivatives in solution [16].

The experiments were performed under ultrahigh vacuum conditions (base pressure of  $10^{-10}$  mbar) at a temperature of 5 K using a homebuilt STM, described in detail elsewhere [17]. The Au(111) substrate was prepared by several cycles of sputtering with Ne ions and subsequent annealing at 800 K. The molecules were deposited by evaporation from a homebuilt Knudsen cell kept at 370 K, and the dosage was monitored via a quartz crystal micro-

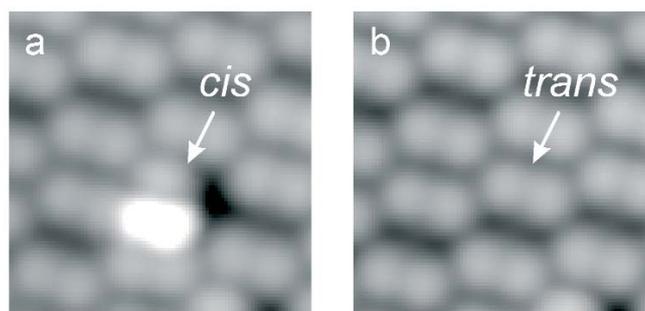
balance. During the deposition of the molecules, the sample was kept at room temperature. All images are recorded in constant current mode with a tunneling current of 0.1 nA and a bias voltage of 1 V on the sample.

An overview STM image of TBA molecules on Au(111) after deposition is shown in **Figure 1b (Page 22)**. The molecules are mobile after adsorption, as they cover step edges and form islands, but are also found isolated on terraces. Islands formed by less than about 40 molecules are disordered, i.e. the molecules are not equally oriented. As the number of molecules increases, the intermolecular interaction leads to the formation of highly ordered islands. The position and orientation of individual molecules inside these islands is shown in **Figure 1c (Page 22)**: The molecules form parallel rows indenting with each other. Isolated molecules (**Figure 1, Page 22**) are always positioned at the elbows of the Au(111) herringbone reconstruction. Even though the molecule itself is not chiral, the molecule-surface system is chiral [18], which becomes clear in the case of a single molecule (d) with a rather rhombic and not a rectangular shape.

Each molecule appears as four lobes with an apparent height of  $2.7 \pm 0.1$  Å arranged in a rhombic shape. According to the dimensions of the molecule in the gas phase, the lobes can be assigned to the tert-butyl groups while the central azobenzene part is not visible. All observed molecules are in the same planar configuration that we assign to the trans isomer (**Figure 1a, Page 22**), which is known to be the energetically favored configuration in the gas phase [11]. The complete missing of cis isomers on the surface is expected, because any heating process (for deposition) increases the fraction of the trans isomers on the expense of the cis molecules [11,13].

We have investigated the isomerization process in the ordered molecular islands, where a large number of molecules is present. To induce the isomerization, we have applied voltage pulses of 2 V with the STM tip positioned above an island. After these pulses, many molecules have changed appearance, showing a larger height of  $4.1 \pm 0.3$  Å. These bright molecules are stable and to let them precisely restore their initial appearance we have to apply a further pulse, as shown in **Figure 2**. As one can see in **Figure 2a**, the isomerization process has no consequence on the neighboring trans molecules, which remain unchanged. The cis form appears with a bright central intensity maximum, while three lateral lobes in an approximately triangular shape can be resolved, completely different from the planar trans conformation. This shows that, in contrast to the trans isomer, the cis isomer is not planar, in agreement with the molecular conformation in the gas phase [11] and as observed by STM [19] for azobenzene molecules on Au(111).

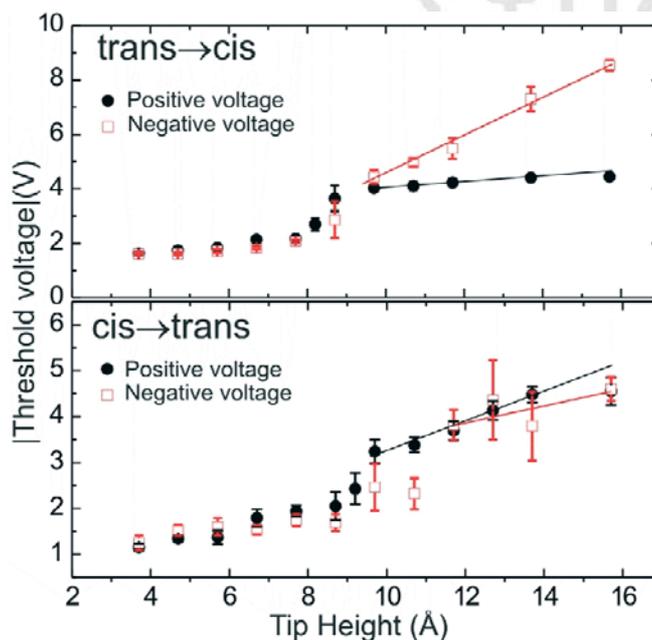
Such switching experiments can be reproduced several hundred times allowing us to conclude that the observed changes are due to the isomerization of single molecules from the trans form to the cis form, and back to the trans form [16]. The reversibility of the experiment and its high reproducibility exclude molecular dissociation or the presence of any contamination as cause for the observed change of the molecular appearance. The switching of an isolated molecule is very rare because, under the effect of



**Figure 2:** Isomerization process from cis to trans. (a) and (b) show STM images (both  $3.5 \text{ nm} \times 3.5 \text{ nm}$ ) before and after the isomerization. The bright molecule in (a) is in the cis state and exactly returns to the trans state in (b), where all visible molecules are trans isomers, after applying a voltage pulse.

a voltage pulse, the molecule can move or rotate thereby efficiently competing with the isomerization process. This effect is avoided in the islands when the molecules are stabilized by each other.

In order to understand the driving mechanism for this isomerization process, we have studied the dependence of the bias voltage, required for the isomerization, on the tip height (**Figure 3**) [16].



**Figure 3:** Plot of the threshold voltage as a function of tip height for the trans → cis isomerization (top) and for the cis → trans isomerization (bottom) for positive (electric field points towards the STM tip) and negative voltage polarities. Reprinted from **Ref. 16**. Copyright 2006 American Chemical Society

The experimental points have been measured by fixing the tip at a specific height, referred to the bare Au(111) surface, and applying a voltage pulse for a fixed time  $t=30$ s. Starting from  $V=0$ , we increased the voltage by increments of 0.1 V until we observed a switching event in a lateral area of  $80 \times 80$  Å from the tip position. Each sequence was repeated 10 times. The data show that switching is possible with positive and negative voltage polarities and the threshold voltage is not a constant value, characteristic in the case of electron resonant tunneling [5], but clearly increases (at tip heights  $>9.5$  Å)

when retracting the tip. The isomerization process occurs also at very large tip distances where no tunneling current is flowing (the tunneling current decreases exponentially with the tip-surface distance). Even in the extreme case when the tip is 36 Å above the surface, we were able to switch molecules from trans to cis (after applying a voltage pulse of 6.8 V)! These results lead to the conclusion that the isomerization of TBA molecules on Au(111) is driven by the electric field in the STM junction, which does not involve the tunneling of electrons. Very recent theoretical calculations of P. Saalfrank et al. [20] for TBA molecules explain this mechanism: the electric field in the STM junction deforms the potential barrier of the molecule in the ground state thereby facilitating the switching process.

The approximately linear dependence of the threshold as a function of the tip height in **Figure 3 (Page 23)**, considering the large tip height regime (points above 9.5 Å), allows to quantize the required electric field. We find values of 0.1 V/Å and 0.7 V/Å for the trans → cis isomerization, while for the cis → trans it amounts to 0.3 V/Å and 0.4 V/Å. Points below 9.5 Å are not included in the plot because in this region there is a change in slope, probably related to electronic effects that come into play at small tip heights (i.e. large currents). These experimental values of the electric field are smaller than the calculated ones (about 1-2 V/Å) [20], which is likely due to the presence of the surface that enhances the permanent dipole and the polarizability of the molecule. It is important to mention the different slopes for positive and negative voltages in the case of trans → cis isomerization as compared to the cis → trans process (where the behaviour is very similar for the two polarities). These differences are presumably caused by the characteristic polarizability of the molecule and the orientation of its intrinsic dipole moment for the trans and cis configuration and intermediate configurations during the reaction.

### Conclusions

We have shown that the isomerization of single azobenzene derivatives can be induced by using a scanning tunneling microscope. Isomerized molecules in the cis state appear brighter within the molecular islands due to their non-planar structure, in accordance with the configuration in the gas phase. The isomerization process is reversible as cis isomers precisely restore the trans configuration after a second voltage pulse. The dependence of this switching process on the experimental parameters shows for the first time that the process can be induced by the electric field in the STM junction and is thus possible without any electric current.

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## STM imaging of molecules on a thin insulating film

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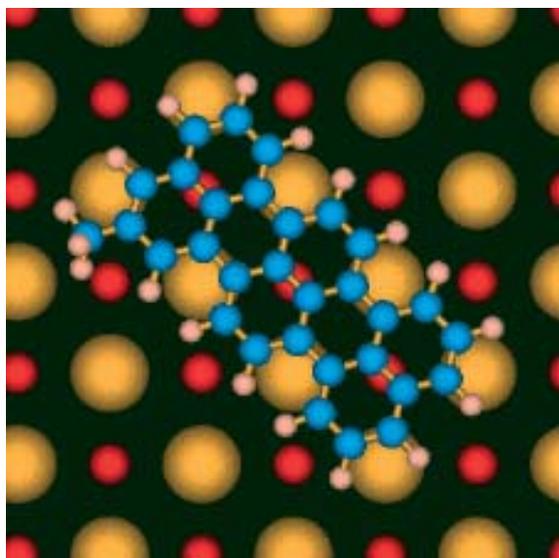
Tomaso Zambelli  
 Laboratory of Biosensors and Bioelectronics, ETH Zurich  
 Gloriastrasse 35, CH-8092 Zurich (Switzerland)

### Introduction

Until recently, STM was the only technique allowing to image individual molecules adsorbed on surfaces. For this reason, single molecule studies were restricted to conducting substrates. Some strategies were developed to allow well defined electrical connexions to single molecules on metals, based on the synthesis of specially designed molecules [1], but these approaches are not suited for further developments, such as planar electrical connexions to a single molecule. The emergence and progress of AFM in the non-contact mode make now possible to image a single molecule on an insulating substrate [2], but this technique is rather difficult and molecular manipulations are not yet well mastered, as for STM. It was realized recently [3-6] that it is possible to use STM to study molecules adsorbed on ultrathin insulating films on conducting substrates. In this situation the insulating film decouples the molecule from the substrate, while still allowing the transport of a weak tunneling current through the structure. These studies constitute an intermediate step which is currently explored in PicoInside (<http://www.picoinside.org>)

A recent achievement in this research area was the imaging of the frontier molecular orbitals of a single adsorbed molecule by STM [5]. When a molecule is directly adsorbed on a conductive surface, the discrete molecular levels are broadened, shifted and mixed by interaction with the electronic continuum of the substrate. As a consequence, many MOs contribute to the tunneling current through the molecule, even when their energies are far away from the Fermi level of the substrate [7]. This phenomenon makes the observation of a well-defined MO by STM exceptional [8]. The key point in Ref. 5 is the use of a NaCl bilayer as an ultrathin insulating layer interposed between the molecule and the substrate. Its role is to electronically decouple the molecule from the supporting metallic substrate. In this way, images that are strikingly similar to the frontier orbitals of the isolated free molecule were obtained for pentacene adsorbed on a NaCl bilayer on Cu(111) [5]. This method provides a systematic and efficient way to visualise MOs. It opens the fascinating possibility to investigate at the submolecular level many of the concepts developed to understand organic chemistry basic rules.

In this paper, we report the first step in a program aimed at exploring substituent effects on a  $\pi$ -electron system at the single molecule level using STM. We chose terrylene, a medium size conjugated molecule and a methyl group as substituent (Figure 1). The methyl group is considered as a weak donor, which should perturb only slightly the frontier orbitals via its hyperconjugative interaction with the terrylene core. The molecules were adsorbed on a NaCl bilayer on Cu(111) and studied by low temperature (5K) STM

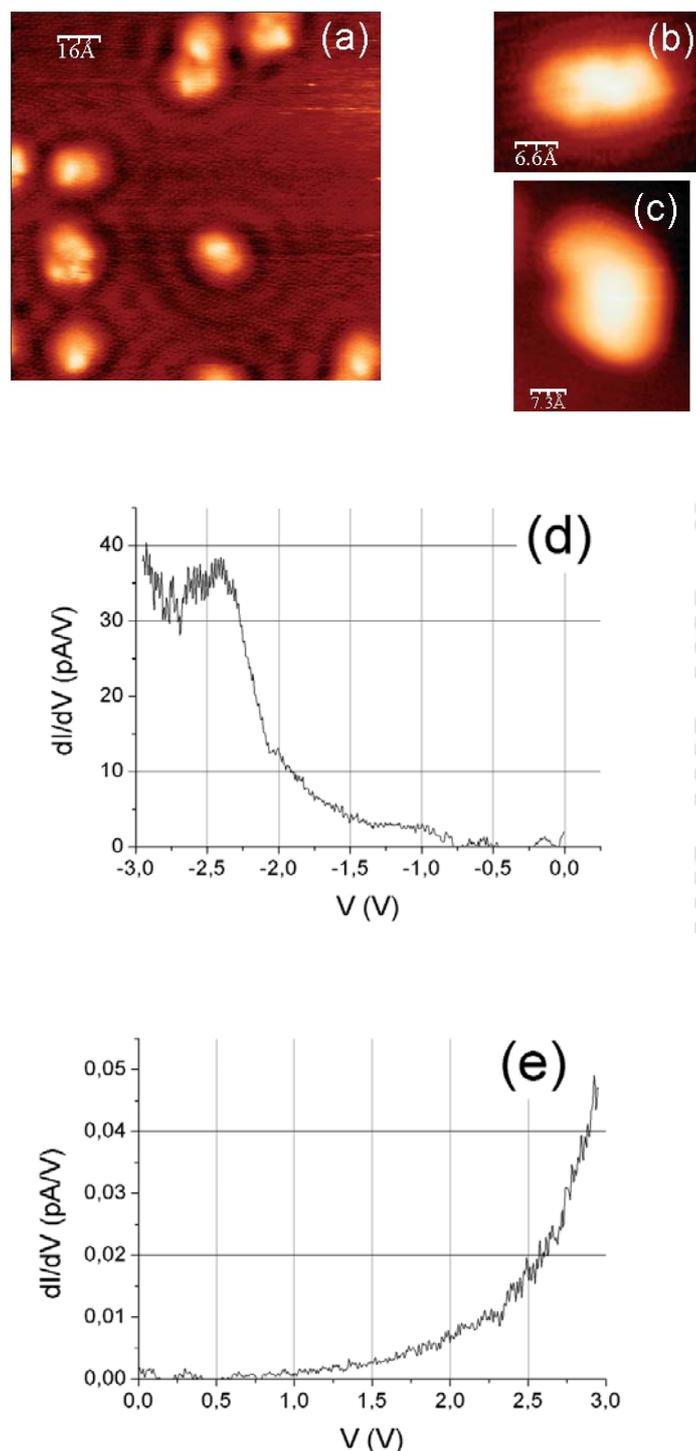


**Figure 1:** Position of methylterrylene (MeT) on the NaCl top layer for the EH-ESQC calculation. Red dots correspond to Na<sup>+</sup> ions, yellow dots to Cl<sup>-</sup> ions.

The results presented in this report are currently submitted for publication.

## Results

STM images of the MeT molecule adsorbed directly on Cu(111) are shown for different bias voltages in Figures 2a, b and c. At low voltage (Figure 2a), the molecules, which interact with the surface state of Cu(111), appear as elongated



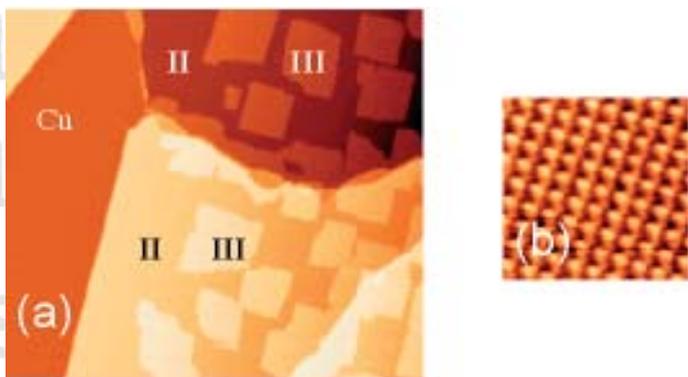
**Figure 2:** Constant-current STM images of MeT adsorbed on Cu(111) at 5K. (a)  $V_t=0.2$  V,  $I_t=10$  pA, (b)  $V_t=-2.5$  V,  $I_t=1$  pA (c)  $V_t=2.5$  V,  $I_t=1$  pA and  $dI/dV$  spectra for (d) occupied and (e) unoccupied states.

gated protrusions, with a size which is of the order of the size of the molecule and only weak internal structure. No significant differences are observed when the bias voltage is changed in the [-3 V, 3 V] range, as shown in Figures 2 b and c.

Differential conductance  $dI/dV(V)$  spectra for occupied (Figure 2d) and unoccupied (Figure 2e) states have the characteristic shape usually observed on metallic substrates.

tes, except for a peak near -2.5 V, which is not systematically observed. These observations are typical for molecules adsorbed on metallic substrates, where due to the mixing of the molecular orbitals mentioned previously, the images are not clearly related to specific, single molecular orbitals.

NaCl was grown on Cu(111) at room temperature from a copper crucible heated to approximately 300 °C (**Figure 3**). The sample was then transferred to the STM and the MeT molecules were deposited by thermal sublimation



**Figure 3:** (a) STM images of a NaCl deposit on Cu(111). Two (II) and three (III) NaCl layers thick areas are observed.  $V_t = -1.5$  V,  $I_t = 1$  pA,  $40 \times 40$  nm<sup>2</sup> (b) Atomic resolution on the NaCl bilayer.  $V_t = 1.5$  V,  $I_t = 50$  pA,  $4 \times 4$  nm<sup>2</sup>

from a tungsten filament on the sample surface held at low temperature ( $T < 10$  K).

Two conductance spectra, acquired above the centre of a MeT molecule are shown in **Figure 4a** (resp. **4b**) for negative (resp. positive) bias voltage. They exhibit two broad peaks, near -2.5 V and +1.4 V, separated by a flat region. The position and the width of these features vary slightly from one molecule to the other. A constant-current STM image obtained at low bias, in the flat spectral region separating the two peaks reflects the overall shape of the molecule (**Figure 4d**). The methyl group is revealed by a protrusion that extends outside the rectangular board of the molecule. The image size is of the order of the geometrical structure of the molecule. The height is around 0.1 nm. No internal structure is discernible.

Much more extended and structured images are obtained when the bias voltage is within or beyond the spectroscopic peaks of **Figures 4a** and **b**. An experimental STM image obtained at negative sample bias is displayed in **Figure 4c**. The image is much larger than in the spectral gap and exhibits well defined lobes separated by dark lines. The height of the image of the molecule can reach 0.2 nm, depending on the value of the bias voltage. The image obtained at positive bias voltage displays similar features (**Figure 4e**). It shows 6 lobes and its height can reach 0.5 nm.

The HOMO of the free molecule, calculated using the semi-empirical Extended Hückel approximation [10], is shown in **Figure 5a** for a value of the orbital electronic probability density  $\rho = 10^{-7}$  Å<sup>-3</sup>. The similarities between the STM image (**Figure 5b**) and the calculated HOMO (**Figure 5a**) are striking. Not only the topology of the orbital's lobes is reproduced but also their size and their

shape. One difference is that the central transversal nodal plane is not visible in the experimental image. This is probably related to a limited resolution of the tip used for this experiment.

These similarities suggest that in the experimental conditions corresponding to **Figure 5b**, the STM probes the HOMO of the adsorbed molecule at a very low density. As seen from the scale in **Figure 5**, this density corresponds to a distance from the board of the molecule of the order of 0.5 nm, unusually large for a MO in the context of chemistry.

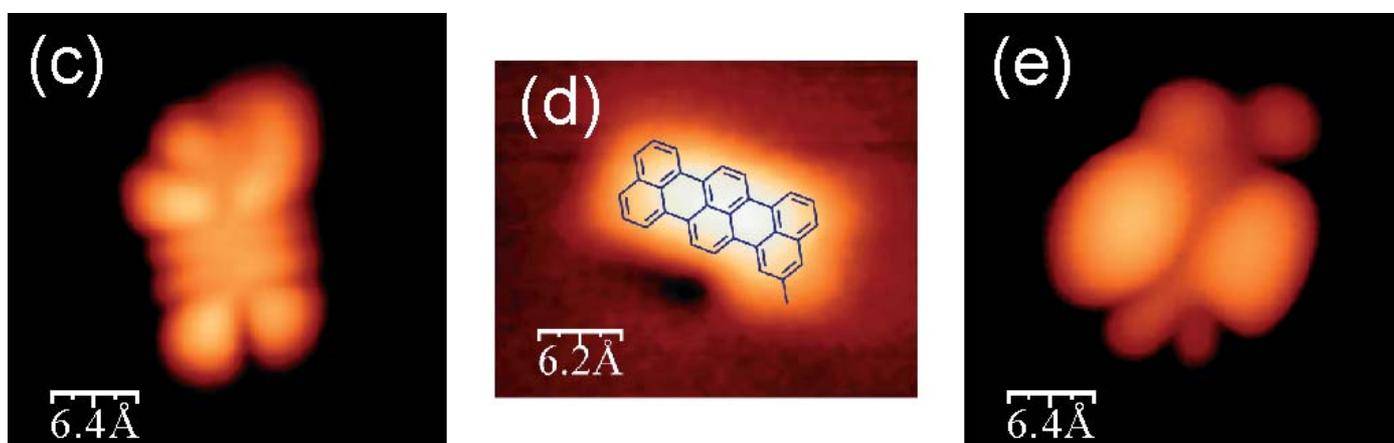
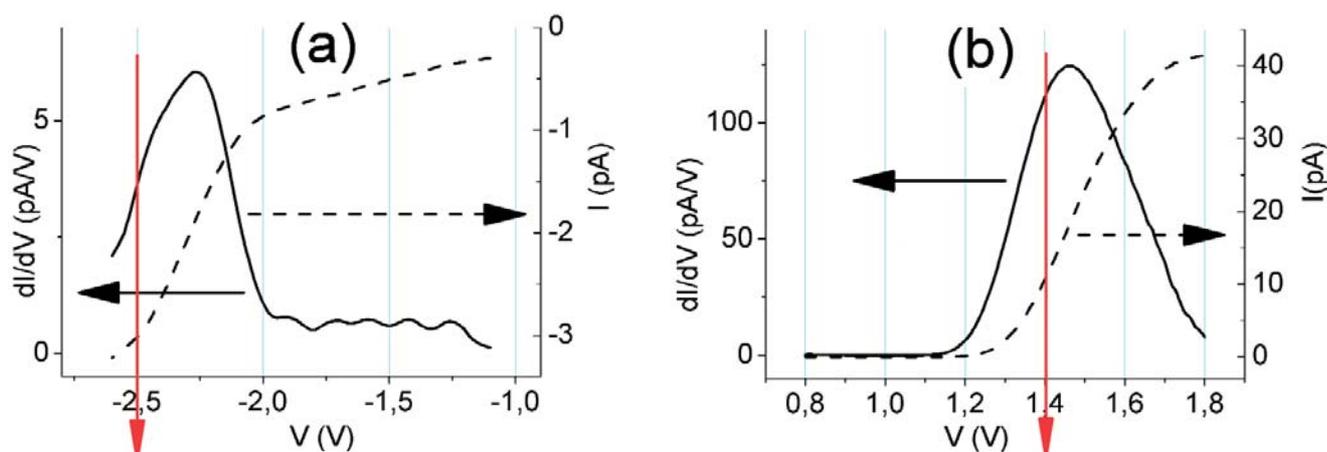
Images calculated by Elastic Scattering Quantum Chemistry (ESQC) calculations [11] are displayed in **Figures 5c** and **6c**. The structure of the system used for the calculation is shown in **Figure 1**. The molecule was positioned at 0.3 nm above the bulk-like and rigid NaCl bilayer. The molecular conformation was deduced from a molecular mechanics optimisation on Cu(111) [12]. This results in a nearly flat molecular board with one of the C-H bonds of the methyl group oriented near a vertical plane. Different tests showed that the calculated images are not very dependent on the precise orientation of the methyl group. The agreement between experimental and calculated images is satisfactory: the size and shape of the orbital lobes are well reproduced, except for the central part of the molecule of **Figure 5b**, as already mentioned. In particular, the two wavy longitudinal nodal surfaces which are observable on the calculated LUMO electronic density do not appear in the calculated STM image.

The LUMO of the free molecule calculated at the same electronic density  $\rho = 10^{-7}$  Å<sup>-3</sup> is shown in **Figure 6a** (**Page 28**). Here again, strong similarities with the experimental image of **Figure 6b** (**Page 28**) appear, except for the middle portion of the two wavy longitudinal nodal surfaces which appear in the calculated LUMO but not in the experimental image.

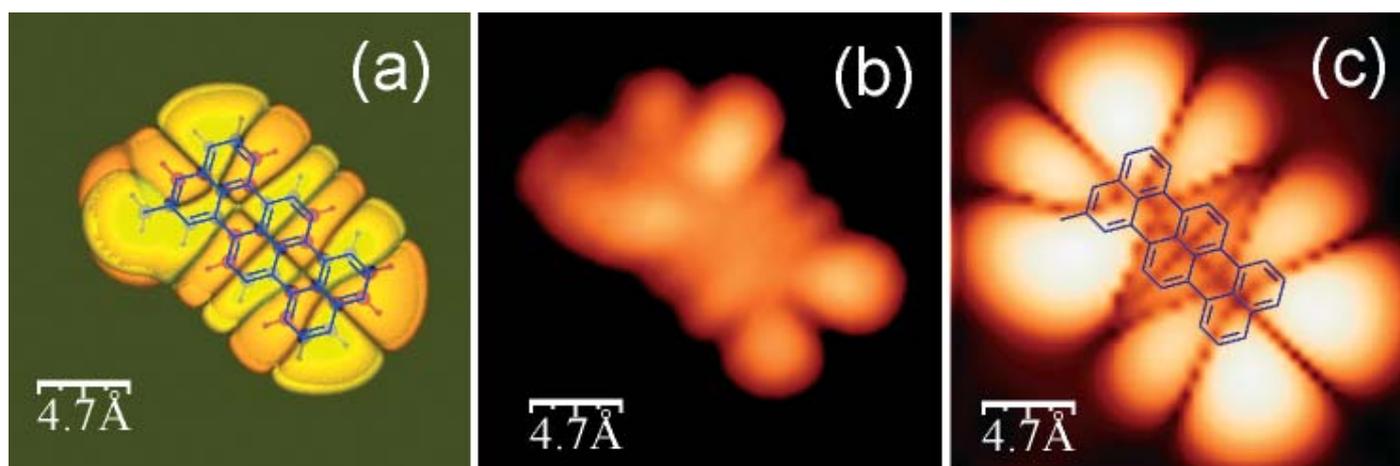
## Discussion

These results confirm the conclusions already reached for the simpler case of pentacene [5]: the peaks observed in the spectra of **Figure 2** are closely related to the HOMO and the LUMO of the molecule. The energy gap separating these resonances is approximately 3.8 eV, quite different from the 2.35 eV observed for the optical HOMO-LUMO gap of terrylene [13]. The reason for this discrepancy is that, as a consequence of the increased lifetime of an electron on the molecule due to the decoupling effect of the insulating layer, these peaks should be considered as characterizing a transient negative ion for the LUMO and a transient positive ion for the HOMO [5]. The ionisation potential and the electron affinity of terrylene are 6.42 eV [14] and 1.66 eV [15]. When referred to the work function of NaCl/Cu(111) which is about 4 eV, the corresponding energy levels are at -2.42 eV and +2.34 eV, but their interaction with the substrate is expected to shift them toward the Fermi level. The observed peak widths (0.3 to 0.4 eV) is not related to the lifetime of the electron but to the coupling of the molecular states with the phonons of the NaCl film [16].

Previous studies showed that even orbitals (atomic or mo-



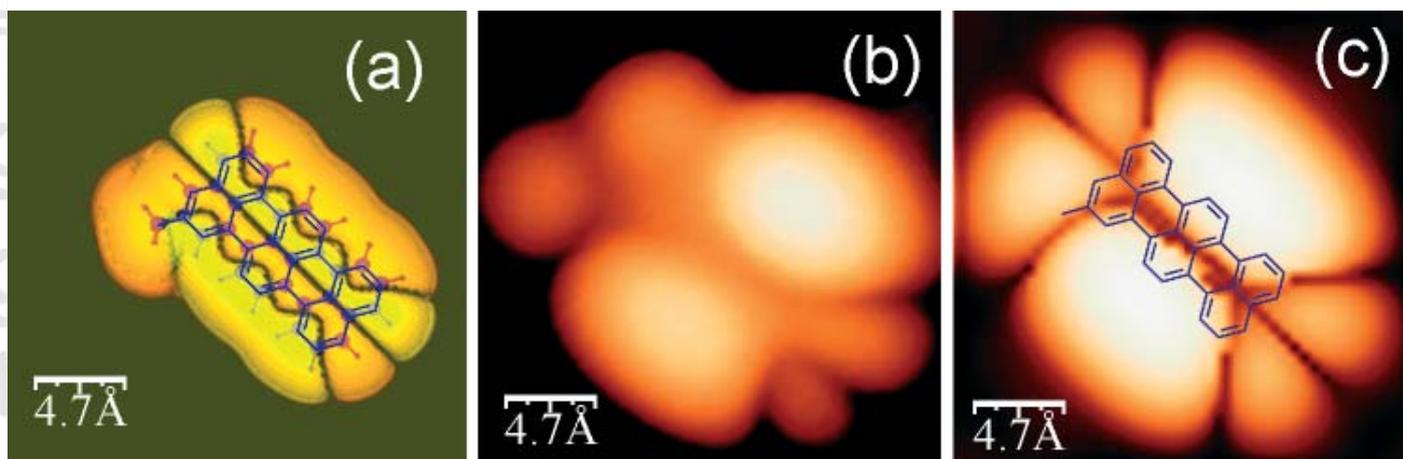
**Figure 4:**  $dI/dV$  spectra for (a) occupied and (b) unoccupied states for MeT on a NaCl bilayer on Cu(111). Constant-current STM images at  $I_t = 1$  pA and (c)  $V_t = -2.5$  V, (d)  $V_t = -1.5$  V and (e)  $V_t = 1.4$  V.



**Figure 5:** (a) Electronic probability density of the HOMO of the free MeT molecule for  $\rho = 10^{-7} \text{ \AA}^{-3}$ , (b) experimental image ( $I_t = 1$  pA,  $V_t = -2.5$  V), (c) calculated image.

molecular) located very far (a few eV) from the Fermi level of the substrate can contribute to the STM image [7,17] at least when the molecule is adsorbed on a metallic surface. The comparison of the experimental and calculated images demonstrates that this is not the case here, due to

the decoupling effect of the insulating layer. It was checked that the MO which have a strong contribution on the methyl group do not contribute to the calculated images of the frontier orbitals of MeT. There is no "direct" contribution of the methyl group, but an "indirect"



**Figure 6:** (a) Electronic probability density of the LUMO of the free MeT molecule for  $\rho = 10^{-7} \text{ \AA}^{-3}$ , (b) experimental image ( $I_t = 1 \text{ pA}$ ,  $V_t = 1.4 \text{ V}$ ), (c) calculated image.

one, which is the consequence of a hyperconjugative interaction between the methyl group and the terrylene core.

As shown for example in Ref. 18, methyl group orbitals of  $\pi$  symmetry can significantly interact with a neighbouring  $\pi$  system.

This work confirms that there are strong similarities between the STM images of a molecule adsorbed on an ultrathin insulating film and its frontier orbitals at very low electronic density. There are nevertheless some differences which are not fully understood. For instance, as mentioned previously, two nodal surfaces which appear on the LUMOs of the free molecule are not observed on the experimental and on the calculated STM images. A truly quantitative understanding of these observations is not yet achieved. Further studies on different and more complex molecules will certainly help in reaching this goal.

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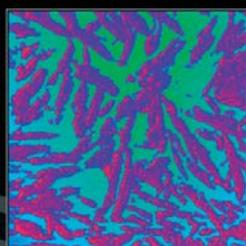
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## High resolution imaging of electronic and molecular structures assembled on InSb(001) c(8x2) surface with LT-STM

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Manipulation and imaging of single organic molecules deposited onto semiconductor surfaces belong to the principal goals of the Pico-Inside project. In order to obtain sub-molecular resolution, STM imaging at low temperatures (down to liquid nitrogen and/or helium temperatures) is used, therefore thermal excitations of the system are reduced to a minimum. In this communication we report on results of the studies performed for 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) molecules assembled on InSb(001) c(8x2) surface. LT STM measurements covered a range of temperatures from 77K up to the room temperature and revealed a sub-molecular structure of individual PTCDA molecules arranged on the substrate in quasi one dimensional chains, as well as a distinct electronic structure of the InSb (001) c(8x2) surface itself which could be interpreted in terms of so called "charge density waves".

The surfaces of AIII-BV compounds are widely used as



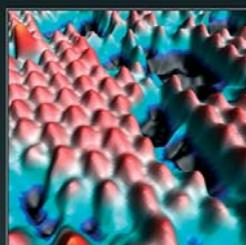
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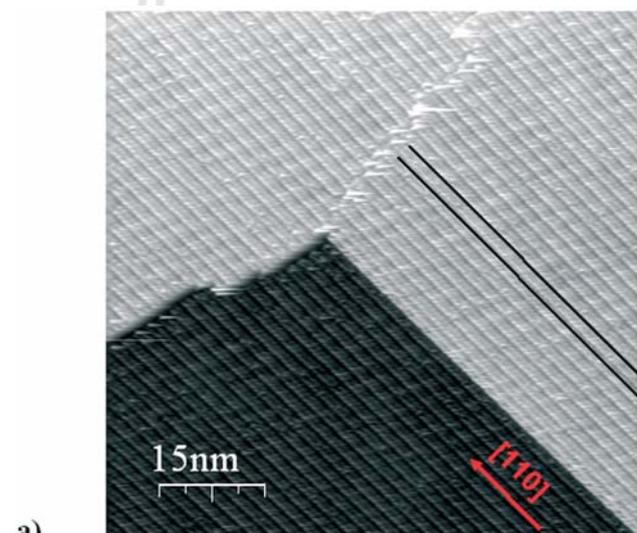
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substrates for thin film growth, and electronic materials processing, therefore, proper understanding of their atomic-scale structure is of significant importance. (001) face reconstruction of these surfaces has been frequently discussed due to their complexity and multitude of possible variations depending on the preparation procedures [1]. The  $c(8 \times 2)$  symmetry is typical for compounds like InSb, InAs and GaAs prepared either by growth in BV-deficient conditions or by ion sputtering and annealing in UHV. The reconstruction model for surfaces of those compounds, so called “ $\zeta$ -model”, was proposed by Lee et al. [2] and Kumpf et al. [3], and later confirmed by a number of experiments [4-7]. According to that model the surface top bilayer has a symmetry of  $4 \times 1$  and comprises All-atom rows running parallel to [110] direction (see Figure 1, Page 30).

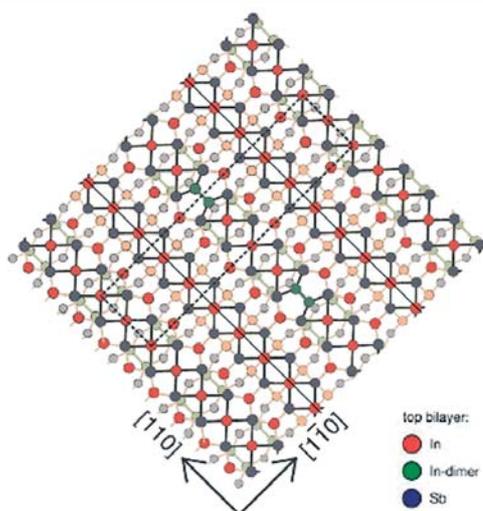
The  $c(8 \times 2)$  superstructure is due to additional All-atom dimerization in the second bi-layer of the crystal. According to a so called “electron counting rule” [8] atoms of the first layer have dangling bonds, unoccupied in indium and occupied in antimony, causing that InSb(001)  $c(8 \times 2)$  surface is quite reactive. This reactivity together with the anisotropy of the surface reconstruction make this system particularly useful as a template for deposition and growth of nanostructures. Our previous studies obtained with NC-AFM at room temperature (see E-Nano Newsletter nr. 6) have shown that small (sub-monolayer) amounts of PTCDA molecules assembled on InSb(001) in a form of chains parallel to the indium reconstruction ridges. Studies at low temperatures using STM enable us to investigate the electronic structure of PTCDA molecules with sub-molecular resolution and, in addition, for identification of a novel surface phase appearing at low temperatures (below 180 K) on InSb (001), whereas exhibiting  $c(8 \times 2)$  symmetry at room temperature.

The real space imaging and tunnelling current spectroscopy were done using Omicron LT-STM instrument with the sample holder mounted directly on the cryostat filled-up with liquid nitrogen. The sample could also be heated up to room temperature. The microscope was operated mainly in constant current mode with a tunneling currents varying from 50pA to 150pA. Etched tungsten tips were used as probes. Epi-ready InSb wafers (Kelpin Crystals, Te-doped) were inserted into the UHV system without any prior chemical treatment. The samples were initially annealed at 700K for several hours and then cleaned by  $\text{Ar}^+$  ion bombardment (ion beam energy of 700 eV, incident angle of 60° off-normal, current density of about  $0.5 \mu\text{A}/\text{cm}^2$ ). The cleaning cycles were performed until a clear  $c(8 \times 2)$  LEED diffraction pattern could be observed. The preparation procedure has been proved to deliver InSb (001) surface with large flat terraces separated by monolayer steps [9].

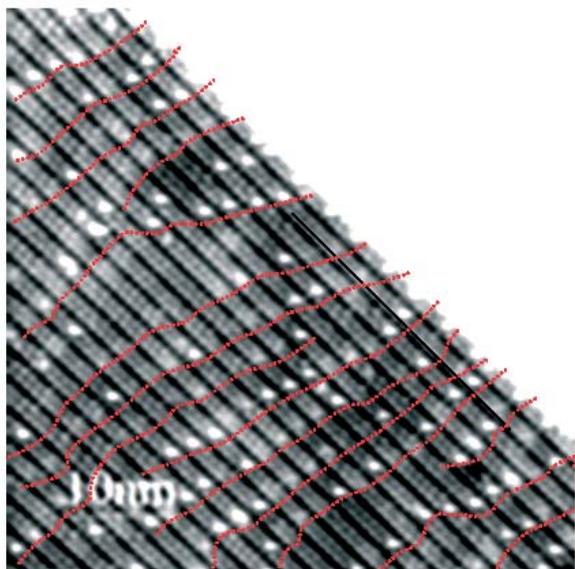
Our STM images taken at room temperature are in good agreement with previous studies, exhibiting  $4 \times 1$ ,  $4 \times 2$  and  $8 \times 2$  symmetries. Typically, the surface is composed of large, atomically flat terraces with edges oriented preferentially along [1 1 0] and [1, -1, 0] crystallographic directions. However, after cooling the sample down to 77K, in addition to this ladder structure, new contrast modulation is seen with an approximate periodicity  $\times 9$  as presented



a)

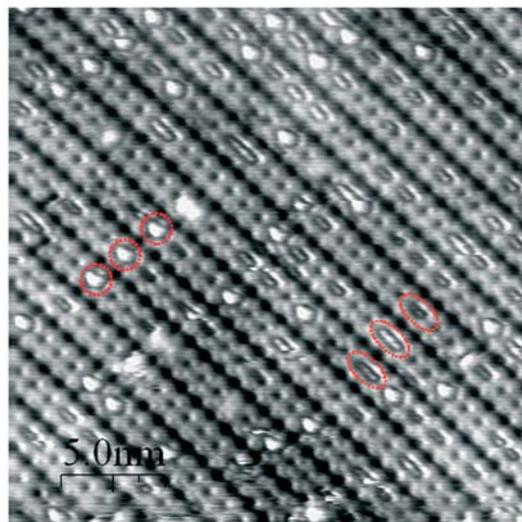


b)



c)

**Figure 1:** STM images of occupied states of InSb(001)  $c(8 \times 2)$  surface at 77K; the surface bias was -0.5V. (a) ladder structure of the surface parallel to  $[110]$  direction with additional contrast modulation; (b) model of  $c(8 \times 2)$  surface reconstruction (due to Kumpf et al.[3]) with black lines marking the reconstruction rows indicated on image a; (c) image with contrast adjusted to the upper terrace level showing wavy-pattern of contrast modulation (marked by red dotted curves) together with the superimposed bright protrusions.

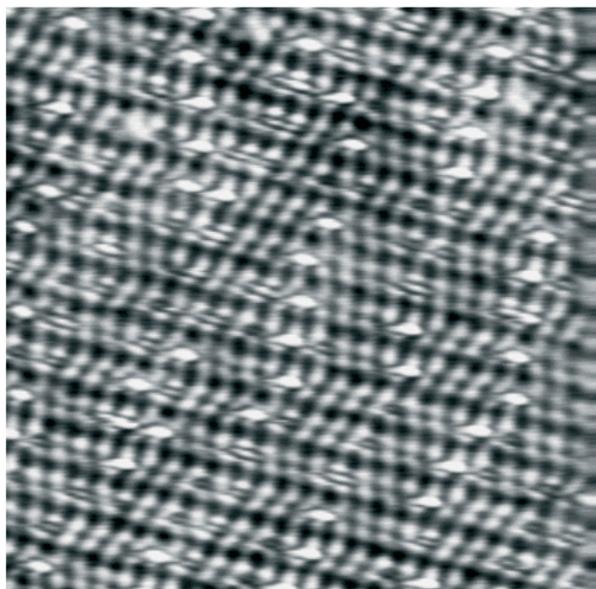


**Figure 2:** High resolution LT-STM image of occupied states on InSb (001) surface demonstrating two types of corrugations: bright (high) protrusions – marked with circles, and elongated features – marked with ovals. The sample bias was -0.4V.

in **Figure 1a-c**. The undulating pattern with superimposed additional bright protrusions is best seen in **Figure 1c** where red dotted lines were drawn to guide the eye. For further identification of the bright features from **Figure 1c** high resolution images of occupied states were taken (see **Figure 2**).

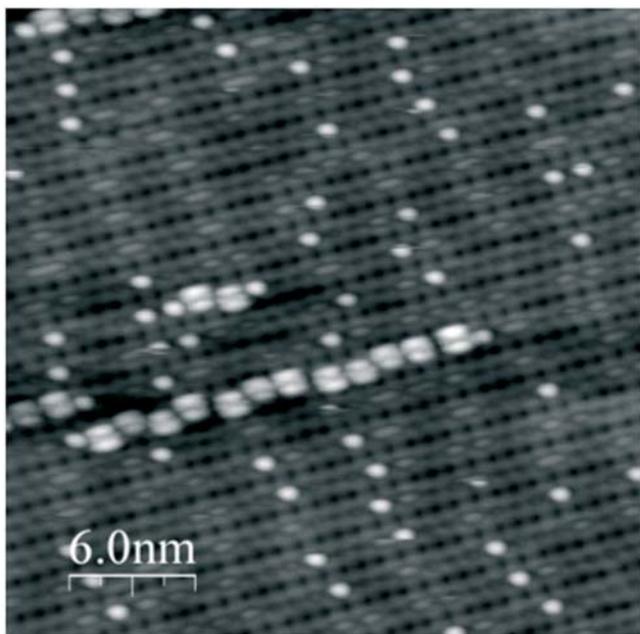
Two types of protrusions could be distinguished: bright ones almost circular in shape, and darker elongated features. In order to exclude possibility that the bright features are due to some adsorbates trapped at the surface from the surrounding environment (vacuum in low  $10^{-11}$  mbar, or better) we have performed repetitive imaging of the same part of our surface for several hours. We found that the average number of the bright features was stable in time. This finding together with the results of bias dependence of our STM images allow us to rule out a possibility of adsorbates and to suggest that bright protrusions are due to structural deformation of the reconstruction rows, whereas the elongated features have character of charge. Appearance of the corrugations described above is often connected with periodic lattice distortion and creation of the domain structure as seen in **Figure 3**. It is striking that the bright protrusions are seen at the domain boundaries.

PTCDA molecules were deposited using a standard effusion cell. The deposition process was done in the  $10^{-10}$  mbar pressure range with the rate of 0,15 ML/min, where the monolayer (ML) is taken as a single layer of molecules similar to that on (102) bulk PTCDA plane of density approx  $8,3 \times 10^{13} \text{ cm}^{-2}$ . After evaporation of sub-monolayer amounts of PTCDA at room temperature and subsequent cooling of the sample to 77K, the bright features with contrast modulation are still observed as shown in **Figure 4**. Interestingly the bright corrugations are present at both ends of nearly each molecular chain and the pinning of the charge density waves by PTCDA molecular chains is clearly seen.  $dI/dV$  images taken using a lock-in technique (see **Figure 5**) confirm further that ordering of the surface charge density distribution and incorporation of the PTCDA molecular chains into overall structure of the sys-



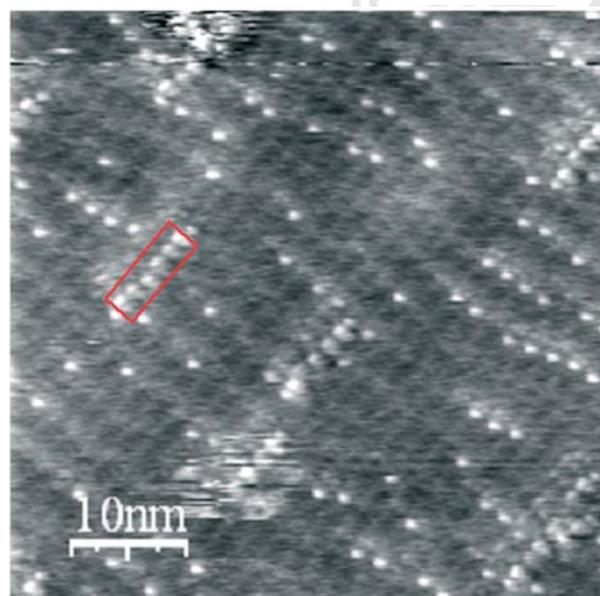
**Figure 3:** LT-STM image ( $25 \times 25 \text{ nm}^2$ ) of occupied states demonstrating a domain-like structure with boundaries formed by bright protrusions and elongated features. The periodic lattice distortion is seen too.

tem take place. Comparison of our results with previous studies of the similar surface (GaAs(001)  $c(8 \times 2)$ ) [7], allow us to suggest that the wavy pattern observed in our experiments at low temperatures is caused by development of charge density waves connected to a quasi-one-dimensional structure of InSb (001) reconstructed surface consisting of topmost indium atom chains running parallel to the [110] direction [10-15].

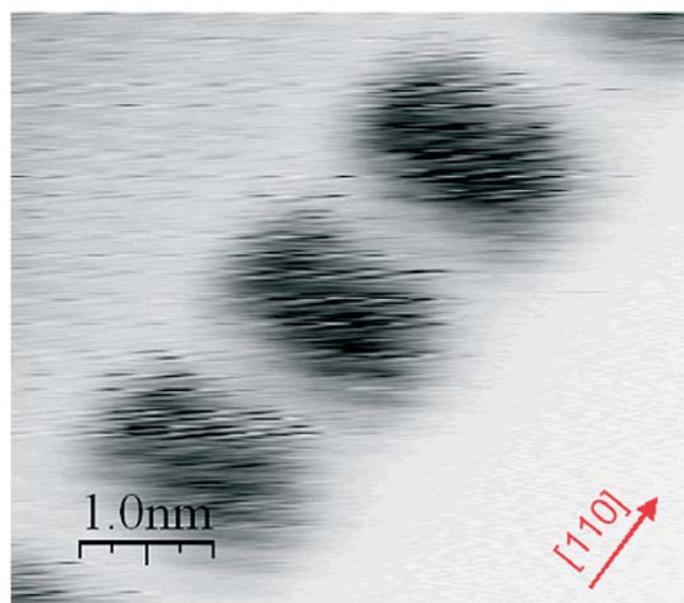


**Figure 4:** LT-STM image of occupied states obtained for submonolayer deposition of PTCDA molecules on InSb(001) reconstructed surface. The sample bias was  $-1.0 \text{ V}$ . PTCDA molecules are seen as double bright protrusions.

Further information on adsorption of PTCDA molecules are obtained by measurements of the tunnelling current with the feedback loop of the microscope switched-off. Geometrical orientation of the molecules with respect to the reconstruction rows is shown in **Figure 6**. The longer



**Figure 5:**  $dI/dV$  map taken with a lock-in technique at the sample bias  $-1.0 \text{ V}$ . The red rectangle marks a chain of PTCDA molecules.



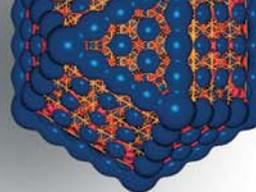
**Figure 6:** PTCDA molecules assembled on reconstructed InSb (001) surface. Tunneling current map taken at  $77 \text{ K}$  with the microscope feedback loop switched-off.

axis of PTCDA seems to be perpendicular to [110] direction.

In **Figure 7 (Page 33)** we demonstrate our ability for imaging of occupied states of PTCDA with sub-molecular resolution using low bias voltages ( $0.5\text{-}0.75 \text{ V}$ ). The results indicate a shift of HOMO states in PTCDA adsorbed on InSb(001) which could be caused by several possible interactions, such as the interaction (attractive) between the molecule and the surface, van der Waals interaction between molecules in the chain, and/or the interaction between the molecule and the tip. In **Figure 7a** one can notice some asymmetry of the orbitals which could likely be explained by tilting of the molecule related to slight elevation of one of the dianhydride groups supported by the topmost ridge of indium atoms (see **Figure 7c**).

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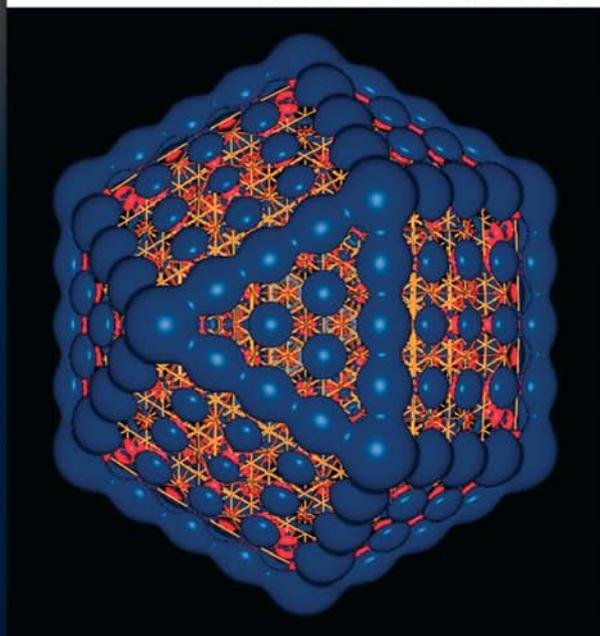
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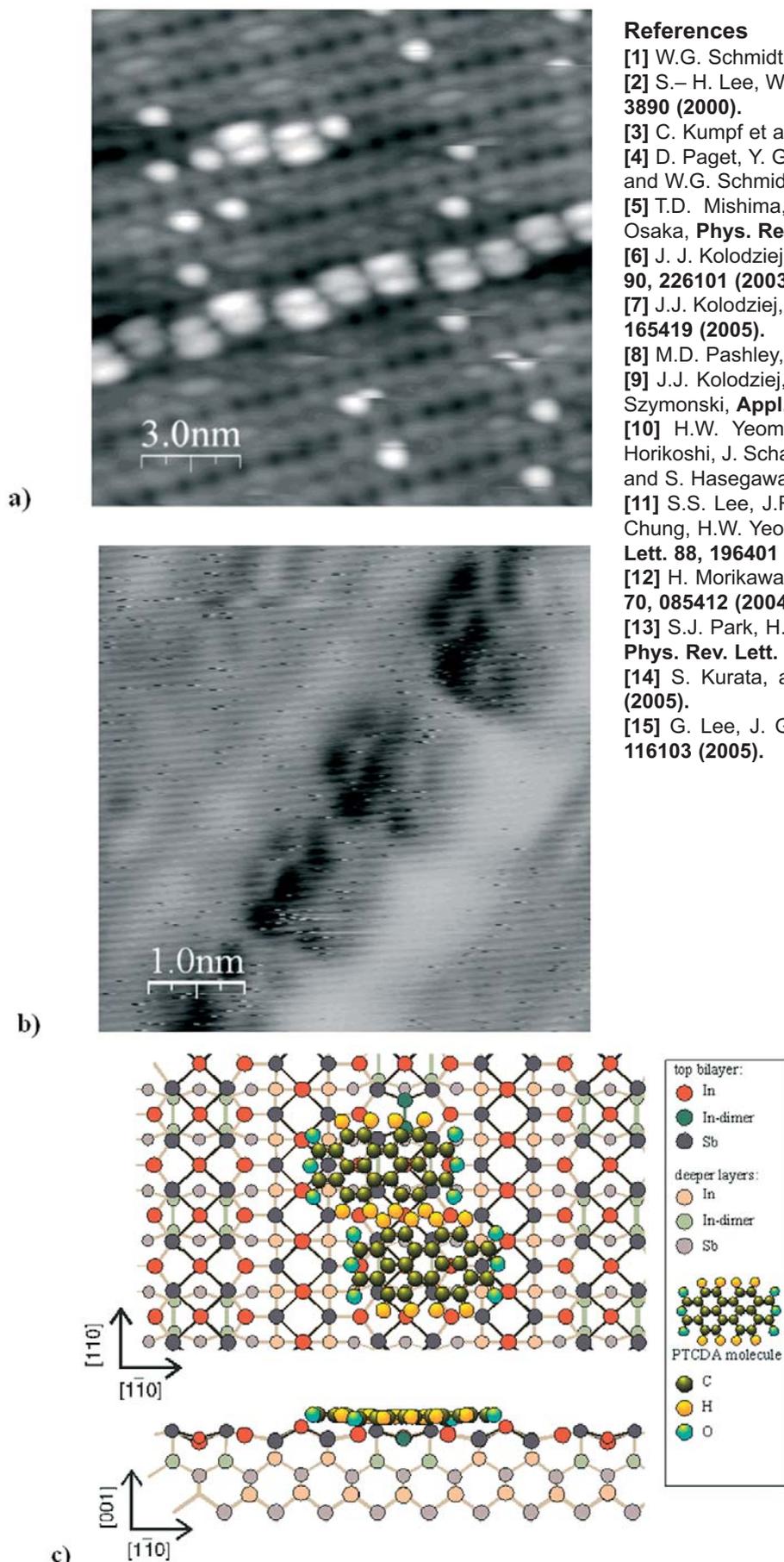
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**Figure 7:** PTCDA molecules assembled on reconstructed InSb (001) surface. (a) Topography map of occupied states taken at 77K and the sample bias -1.0V; (b) Tunneling current map taken at 77K and the sample bias -0.75V; (c) Schematic model illustrating possible adsorption sites of PTCDA molecules on  $c(8 \times 2)$  InSb (001) surface.

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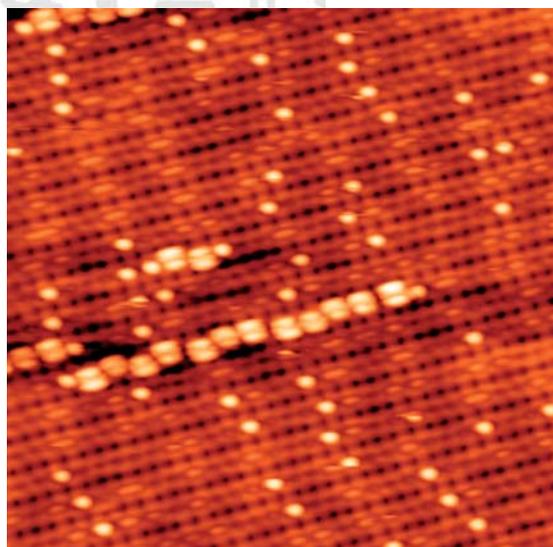
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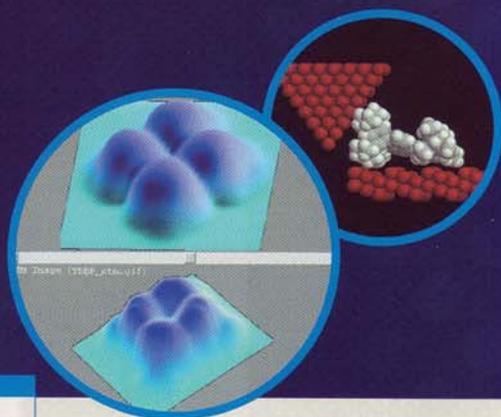
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LT STM image of occupied states of PTCDA molecular chain pinning charge density waves on  $c(8 \times 2)$  InSb(001) surface at the sample bias of -1.0V. PTCDA molecules are seen as double bright protrusions.

G. Goryl, S. Godlewski, J.J. Kolodziej and M. Szymonski

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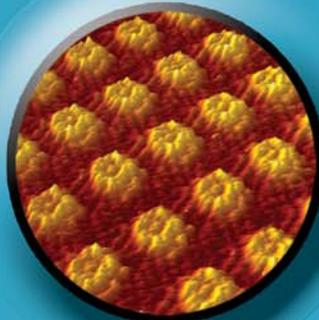
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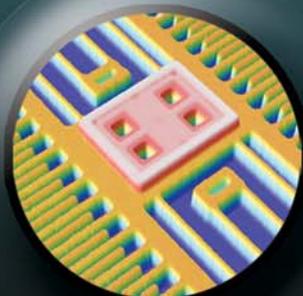
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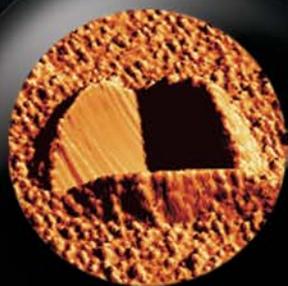
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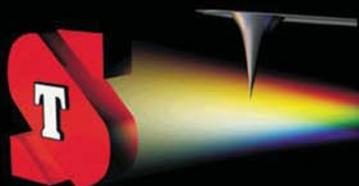
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