nano newsletter

nº 5

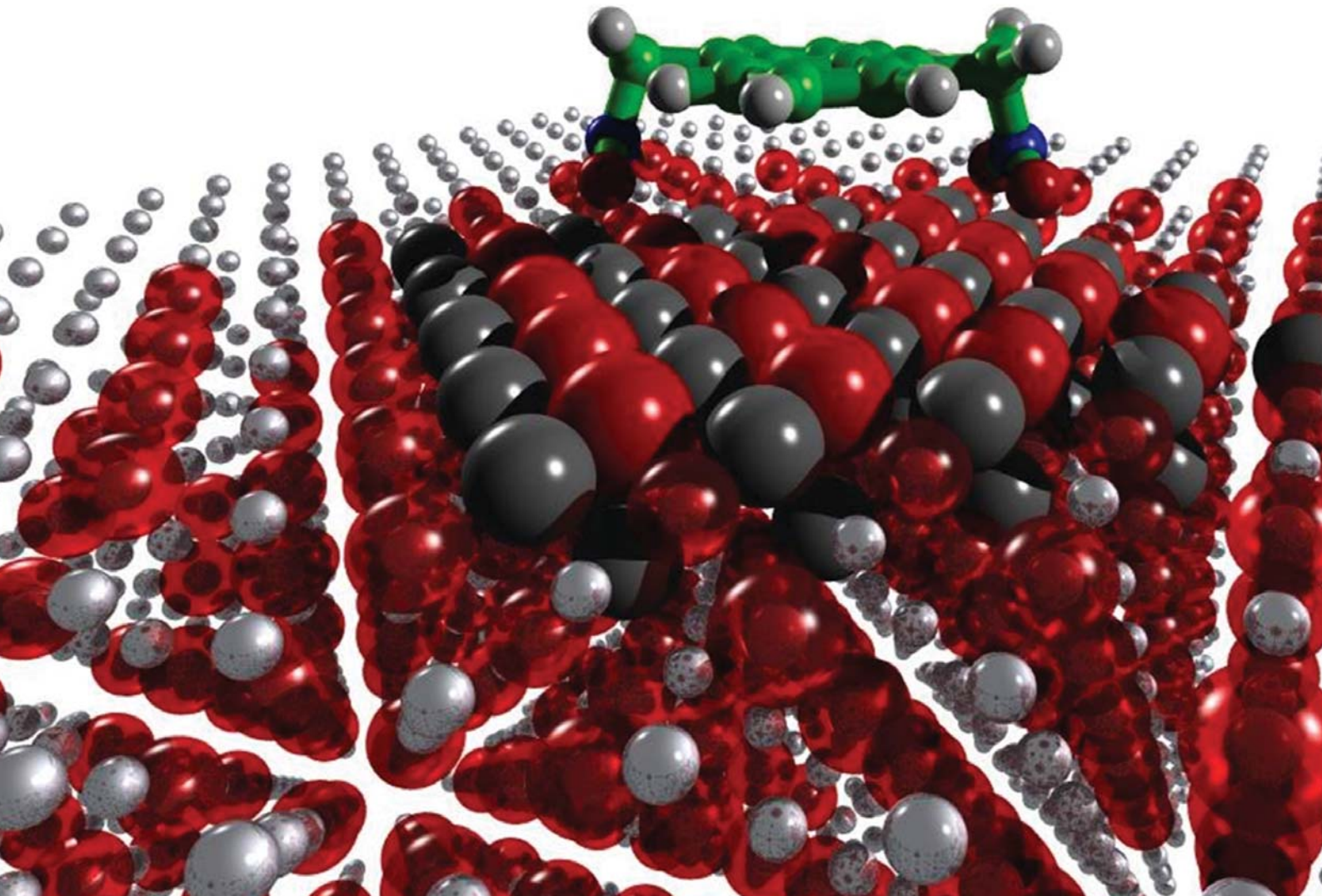
September 2006
http://www.phantomsnet.net

The NID Initiative

Emerging Nanopatterning Methods

Atomic Scale Technologies

Theory and Numerical Simulation for Molecular Electronics



NANOTEC
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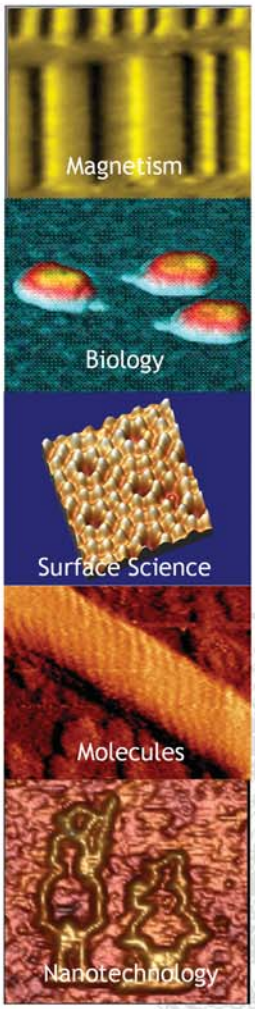

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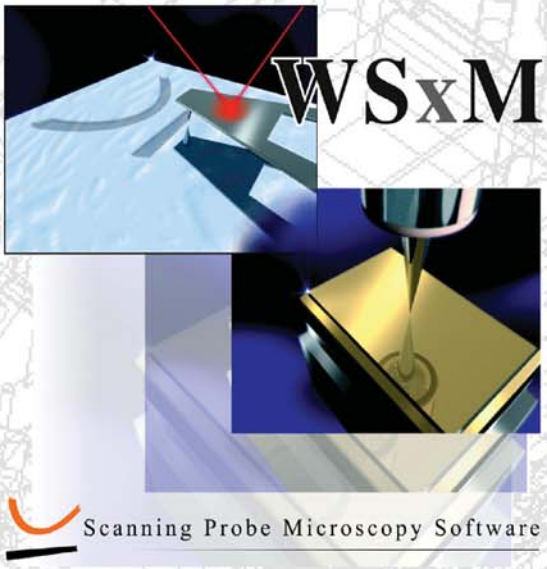

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E nano newsletter

Dear Readers:

Nowadays, and as already mentioned in the last E-Nano issue, modelling the behaviour of possible nanodevices is becoming crucial to understand certain phenomena and to develop new processes.

This E-Nano Newsletter number provides insights on these issues within two EU funded projects: NaPa (NMP) and Pico-Inside (IST).

Modelling and simulation within the NaPa project deals with the elaboration of models and computer simulation of new nanopatterning processes such as nanoimprint lithography, MEMS-based processes, soft lithography and self-assembly.

Atomic scale technology also requires a lot of modelisation. As an example, we present here the results of a Pico-inside unit exploring the theoretical problems related to adsorption of large molecules on perfect and hybrid crystal surfaces.

In addition, two scientific policy articles are proposed:
- A survey summarising the results of the "Nanotechnology Information Devices" (NID) proactive initiative launched in 1998.
- A report from a consultation meeting on "Atomic Scale Technologies" aiming at identifying main challenges and promising research directions in this emerging area.

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

Dr. Antonio Correia

E *nano* *newsletter* Editor
PHANTOMS Foundation

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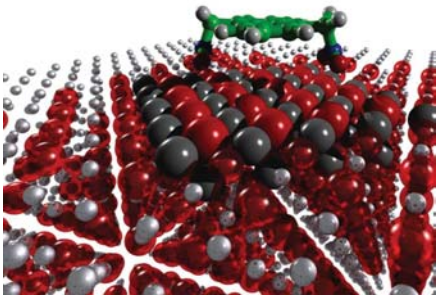

Cover picture:
Illustration of a "Single organic molecule positioned on a surface" system configuration in an embedded cluster calculation (Courtesy: T. Trevethan, M. Watkins, M.L. Sushko and A.L. Shluger - University College London, UK)

EDITORIAL INFORMATION

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The NID Nanotechnology Information Devices Initiative (1999-2003)

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When the NID initiative was conceived in 1998, the ITRS roadmap of standard CMOS semiconductor device shrinking was facing escalating roadblocks. Research into radically new physical implementations of information processing systems appeared urgently needed. At the same time, instruments were starting to be available to visualise, characterise, manipulate, and functionalise matter at scales of about 10 nm, and to perform electronic measurements on samples at this scale. The goal of the NID programme was to investigate how these emerging capabilities could be exploited to develop elementary information processing devices, in a first instance to perform logic and memory operations.

NID in Figures:

1st phase: Call 1 (1999)
FET Open (1999-2000):
22 projects, 23 M€

2nd phase: Call 2 (2001)
FET Open (2001-2002):
28 projects, 37 M€
128 participations

Two calls for proposals were opened, in 1999 and 2001 **(1)**; the turnout was very positive; many proposals submitted to the bottom-up open calls in FET addressed related topics and complemented the initial set of projects. As a result, a vibrant community was created in Europe to pursue the quest for disruptive approaches to information processing hardware.

The NID initiative was truly multidisciplinary, attracting researchers from the fields of electronics, physics, chemistry and biology. It attracted researchers from a majority of EU-15 and associated countries, with intensity commensurate with the relative weight of national efforts in nanotechnology. Even though the participation was expected to come primarily from academic and research centres, the participation of large industrial companies was not negligible.

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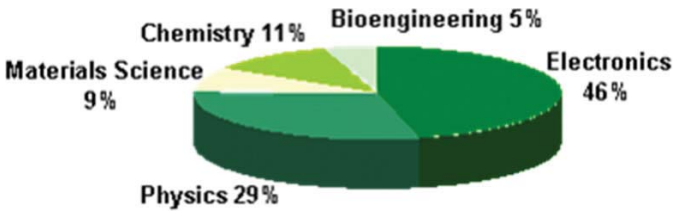


While the ultimate scientific and technological goal was and still is to reach information processing at the level of single molecules or atoms, most of the initiative concentrated on information processing based on structures with dimensions on the order of 10nm. This area seems to offer the best exploitation potential in information processing systems with a time to market of 10-15 years.

NID was a pro-active initiative in Future and Emerging Technologies in the EU's 5th Framework Programme (1998-2002).

Many prominent scientific results have been reached and published by the participants in the initiative, and some of them have also been echoed in the non-technical press. The transfer of the successful results to industrial research is in general not among the primary objectives of FET proactive initiatives. Nevertheless, several participants in the initiative contribute to the discussions of the ITRS roadmap Emerging Research Devices section, and have helped establish this area as a genuine section of the roadmap document.

When compared with similar programmes in the US and Japan, the NID initiative shows a marked difference due to its "bottom-up" character, where the other programmes show a stronger top-down structuring. However, the quality of research in Europe compares well with that of the other continents, with certain weak spots such as in small-scale silicon device research or in computing architectures. Ongoing EC programmes in the context of FP6 are contributing to redress these imbalances.

A recently compiled brochure summarises the projects and results of the second phase of the initiative (2001-2003). The brochure covers a perspective of the initiative in a longer-term context, an objective description of its activities and participants and a subjective assessment of the whole initiative and lessons learned for future R&D programmes. In this article, we only cover a map of the individual projects in the second part of the initiative.

Objectives of NID

The aim of the call for proposals for Nanotechnology Information Devices, published on 27 January 2001, was to promote research into innovative concepts for information processing systems operating at the nano-scale. NID aimed at broadening the scope of earlier device research to bring contributions from fields such as quantum electronics, nano-mechanics and biology. It emphasised radical approaches and cross-disciplinary integration.

The NID initiative promoted three inter-related objectives, namely

- The development of novel architectures and designs for information processing systems that are adequate for nano-scale implementation:
- The development of novel devices that would provide scalability, low power consumption, and potential for room temperature operation.
- The development of tools and techniques for the fabrication of structures with critical dimensions below 10 nm, having in mind scalability and cost issues.

NID Research Projects

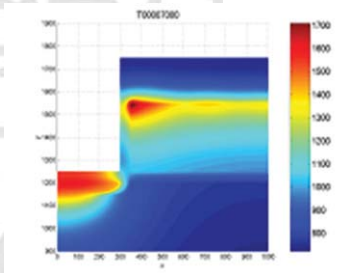
Together with projects from FET Open, 28 projects started between end 2001 and early 2003, represent a total of 128 participations and a total EC funding of 36.6 M €.

The largest number of projects (17) concentrated on the development of new or improved devices for logic, memory, or other functions. Seven projects tackled new concepts of architectures, and four projects concentrated on tools or manufacturing processes. Most of the projects included research on a combination of the above topics. For example, projects researching ultimate scaled devices also needed to research on methods to produce laboratory samples to demonstrate their concepts. The following sections provide the details of topics covered by the individual projects.

Logic and Memory Devices

Projects covered a range of "time-to-market" and novelty scales. Three projects worked on focused incremental innovations for the CMOS architecture, namely low Schottky barrier contacts for CMOS source/drain in SODAMOS, self-assembled Single Electron CMOS memories in SASEM, and laser processing for 65nm CMOS manufacturing in FLASH.

The FLASH project demonstrated superior yield for MOSFET devices using Excimer Laser Annealing for manufacturing of MOSFET transistors at the 65 nm node and below.



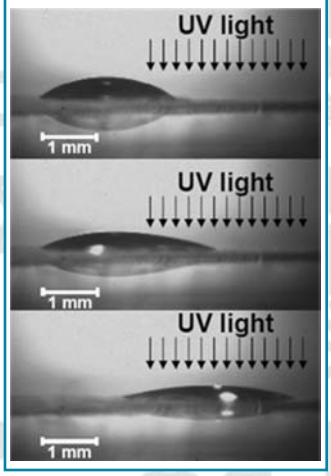
Thermal field in a laser irradiated MOSFET cross section simulated by CLASS.

A number of projects worked on new memory devices, using technologies such as molecular in FRACTURE, phase-change in PC-RAM and phase change with parallel access through cantilevers in INPROM. Bio-inspired devices were proposed in several projects, including DNA wires in DNA-BASED NANOWIRES, switches using magnetic beads on bio-molecules in MOLSWITCH and switches based on organic molecules between electrodes in SAMBA. Ultimate molecular electronic devices were targeted in NICE and CHIC while spin injection, a critical factor in spintronics, was addressed in SPINOSA.

Additional Functions

In addition to the traditional logic and memory functions targeted by the above projects, a number of projects addressed research into additional functions to be incorporated in advanced circuits. Several projects addressed the realisation of high-frequency functions, through cooled RSFQ circuits for AD converters in SUPER-ADC, through various implementations of Resonant Tunnelling Devices (RTD) in QUDOS, NEAR and NANO-TERA, and with Carrier Velocity Modulation transistors in EXTRA.

The MECHMOL project developed a new technique that is able to move macroscopic objects using rotaxane molecules as molecular motors.



A number of projects also addressed the new perspectives of bio-sensing offered by the possibility to manufacture devices at scales similar to those of bio-molecules. They include sensing using a molecular switch in SAMBA, or using an extremely sensitive nano-cantilever in NANOMASS II. A nanoscale DNA sequencing tool was researched in MOL SWITCH, and a microsystem for cell sorting was developed in MEDICS.

Finally, two projects addressed the fascinating opportunities of light as a driver for changes at the molecular level, and of its use as a gating effect for electrical or chemical output in LIMM, or as a trigger of macroscopic motion in MECHMOL.

Novel Fabrication methods

Long-term fabrication innovations were proposed, such as nano-imprint in NEAR, bio-templated interconnects in MINT, self-assembly in ESCHER and in DNA-BASED-NANOWIRES, atomic deposition in NANOCOLD and ultimate atomic manipulation in NICE and CHIC.

Architecture

Fault-tolerant architectures will be required to implement reliable circuits based on nanoscale devices that could be unreliable. FRACTURE and FT-EA developed such architectures. 3-D stacking of CMOS-based circuits were addressed in HIGH-TREE and FRACTURE. Longer term architectures based on self-assembly were addressed in ESCHER, MINT and SAMBA. Finally, the CHIC project proposed a radically new architecture for computation inside a single molecule.

Other actions

In parallel with the R&D projects listed above, two "thematic networks" were also supported by the NID initiative. The objective of the CERION-2 action was to encourage cooperation among teams in the EU and in Canada. MOLCONET supported interactions among teams active in molecular computing. These two contracts provided support for meetings and the organisation of workshops by the participants, but not for research itself.

NID Coordination and the PHANTOMS Thematic Network

The PHANTOMS Thematic network (2000-2004) provided a coordination framework for the whole NID initiative. While the consortia of the 28 research projects of the NID initiative each developed cooperative research towards their own specific objectives, an overall coordination of the cluster of projects was provided by this network.

This initiative supported a very wide range of activities that encouraged researchers across the various projects to exchange information, meet, work together, draw up research agendas, and develop a vibrant European community around NID.

The PHANTOMS network was instrumental in nurturing the NID community. Its efforts have been widely recognised, including in a recent opinion of the European Economic and Social Committee on the Communication from the Commission on "Nanosciences and nanotechnologies: An action plan for Europe 2005-2009".

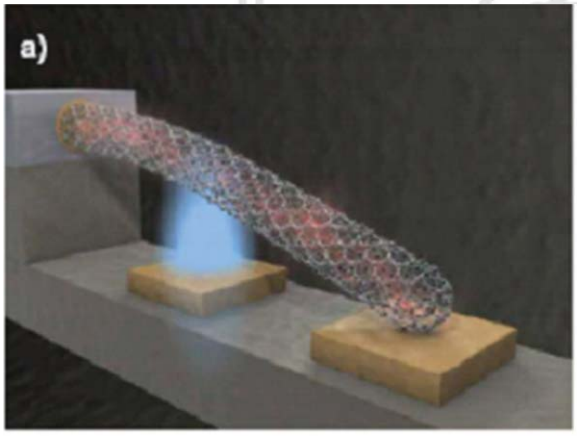
Follow-up of the NID Initiative-FET Emerging Nanoelectronics

The success of the NID initiative led to the take-up of evolutionary developments closer to industry-led initiatives were as part of the main strategic objective on CMOS technology in Framework Programme 6 (FP6) while further advanced were taken up in the Emerging Nanoelectronics Initiative in FET. Developments on materials and instrumentation were further pursued in the new Nanotechnology, Materials and Production programme

The FP6 call for proposals for Emerging Nanoelectronics was clearly set in the context of the Emerging Research Devices section of the ITRS roadmap, and was published on 15 June 2004 to advance research in hybrid and molecular electronics, and prepare the bases for an extension of integrated circuit technology beyond the limits of CMOS scaling. Two large proects were started in 2005 as a result of the call. The NODE project concentrates on nanowires, which are self-assembled

crystalline structures with sizes of 10 to a few tens of nanometres, and on their applications in electronics and opoelectronics.. The PICO-INSIDE project supports disruptive technologies that operate at the atomic scale. These two projects are complemented by a number of smaller FP6 projects arising from the FET Open call for proposals. These projects also cover research on nanotubes; in particular, the CANEL project, started in 2004, addresses CNT applications in nanomechanics. Most of the FP6 projects only started recently and will report on their results at a later point in time.

The FP-6 CANEL project investigates Carbon-based nanoelectromechanical devices that could be applied e.g. as volatile and non-volatile low-dissipation memory elements (short term), tunable RF components for cellular phones (medium term), or mechanical qubits (long term). Structures like in the figure above have already been fabricated using methods of nanoprocessing. The structures were characterized electrically and mechanically showing promising results. Several switching cycles could be demonstrated. The challenge beforehead is the reliable manufacturing of many of these structures and the integration onto a common substrate together with conventional electronic devices.



A singly-clamped conducting Carbon nanotube (diameter about 10 nm) is electrostatically bent by an electric field originating from the gate electrode to close the electric circuit between the source and drain electrodes.

Towards Framework Programme 7

The 7th Framework Programme for Research and Technology Development for the period 2007 – 2013 is currently being discussed. A wide consultation on future ICT challenges was organised by the "Beyond The Horizon" action **(2)**, coordinated by ERCIM. In the strategic area "nanoelectronics and nanotechnology", six challenges were identified:

System-ability of Emerging ICT Technologies and Devices;
Interfacing Cell-Level Biology with Nanoelectronics;
Future interconnects for System Integration;
Post-CMOS Devices and Storage
Nano ElectroMechanical Systems (NEMS)
Atomic Scale Information Technology

Further details of the consultation can be found on the web site of the initiative.

(1) Final EU Reports available for download at:
http://www.phantomsnet.net/Enano/euprojectreports.php
(2) IST-FP6-006622 Beyond-The-Horizon Coordination Action, 23/12/2004-30/06/2006, "Anticipating Future and Emerging Information Society Technologies,

Emerging Nanopatterning Methods

C. M. Sotomayor Torres, H. Wolf, J. Brügger, F. Reuther, G. Lecarpentier, J. Greer, P. Majander and J. Ahopelto

Introduction

In the end of the last century nanotechnology and nanoscience was branching out and new research fields emerged. This progress created demand for new nanopatterning methods. In the mid-90's the investigation and development of new patterning methods was activated in Europe through European and national projects. These efforts were brought together in the Sixth Framework Programme Integrated Project "Emerging Nanopatterning Methods (NaPa)". The consortium integrates well over 80 % of the viable existing European know-how in emerging nanolithography, the leading institutes and companies active in the field of nanopatterning by imprint, soft printing/self-assembly and MEMS-based nanopatterning, both anticipating and responding to the increasing need for technologies, standards and metrology required to harness the new application-relevant properties of engineered structures with nm-scale features.

To achieve this, research in three technology strands is being carried out: **nanoimprint lithography**, **soft lithography & self-assembly** and **MEMS-based nanopatterning**. Research and development is also being undertaken in three overarching themes required by all strands: **Materials**, **Tools** and **Simulation**. Thus, thematically, the consortium embraces and pushes forward the state-of-the-art developments in the physical and engineering sciences with the object-driven mission to provide European industrial and academic researchers with a library of novel nanopatterning processes needed to underpin radical innovations and further scientific developments in nanotechnology.

The consortium integrates SMEs, corporate and national research labs, and university partners to insure a strong presence and interaction of varied innovative enterprises to allow a pipeline from strategic research to commercial exploitation.

The outcome of NaPa project will finally be process libraries with standards for nanoimprint lithography, soft lithography & self-assembly and MEMS-based nanopatterning. Also we will create a simulation packages that can be used for optimisation of fabrication processes. Very important objective is to design and construct production tools dedicated for manufacturing products using the emerging nanopatterning processes. The whole manufacturing chain will be tested by fabricating devices and demonstrators in the fields of nano-optics, bioapplications and nanoelectronics.

The duration of the project is 48 months and the total volume is 31 M€. The total number of groups is 35, coming from 14 countries. Of the partners one third comes from industry, one third are research institutes and one third universities.

The progress during the first two years in the six subprojects are briefly described in the following sections. Within Nanoimprint lithography approaches and tools for benchmarking and metrology have been developed. This work aims to establishing standards for the technology. The subproject has produced several demonstrators/proof-of-concepts during the first half of the project. Soft lithography and self-assembly has concentrated on development of large area lithography, of low diffusion inks and of processes related to functionalised nanoparticles. Particle assembly through capillary forces has evolved into a mature state. MEMS based nanopatterning fabricated a system for nanodispensing and investigated the possibility to combine nanostencil deposition with CMOS technology. Two technical solutions with reservoirs for inks have been demonstrated for nanodispensing. In Materials several new polymers dedicated to nanoimprinting have been developed. In addition, various functionalised materials, including polymers with modified surface and materials loaded with semiconductor nanoparticles, have been synthesised for imprint and soft lithography, self-assembly and nanodispensing. Tools subproject has finalised a new imprinting tool capable to cold and hot nanoimprinting. Also a prototype system for stencil alignment and fixation has been developed. The Modelling subproject has concentrated on modelling the imprint process, on investigation of the effect of stress building up in the stencil mask during evaporation and on interaction of self-assembling molecules with surfaces.

One of the great successes of the project has been the **PANAMA** school for "**PA**ttering at the **NA**noscale – **M**ethods and **A**pplications", the first one arranged in Toulouse in June 2005. The format was a small school (25 students), combining one week of practical training on Emerging Nanopatterning Methods and one week of magisterial courses on nanopatterning, applications in industry and ethical and societal issues. The school was extremely well received and the second edition was arranged in July 2006.

1. Nanoimprint lithography

Nanoimprint lithography is a polymer embossing process requiring a stamp, a polymer film, and a defined temperature and pressure cycle. It is capable of delivering sub 10nm resolution and has been listed as on of the top 10 technologies for the 21st century. The key objective of this subproject is to establish a library of processes for applications of NIL in photonics and nanobiotechnology, in the first instance. The subproject is further developing NIL in order to enhance throughput as well as to set metrics and standards.

Achievements of NaPa in NIL:

Four processes have been entered in the NaPa process library:

- Biochips in a single NIL step, including process flows for stamps, biochip and lid fabrication.
- Large area imprinting masters for microfluidic substrates.
- Printed DBR gratings for laser diodes for gas sensor applications.
- Printed optical encoders

Moreover, three demonstrators have been delivered:

(a) DBR laser diodes for gas sensing applications with imprinted, instead of electron-beam written, Bragg gratings (sub 100 nm wires 400 nm pitch)

(b) Fluidic chip with imprinted diffraction grating in lieu of NIL photonic structures on 100 mm wafers.

(c) High accuracy optical encoder, 20 mm long with pitch down to 160 nm pitch. Targeted accuracy better than +/-0.5 mm and resolution near 1 nm.

Below some of the research highlights.

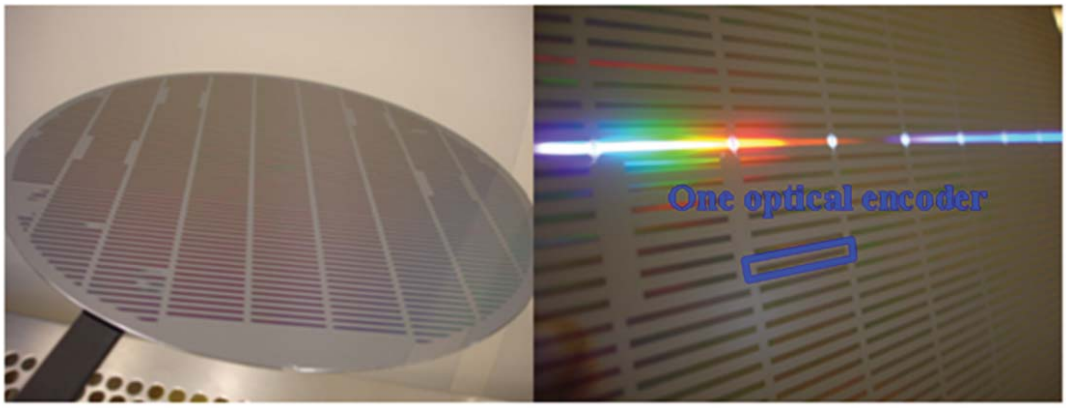


Fig. 1.1 Wafer-scale Nanoimprint lithography for optical applications. Full 200 mm silicon stamps and closer view of several optical encoders. Minimum feature size is 250 nm. (S Merino, Tekniker, and S Landis, LETI)

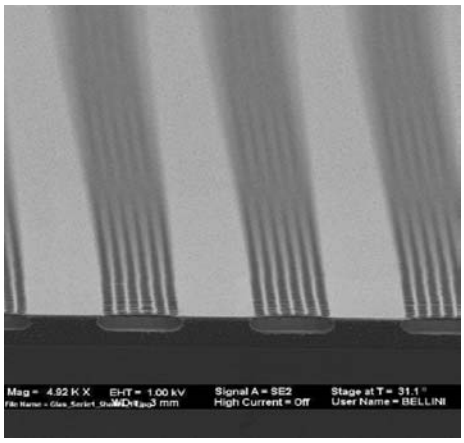


Fig. 1.2 Nanoimprinting for microfluidics. SEM micrographs of the processes samples with the new design. Long lanes of pores, ordered in groups of 3 or 5 rows, where imprinted. By dissolving the LOR (Lift-off-resist) below the pores, long channels are created which serve for fluid transport. (H Schift et al, PSI)

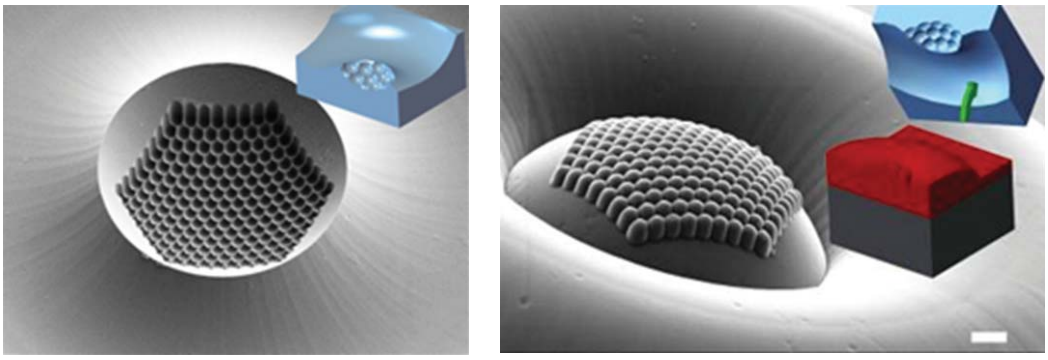


Fig. 1.3 Left: Towards 3D nanoimprinting. Fabrication of three-dimensional stamps by electro-beam lithography, focused ion beam and wet etching. Right: Structure of compound eyes fabricated by hot embossing on the thermoplastic polymer Zeonex. (M Tormen et al, TASC)

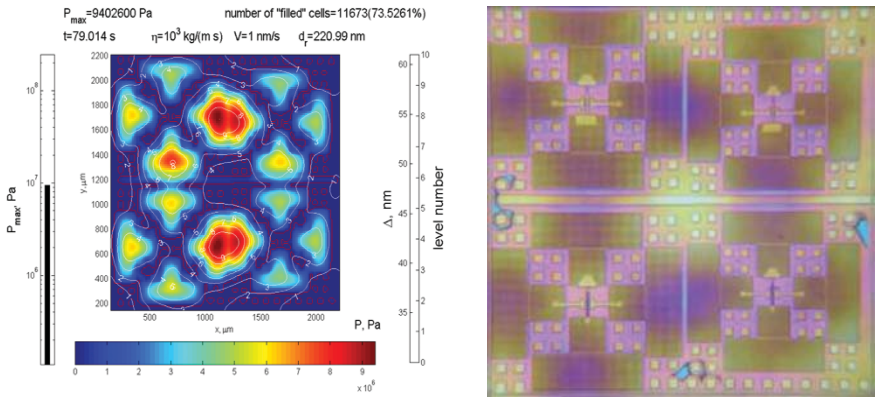


Fig 1.4 Simulations in Nanoimprint Lithography. Pattern transfer in nanoimprint lithography (NIL) is largely dependent on the distribution of cavities and protrusions on the NIL stamps. A homogeneous residual layer thickness can be achieved by optimising the stamp geometry using viscous flow simulation. For real stamps, the viscous flow simulation based on the solution of Navier-Stokes equations requires unreasonable large computational costs. We have developed a coarse-grain method, which makes it possible to simulate the imprinting process adequately even using personal computers. (S. Zaitsev et al, IMT)

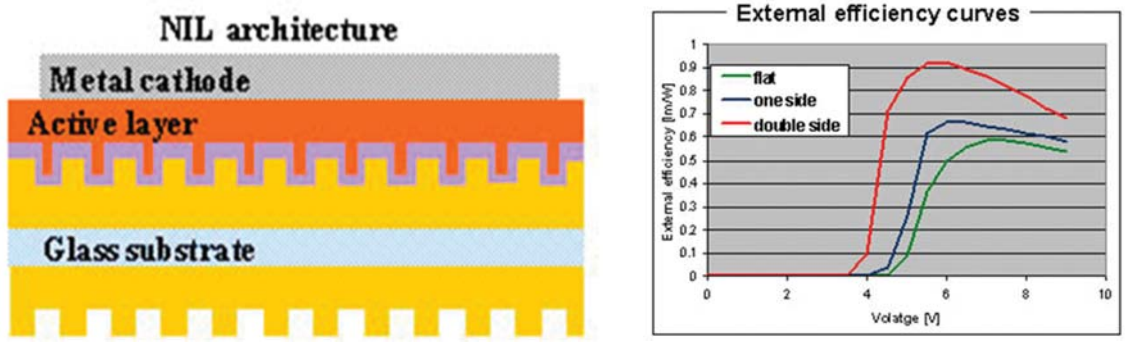


Fig. 1.5 Nanoimprint applications in organic opto-electronics. The NIL introduction in the light emitting technology allows the fabrication of high performance substrates on large area with a low cost process. A high increment of performances is obtained with double layer nanostructuring of the devices. (V Lambertini et al, CRF)

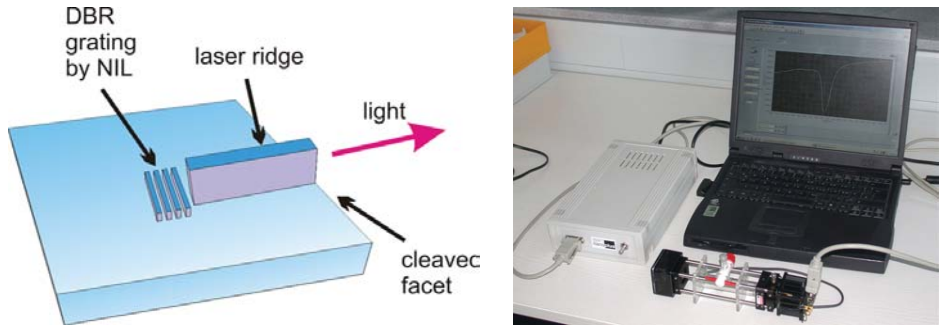


Fig. 1.6. Applications of NIL in optoelectronics for gas sensors. Schematics of a DBR laser diode. The DBR grating in this device concept is fabricated by using nanoimprint lithography. The DBR laser diode and its control electronics. (Nanoplus GmbH)

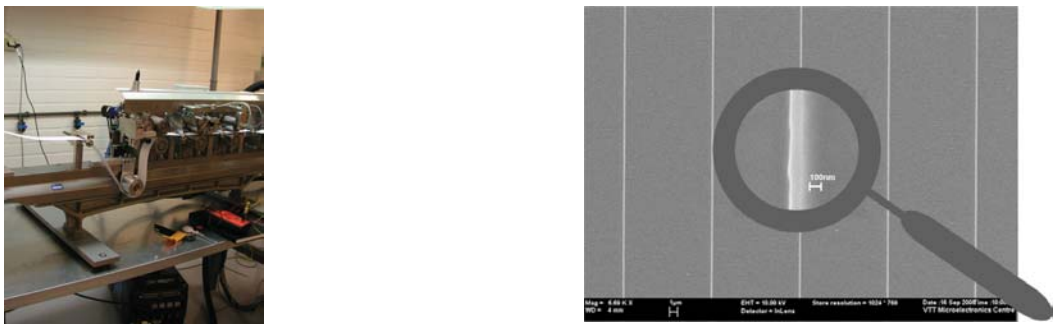


Fig. 1.7 Left: Roll-to-roll printing. Flexo unit tested using printing inks and polyaniline-toluene on paper . Right: SEM image of Ni stamp with 100 nm wide and 170 nm high ridges. (T Makela et al, VTT)

Highlights in publications:

B. Bilenberg, M. Hansen, D. Johansen, V.Özkapici, C. Jeppesen, P. Szabo, I. M. Obieta, O.Arroyo, J. O.Tegendfeldt, and A. Kristensen, Topas Based Lab-on-a-chip Microsystems Fabricated by Thermal Nanoimprint Lithography, Journal of Vacuum Science and Technology B, Vol. 23 (2005) 2944-2949.

N. Kehagias, M. Zelsmann, C. M. Sotomayor Torres, K. Pfeiffer, G. Ahrens and G. Gruetzner, 3D Polymer Superstructures fabricated by UV-Curing Imprint Llithography, J. Vacuum Science and Technology B 23 (6) 2954-2957, Nov/Dec 2005

C. Gourgon, C. Perret, J. Tallal, F. Lazzarino, S. Landis, O. Joubert, R. Pelzer, Uniformity across 200 mm silicon wafers printed by Nanoimprint Lithography, J. Phys. D: Appl. Phys 38 (2005) 70-73.

K. Seunarine , H. Morgan , N. Gadegaard , C. D.W. Wilkinson and M. O. Riehle, Super-hydrophobicity and super-hydrophilicity of regular nanopatterns: E. Martines, Nano Letters **5** (10) 2097 (2005).

A Pozzato, S. Dal Zilio, G. Fois, D. Vendramin, G. Mistura, M. Belotti, Y. Chen, F. Natali, Superhydrophobic surfaces fabricated by nanoimprint lithography , Microelectron. Eng. 83, 884 (2006)

2. Soft Lithography & Self-assembly

The SLASA subproject develops large area, low-cost nanopatterning processes making use of soft elastomeric patterned stamps and self-assembly techniques. The focus lies on soft UV-NIL and microcontact printing (μCP). Soft UV-NIL allows nanopatterning on wafer scale in a single imprint step at room temperature and at low imprint pressures (<1 bar). μCP uses elastomeric stamps to transfer an ink pattern to a substrate. The scope of inks applied extends from small molecules (alkanethiols) over biomolecules, dendrimers, and polymers to even nanoparticles. Self-assembly methods are explored to complement and optimize large area patterning with functionalized nanoparticles. Applications for the methods developed in the SLASA subproject are envisaged in sensors, diagnostic devices, photonics, photovoltaic and post-CMOS electronic devices.

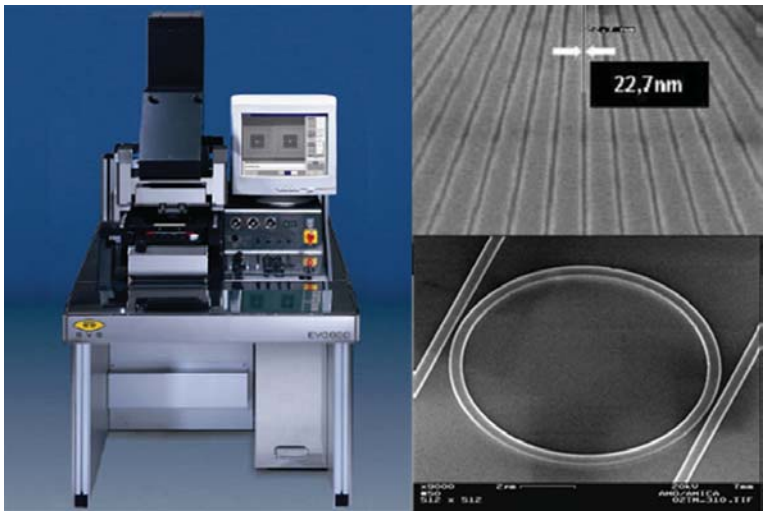


Fig. 2.1 EVG620 tool for soft UV molding (left). Imprinted high resolution pattern (upper right) and optical ring resonator structure (lower right). (Images courtesy of EV Group and AMO GmbH)

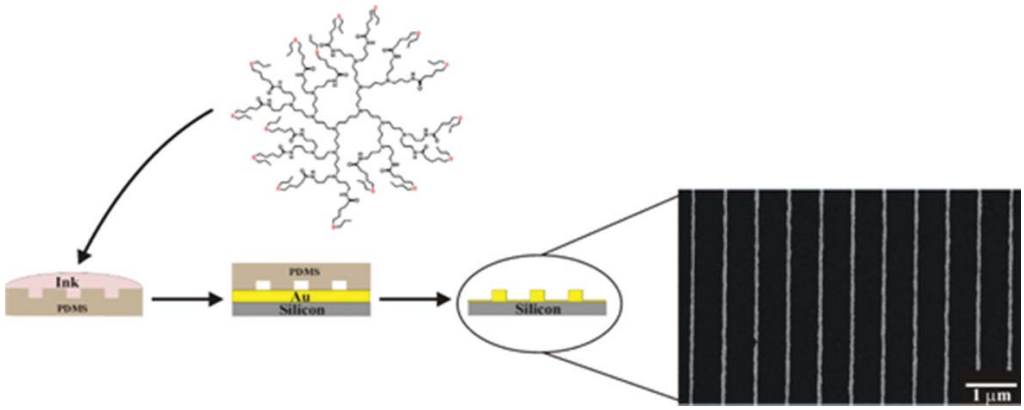


Fig. 2.2 100 nm wide lines produced by positive CP with dendrimer inks (image courtesy of University of Twente)

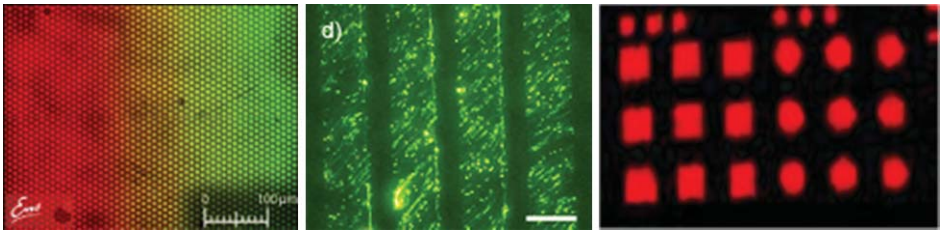


Fig. 2.3 µCP of a double gradient of proteins for bio-chip applications, BSA-FITC in green, BSA-Cy3 in red (left image). µCP of stretched lamda-DNA complexed with a fluorescent conjugated polyelectrolyte (scale bar 15 µm) (center image). µCP of oligonucleotides for bio-chip applications (right image). (images courtesy of CNRS-LPN, Linkoeping University, and CNRS-LAAS)

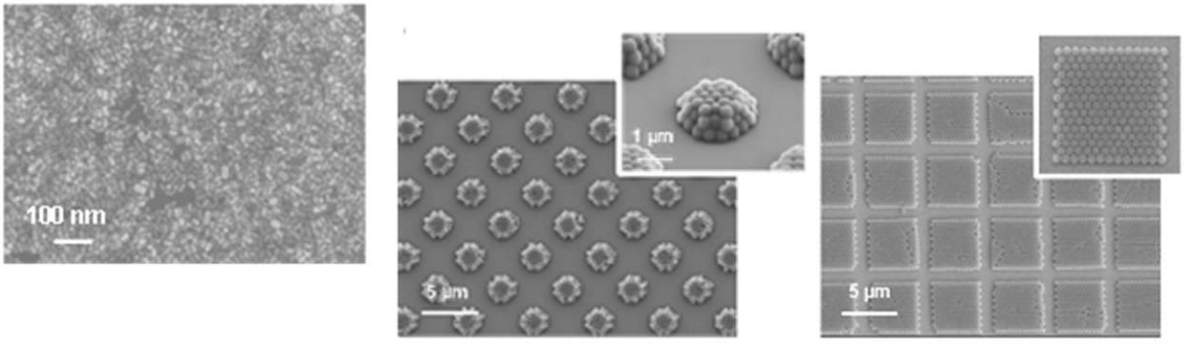


Fig. 2.4 Gold nanorods deposited by convective assembly (left image). Polystyrene particles (500 nm) assembled on an elastomer stamp and then printed on a gold coated silicon substrate (center and right image). (Images courtesy of CNR-IPCF and IBM Research GmbH)

The tools and processes developed in NaPa for soft UV-NIL allowed to fabricate structures with sub-50 nm feature size on 4 and 6 inch wafer scale setting a new standard to the state of the art.

Heavyweight dendrimer inks with low surface diffusion enable high resolution μCP with high pattern fidelity (100 nm wide lines). A high-speed mCP-tool developed in Napa SLASA was used to demonstrate for the first time that self-assembled monolayers (SAMs) of alkanethiols can be printed within milliseconds, an important achievement towards a high throughput printing process.

Biomolecules and biomolecule-polymer complexes were aligned and printed with elastomer stamps for future multiplexing biosensor applications.

A variety of nanocrystals from semiconductor materials and metals was synthesized with control of shape and functionality. Nanocrystals with reactive chemical functionalities, host-guest chemistries as well as bioconjugated particles are used for self-assembly processes. Nanoparticle assembly is achieved through topographical and chemical patterns.

Representative publications from the SLASA subproject

Perl et al. "Heavyweight dendritic inks for positive microcontact printing" *Langmuir* **2006** in press

Helmuth et al. "High-speed microcontact printing" *J. Am. Chem. Soc.* **2006**, *128*, 9296-9297

Cozzoli et al. " Synthesis of TiO2–Au Composites by Titania-Nanorod-Assisted Generation of Gold Nanoparticles at Aqueous/Nonpolar Interfaces" *Small* **2006**, *2*, 413 – 421

Thibault et al. " Microtransfer molding of hydrophobic dendrimer" *Microelectronic Engineering* **2006**, *83*, 1513–1516

Kraus et al. " Closing the Gap Between Self-Assembly and Microsystems Using Self-Assembly, Transfer, and Integration of Particles" *Adv. Mater.* **2005**, *17*, 2438-2442

Foley et al. " Microcontact Printing of Proteins Inside Microstructures" *Langmuir* **2005**, *21*, 11296-11303

Kraus et al. "Printing chemical gradients" *Langmuir* **2005**, *21*, 7796-7804

Balmer et al. " Diffusion of Alkanethiols in PDMS and Its Implications on Microcontact Printing (mCP)" *Langmuir* **2005**, *21*, 622-632

Onclin et al. " Molecular Boxes on a Molecular Printboard: Encapsulation of Anionic Dyes in Immobilized Dendrimers" *Small* **2005**, *1,* 852 –857

Bruinink et al. "Supramolecular microcontact printing and dip pen nanolithography on molecular printboards" *Chem. Eur. J.* **2005**, *11*, 3988-3996

Maury et al. "Patterned self-assembled monolayers in silicon oxide prepared by nanoimprint lithography and thei applications in nanofabrication" *Adv. Funct. Mater.* **2005**, *15*, 451

Maury et al. "Directed Assembly of Nanoparticles onto Polymer-Imprinted or Chemically Patterned Templates Fabricated by Nanoimprint Lithography" *Adv. Mater.* **2005**, *17*, 2718–2723

Plachetka et al. "Single step soft UV-nanoimprint process for 4 inch wafer patterning" *Japan. Electr. J.* **2005**, *3*, 80-83

Depalo et al. "Cyclodextrin mediated phase transfer in water of organic capped CdS nanocrystals" *Synthetic Metals* **2005**, *148*, 43-46

Cozzoli et al. "Low dimensional chainlike assemblies of TiO_2 nanorod-stabilized Au nanoparticles" *Chem. Comm*. **2005**, 942-944

Cozzoli et al. "Efficient charge storage in photoexcited TiO_2 nanorod-noble metal nanoparticle composite systems"Chem Comm **2005,** 3186-3188.

Cozzoli et al. "Shape and Phase Control of Colloidal ZnSe Nanocrystals" *Chem. Mater*. **2005**, *17*, 1296-1306

Mahalingam et al. "Directed Self-Assembly of Functionalized Silica Nanoparticles on Molecular Printboards through Multivalent Supramolecular Interactions" *Langmuir* **2004**, *20*, 11756-11762

3. MEMS-based nanopatterning
(The mechanical zoom to nanoscale)

The subproject MEMS deals with the development of new micro-mechanical tools for the patterning of surfaces either by local liquid dispensing through nanoprobes (NADIS, BioPlume), or by local material deposition through miniature shadow-masks (nanostencils). The patterning techniques have several distinct advantages with respect to conventional photolithography methods: they are a) scalable, b) use simple equipment, c) can be applied to all sorts of substrates including elastic, and d) are entirely additive methods. The local material deposition aspect is probably to most noteworthy in that it drastically eliminates cross-contamination. Micromechanical devices have the following distinct assets for use as nanopatterning tools. Due to their small size and mass they have a high resonance frequency (kHz-MHz) making them immune against vibration and thermal noises and applicable for rapid interactions with features on surfaces. The cantilevers and membranes are mechanically compliant with low spring constants, which allow creating soft-contacts between probe and surface and reduce the risk to damage fragile substrates. MEMS tools can be micromachined using wafer manufacturing methods with integrated sensor and actuators enabling the conception of parallel probe arrays that will speed up the probe-surface interaction of single tips.

Application to soft and/or fragile surfaces makes MEMS based nanopatterning versatile and useful for application in bio/nanotechnology, surface materials science, solid-state physics, nanoelectronics/molecular electronics, spintronics. MEMS-based pattering is excellent for rapid prototyping, but are scalable to full wafer scale.

The NADIS / BioPlume approach (fluidic nanopatterning)

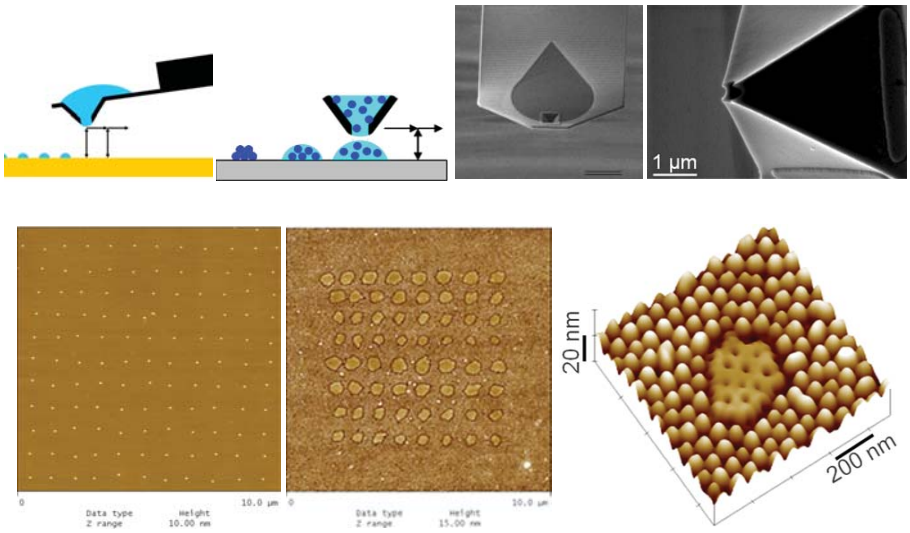


Fig. 3.1 Images showing the NADIS concept and representative results. Top row from left to right: Conceptional sketch of nanoscale dispensing (NADIS) using a specific AFM probe; Nanoparticles or biomolecules can be deposited on the surface by using the liquid as transport medium; SEM micrograph showing the loading area for the liquid of an NADIS probe; Close view of the tip of an NADIS probe, at the apex is located a small aperture that allows the transfer of liquid towards the sample surface. Bottom row from left to right: AFM micrograph of an array of clusters made of a few nanoparticles each, deposited by NADIS; Besides the deposition of nanoparticles, NADIS can also be used to induce local morphological changes on a responsive surface such as micellar layers; AFM micrograph showing the detail of one spot of inversed micelles. (Images courtesy of CSEM).

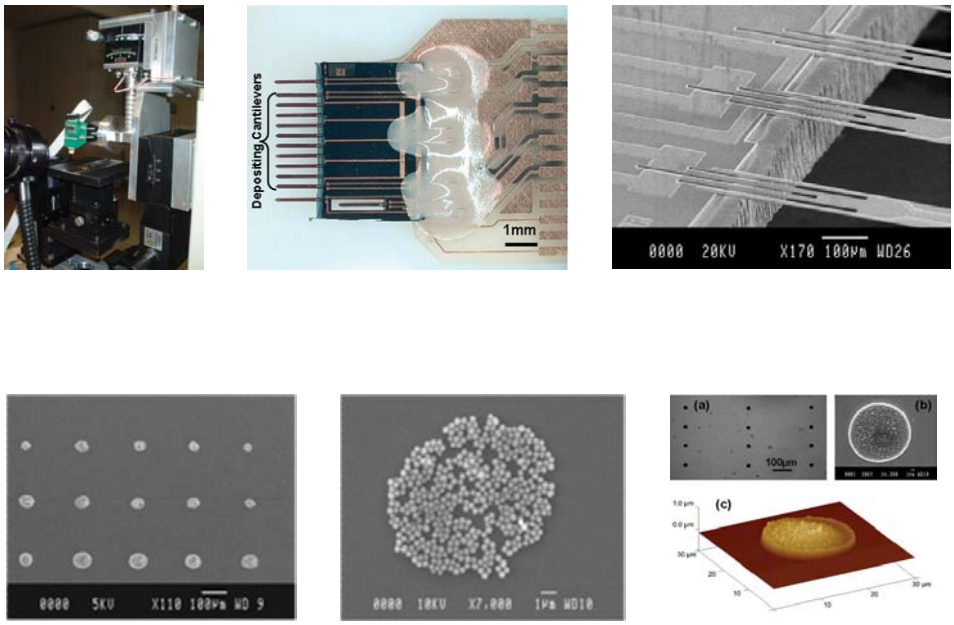


Fig. 3.2 Images showing the Bioplume concept, device and representative results. Top row from left to right: Bioplume depositing system relying on a direct-contact method and including the silicon chip bearing microcantilevers, the dedicated electronics for force control during deposition and the automated home-made spotter; Picture of the Bioplume chip with ten depositing microcantilevers and two tilt control cantilevers on the side; SEM close up view showing the location of the piezoresistor integrated onto the force sensing cantilevers. Bottom row from left to right: SEM picture of rows of silica colloid spots deposited with Bioplume; Close-up view of a single spot showing the nanoparticles; SEM (a, b) and AFM (c) pictures of electrodeposited copper dots using the special electrochemical feature offered by Bioplume (Images courtesy of CNRS).

The stencil lithography approach (shadow mask deposition)

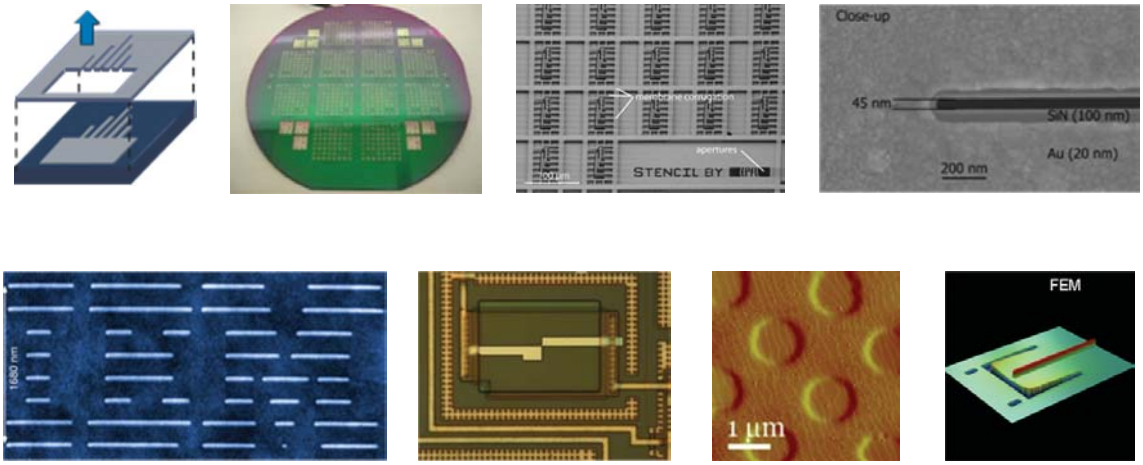


Fig. 3.3 Images showing the nanostencil method with representative results. Top row from left to right: schematics of stencil lithography (shadow masking), 100-mm wafer containing stencils, SEM image of rim-reinforced stencil membranes, SEM image of high resolution nanostencil with 45 nm apertures. Bottom row from left to right: 40 nm wide lines of Cu on SiO2 deposited in UHV, sub-micrometer mechanical device patterned by nanostencil on a full CMOS wafer, AFM image of Ni pattern deposited by pulsed laser deposition though nanostencil, image showing optical profilometer image of rim-reinforced stencil for comparison with finite element analysis. (Images courtesy of EPFL, CNM-CSIC, MESA+ Uni Twente, IBM Research GmbH, Tyndall Cork)

One of our objectives is to create a generic platform with low technical and financial threshold that makes top-down nanopatterning accessible for R&D to overcome the bottleneck of conventional high resolution photolithography. The methodology furthermore includes the development of new tools, methods, and processes to enable dispensing expensive functional materials with no waste.

Current achievements include among others stencil lithography resolution below 100 nm for a variety of materials (e.g. C60, NaCl, metals, SiO2, magnetic alloys), full wafer scale stencil lithography with 1 micrometer alignment accuracy, compatibility with CMOS circuitry. Liquid nanodispensing of functional materials (e.g. 50/50 water/ glycerol, TEG, PS nanoparticles, aqueous solution, solvents, other NPs and biomolecules); Parallel probes (up to 12) with micro/nanoscale apertures, droplet size 100 nm - 20 um.

NaPa

List of representative publications from the MEMS-based nanopatterning subproject

M.A.F. van den Boogaart, M. Lishchynska, L.M. Doeswijk, J.C. Greer, J. Brugger, *"Corrugated membranes for improved pattern definition with micro/nanostencil lithography"*. Sensors and Actuators A, 130-131, pp. 568-574 (2006)

N. Takano, L.M. Doeswijk, M.A.F. van den Boogaart, J. Auerswald, H.F. Knapp, O. Dubochet, T. Hessler, J. Brugger, *"Fabrication of metallic patterns by microstencil lithography on polymer surfaces suitable as microelectrodes in integrated microfluidic systems"*, Journal of Micromechanics and Microengineering, 16(8), pp. 1606-1613 (2006)

E.A. Speets, P. te Riele, M.A.F. van den Boogaart, L.M. Doeswijk, B.J. Ravoo, G. Rijnders, J. Brugger, D.N. Reinhoudt, D.H.A. Blank, *"Formation of Metal Nano- and Micro-patterns on Self-Assembled Monolayers Using Pulsed Laser Deposition through Nanostencils and Electroless Deposition"*, Advanced Functional Materials, Adv. Funct. Mater. 2006, 16, 1337-1342

M.A.F. van den Boogaart, G.M. Kim, R. Pellens, J.-P. van den Heuvel, J. Brugger. *"Deep-ultraviolet-microelectromechanical systems stencils for high-throughput resistless patterning of mesoscopic structures"*. Journal of Vacuum Science and Technology B, 22(6), pp. 3174-3177 (2004)

J. Arcamone, G. Rius, G. Abadal, J. Teva, N. Barniol, F. Pérez-Murano *"Mechanical resonator for distributed mass sensing and capacitive detection"* Microelectronic Engineering, 83, 1216-1220 (2006)

Julien Arcamone, Marc van den Boogaart, Francesc Serra-Graells, *Sven Hansenc Jürgen Brugger, Francesc Pérez-Murano, "Full wafer integration of NEMS on CMOS by nanostencil lithography"*, accepted for presentation at IEDM 2006, San Francisco

A. Meister, M. Liley, J. Brugger, R. Pugin, H. Heinzelmann. *"Nanodispenser for attoliter volume deposition using atomic force microscopy probes modified by focused-ion-beam milling"*. Applied Physics Letters, 85(25), pp.6260-6262 (2004)

A. Meister, S. Krishnamoorthy, C. Hinderling, R. Pugin, H. Heinzelmann; *"Local modification of micellar layers using nanoscale dispensing"*. Microelectronic Engineering, 83, 1509-1512, (2006)

T. Leïchlé, M.M. Silvan, P. Belaubre, A. Valsesia, G. Ceccone, F. Rossi, D. Saya, J.-B. Pourciel, L. Nicu, C Bergaud; *"Nanostructuring surfaces with conjugated silica colloids deposited using silicon-based microcantilevers"*. Nanotechnology, 16 (4), pp. 525-531 (2005)

T. Leïchlé, L. Nicu, E. Descamps, B. Corso, P. Mailley, T. Livache, C Bergaud; *"Copper electrodeposition localized in picoliter droplets unsing microcantilever arrays"*. Applied Physics Letters, 88, 254108 (2006)

P. Zahl, M. Bammerlin, G. Meyer, and R.R. Schlittler; *"All-in-one static and dynamic nanostencil atomic force microscopy/scanning tunneling microscopy system"*. Rev. Sci. Instrum. 76, pp.023707-1 - 023707-5 (2005)

Advertisement

4. Materials

In the Materials subproject tailored and functional materials are designed, which meet the requirements of the emerging nanopatterning methods. Only the availability of such materials allows to fully exploiting the whole potential of the emerging technologies. The emphasis in the subproject is on materials for Nanoimprint Lithography.

Three main routes are followed as shown in the scheme.

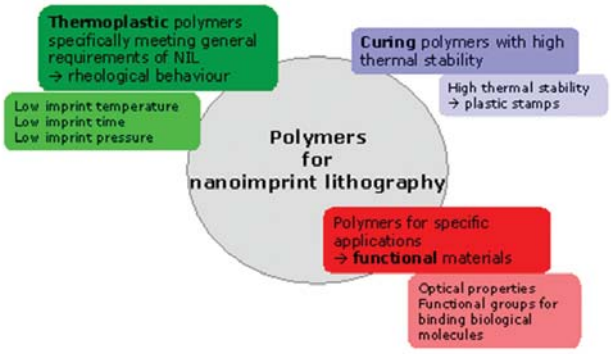


Figure 4.1: Approaches to polymers for nanoimprint lithography

Related to the thermoplastic materials, the subproject is focused on the development of new polymers (or copolymers) surpassing the properties of the currently used polymers (related to thermal/ optical/ flow behaviour, biocompatibility, hydrophobicity, and others).

Examples are shown in the next table.

Table : New thermpolastics for NIL

mr-I 7000E*:	Thermoplastic, T_g 60 ºC, with improved imprint behaviour for pattern transfer
mr-I 8000E*:	Thermoplastic, T_g 115 ºC, with improved imprint behaviour for pattern transfer
mr-I T85*:	hermoplastic, Tg 85 ºC, with outstanding chemical stability for Lab-on-a-chip, microfluidics and optical applications
Thermoplastic, Tg 80 ºC	Thermoplastic, Tg 80 ºC, for nanopatterning of optically active nanocomposites
Thermoplastic, Tg 108 ºC	Thermoplastic, Tg 108 ºC, functionalized for nanopatterning of biomolecules

* already commercially available

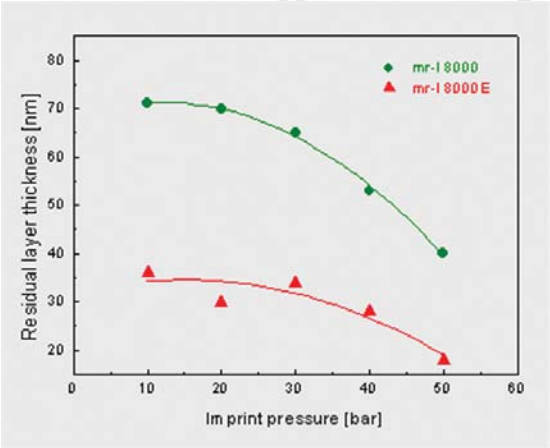


Figure 4.2: Residual layer thickness of new mr-I 8000E in comparison with "standard" mr-I 8000 as a function of imprint pressure, film thickness: 200 nm,
Imprint: 10 s @ 160 °C, incomplete filling of stamp cavities

Surface modification of nanoimprinted PMMA by growing polymer brushes allowed controlling the surface energy of the polymer as detected by the water contact angle.

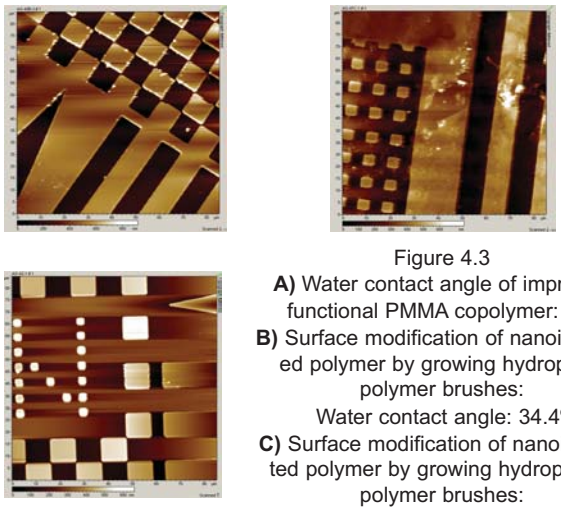


Figure 4.3
A) Water contact angle of imprinted functional PMMA copolymer: 88º
B) Surface modification of nanoimprinted polymer by growing hydrophilic polymer brushes:
Water contact angle: 34.4º
C) Surface modification of nanoimprinted polymer by growing hydrophobic polymer brushes:
Water contact angle: 115º

The incorporation of colloidal nanocrystals (semiconductor, oxide or metal), with size dependent optical and electronic properties in the polymer matrix allows to add new functionalities to thermoplastic and cured materials towards permanent applications.

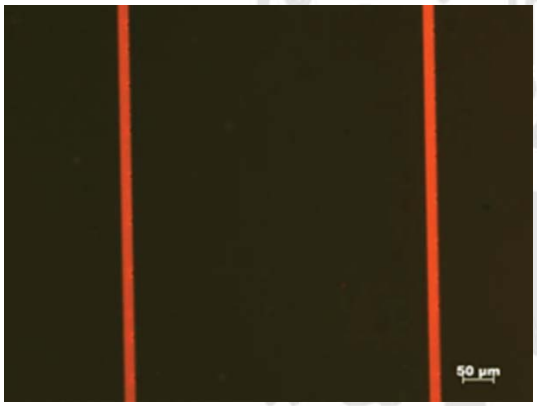


Figure 4.4: Waveguide imprinted in luminescent NC doped PMMA

New curing polymers offer a chance of nanoimprinting at low temperature and short cycle times. The novel epoxy-based curing polymer mr-NIL 6000 was developed and is already commercially available. The curing reaction is initiated by UV exposure and can be beneficially performed during imprinting, i.e. in the imprinter.

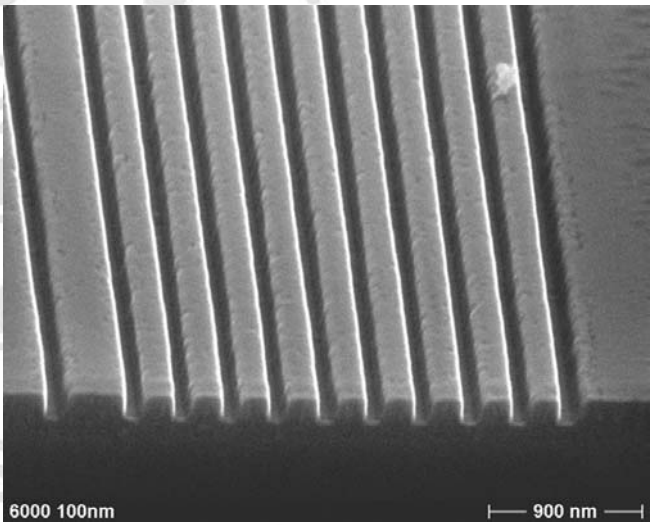


Figure 4.5 : mr-NIL 6000 test pattern, 100 nm trenches, 300 nm pitch, 200 nm film thicknes

List of selected Papers and conference contributions

Mike Kubenz et al.,Polymer Stamps for Nanoimprint Lithography with Good Release Properties (Poster). Forth International Conference on Nanoprint and Nanoimprint Technology, Nara, Japan, 2005

Freimut Reuther et al., Nanoimprint Lithography - General Considerations and Polymer Properties (Invited lecture). Seminar on Alternative Micro- and Nanofabrication, Industrial Materials Institute – NRC, Boucherville, Quebec, Canada, July 7-8, 2005

Freimut Reuther et al., Development of thermosets for thermal nanoimprint lithography at decreased temperatures, Proc. SPIE 5751 (2005), 976-985

Freimut Reuther,Towards functional polymers for nanoimprint lithography – Strategies and achievements of the NaPa Materials subproject Ultimate Lithography and Nanofabricationfor Electronics and Life Science, Marseille, France, 26-30 june 2006

Isabel Obieta, Plasma treatments of NIL polymers to enhance anti-adhesion properties, Ultimate Lithography and Nanofabricationfor Electronics and Life Science, Marseille, France, 26-30 june 2006

Maria Lucia Curri, Colloidal Nanoparticles: Novel Perspective for Nanopatterning Ultimate Lithography and Nanofabricationfor Electronics and Life Science, Marseille, France, 26-30 june 2006

5. Tools

The subproject “TOOLS” includes three work packages:

WP15: Step & Stamp Nano Patterning Tool

For hot and cold embossing, with an alignment accuracy < 250nm.

-SUSS MicroTec SAS
-VTT Technical Research Centre of Finland

WP16: Stencil Mask Alignment and Fixation Tool

Accuracy of 1µm at the first and 250nm at the final stage

-SUSS MicroTec Lithography GmbH
-EPFL (Ecole Polytechnique Fédérale de Lausanne)
-CNM (Consejo Superior de Investigaciones Científicas)

WP17: Overlay Accuracy in NIL

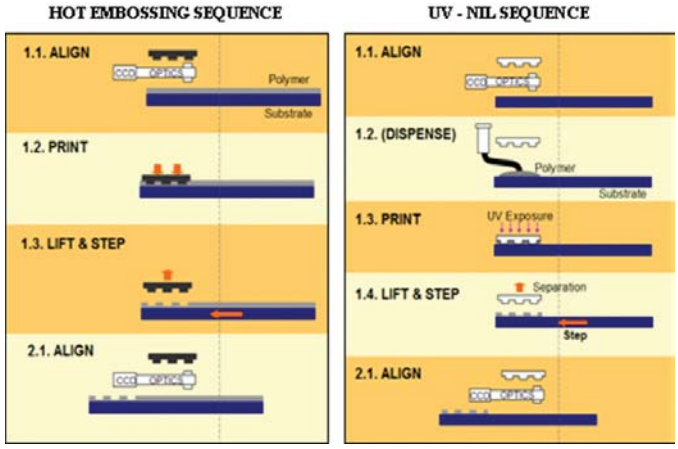
Development of an alignment system with an overlay accuracy < 20nm at wafer scale and optionally for the Step and Stamp Nanoimprint Lithography Tool

-Obducat
-Lund University

Work Package #15: Step & Stamp Nano Patterning Tool

Step & Stamp Imprint Lithography mimics the operation of an optical stepper in which the substrate is exposed chip by chip. The optics and the reticule are replaced by the imprinting arm and a stamp/template. Sequential imprinting methods can be used to pattern large areas.

The mode of operation is illustrated below for both UV – NIL imprinting and Hot embossing sequence. The alignment can be performed before each imprinting step to provide the highest alignment accuracy. For applications which do not require so high accuracy overlay, it is possible to align the stamp/template with the wafer only before the first imprint, and then repeat the imprinting without having to realign each step; in such case, the accuracy is the accuracy of the XY stage.



General description of the Nano Imprinting Stepper (NPS300)

The Nano imPrinting Stepper Model NPS300, developed for the NaPa project (FP 6 NMP4 CT2003500120) is a versatile machine addressing R&D requirements as well as Production needs. It performs Hot Embossing or UV-Nano Imprinting on large area using a step and print approach.

In its R&D version, the degree of automation allows a fully automatic imprint of a complete wafer, including loading of the stamp, single or multiple alignment, multiple imprints and unloading of the stamp; the wafer is loaded and unloaded manually by the operator. The automatic wafer loading required for Production was not included in the initial development.

Main specifications:

Alignment XY Stage: Resolution: XY 10 nm, Theta 0.8 µradian

Heating chuck: 200 x 200 mm (Diameter 300 mm available on request), Temperature up to 450°C

Alignment optics: Top & Bottom Viewing Microscope, FOV: 870 x 690 µm (20X); Alignment accuracy: 100nm; Overlay Accuracy: 250 nm with Automatic alignment

Imprinting Arm: Force 5 N ~ 4,000 N; Z resolution: 50 nm; Pre-leveling < 20µrad; Self-leveling system

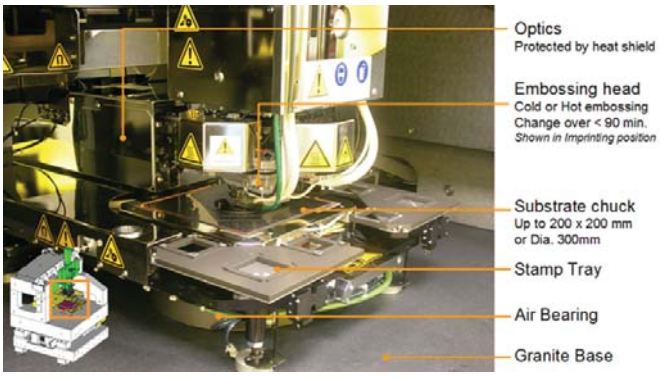
Cold Embossing Head: Stamp Square 50 ~ 65 mm; Force up to 200N (more on request); Exposure area 40 x 40 mm, Wavelength: 375 ± 15nm, > 120mW/cm^2, Uniformity 5%

Hot Embossing Head: Stamp Square 50 ~ 65 mm; Force up to 4,000 N; Temperature up to 450°C

Fluid dispenser for cold embossing: Jet System

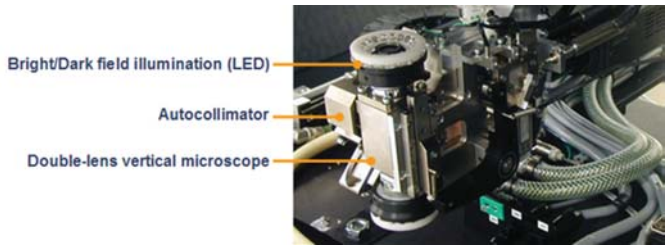
NPS 300: Main modules

The main modules of the NPS300 are a high accuracy alignment stage, a microscope for alignment and an imprinting arm equipped with two different of imprinting heads depending upon which process is used



Parameters to control are: stamp-to-wafer leveling, alignment, force profile, temperature, UV-exposure and Material Dispense

Stamp-to-substrate aligment



Stamp-to-Substrate alignment is performed using an Inter-Substrate Microscope which aligns features of the substrate to features of the stamp. The optics XY stage moves on air bearing to maintain the parallelism of the optical axis during displacement.

The microscope, built low CTE material is protected by heat shield to minimize the impact of the temperature while performing hot embossing. The automatic alignment aligns stamp-to-substrate within 100 nm allowing an overlay down to 250nm.

Leveling System

A build in autocollimator pre-levels the stamp-to-substrate within 20 µradians using a motorized ball cup system. Since Nano Imprint requires parallelism about two orders of magnitude better, a self leveling system using a Flexure Stage supplements the active leveling.

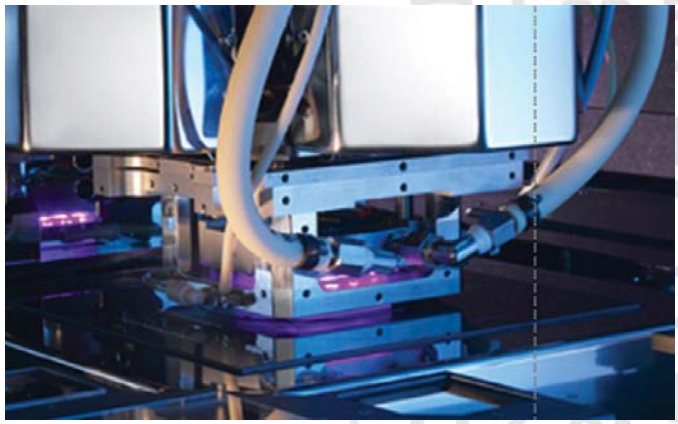
Force Control Principle

The Imprinting Arm is attached to the upper granite bridge of the machine which also supports the optics stage. The up/down movement is controlled by a DC motor. The information of the force sensor included in the imprinting head is included in a close loop system to accurately monitor and profile the imprinting force.

Temperature Control (Hot Embossing)

Heating chucks are included in the system to control independently the temperature of the wafer and the temperature of the stamp. The wafer chuck uses Halogen Lamp to increase by radiation the temperature of an Optical Polished Silicon Carbide top plate which holds the wafer in place by vacuum. The Imprinting Head includes ceramic heaters. The stamp holder is an Optical Polished Silicon Carbide tool. Water jacketing is provided on both chucks to maintain the housing at room temperature and avoid thermal drift.

UV-Exposure (Cold Embossing, UV-NIL Head)



Ultraviolet light is generated directly inside the imprinting head by an array of 25 UV-LED Arrays.

The LED offers the advantage of being easy to control by adjusting the current. It can be pulsed for high peak irradiance if needed. It supplies pure spectral light with no infrared which could heat up the imprinting material or the stamp. Various wavelengths are available (375nm, 395nm and 365nm under development). The current machine is configured with 375 ± 15 nm LED.

Material Dispense (Cold Embossing)
The dispense volume required for Step & Print is small. For instance, a stamp 10x10mm used to transfer pattern with 300nm topographies representing 50% of the stamp surface would need only 20nl if the residual layer requirement is 50nm. In addition, for a better flow control of the fluid during the imprinting sequence, multiple droplets dispense is preferred to a single droplet. The current system allows dispensing of 100µm droplets with a pattern which can be programmed by the operator according to his stamp design.

Work Package #16: Stencil Aligner

The stencil aligner uses the well known and proven base of the SUSS Mask Aligners. It has been adapted to meet the following requirements:
- tAlignment from backside or topside; accuracy down to 250nm
- Adapter frame for stencil tooling prepared for 8-inch fixtures
- To achieve a high alignment accuracy the movement after the alignment is minimized; Alignment gap down to 20µm
- Self leveling is performed by flexure stage

6. Simulation

Modelling and simulation within the NaPa project deals with the elaboration of models and computer simulation of new nanopatterning processes such as nanoimprint lithography (NIL), MEMS-based processes, soft lithography and self-assembly. A process library for NIL through a combination of advanced characterization techniques, including mechanical, tribological, and adhesive/stiction/wettability, combined with modelling is under construction. Simulations for wafer scale modelling of the NIL process have been undertaken by applying coarse grain averaging over the feature scale. Modelling for MEMS-based nanopatterning focuses on the stabilization of membranes used as stencils during the deposition process, and the effects of material deposition on the stencil. Effects of membrane deformation and the material build-up on the masks are correlated to the resolution and shape of patterns deposited onto substrates. In support of soft lithography activities including patterning of self-assembled mono-layers (SAMs) and deposition of nanodroplets onto surfaces, molecular dynamics (MD) simulations are being performed to provide fundamental insight into the design of molecular scale patterning processes. MD applications include molecular diffusion studies within SAMs, surface wettability, droplet formation, and chemical reactivity at patterned molecular surfaces.

Objectives

A primary goal is to create a process library and software tools useful in NIL applications for the definition of processing windows. It is important to extend the constitutive behaviour of polymers to nanometre length scales and apply this knowledge to the prediction of feature-scale profiles of nanopatterns produced by NIL. Correlation of thermomechanical and deposition induced stresses in patterned membranes to the shape of structures deposited via nanostencils is the goal of the simulation work supporting MEMS-based lithography. Application of MD simulations to the design and patterning of organic layers and nanoparticles is the aim of the simulation studies undertaken in support of the soft lithography and self-assembly activities.

Recent Achievements

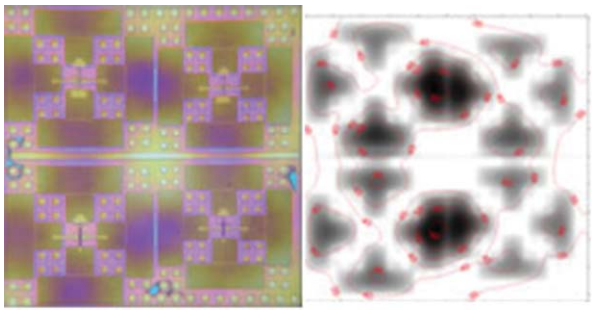


Fig. 6.1 – Coarse grain simulations of NIL patterned transfer compared to experiment. Left: Imprint (violet colour relates to thicker residual layer), Right: Results of modelling of pressure distribution in resist film and calculated distribution of elastic deformation of stamp in nanometres during imprinting. Simulation courtesy of Institute of Microelectronics Technology (IMT), Russian Academy of Science, experimental results courtesy of TASC-INFM.

Characterisation of polymer resists on a nanometre scale and new models have been elaborated for NIL, and additionally the development of a coarse-graining strategy that permits simulation of the NIL process on a wafer-scale enabling the identification of trouble spots has been achieved.

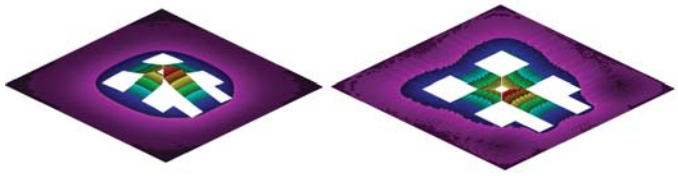


Fig. 6.2 – Side by side comparison of the stabilisation of MEMs membranes using corrugation rims. Left: Unstabilised, Right: Stabilised. Simulation work courtesy of Tyndall National Institute, performed in collaboration with fabrication of the membranes at EPFL.

For prototype nanostencils, a design methodology has been devised that permits stabilisation of the stencils to within prescribed tolerances. Correlation of pattern blurring due to stencil deformations arising from residual and deposition-induced stresses has been accomplished. Currently, these results are being extended to more arbitrary patterns cut from the stencil membranes.

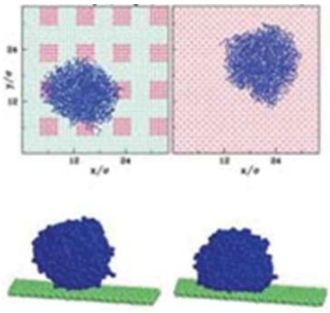


Fig. 6.3- The effect of surface patterning on droplet formation. Figure courtesy of Warsaw University of Technology and the Institute of Physics, Polish Academy of Science.

MD simulations of surface wetting resulting from molecule-molecule and molecule-surface forces have been investigated and the impact on droplet shape determined. These simulations have also begun for droplet formation on patterned surfaces and as well, investigation of fluid flows in the vicinity of patterned surfaces is being explored for applications including

nano-dispensing. Molecular specificity for surface-functionalized SAMs has been calculated for molecular printboard applications, for the determination of appropriate “inking” behaviour.

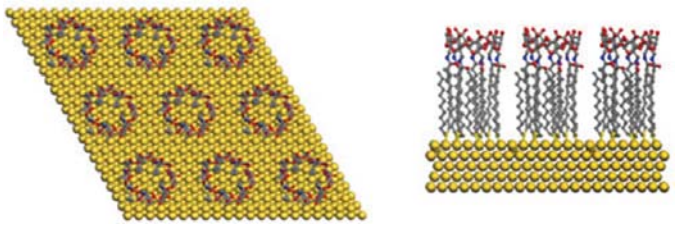


Fig. 6.4 - Plan and side-on views of a molecular printboard, a hexagonally-packed array of beta-cyclodextrin molecules anchored to gold using alkane-thioether chains. MD simulations provide atomic scale information on the stability and flexibility of such arrangements. Simulations performed at Tyndall National Institute in collaboration with the experimental work at Mesa+, University of Twente.

Recent representative publications:

NIL wafer-scale simulation © Institute of Microelectronics Technology, Russian Academy of Science, 6, Institutskaya Street, Chernogolovka, Russia.

Multi-scale modelling of nano-imprint lithography, David Mendels, Ultimate Lithography and Nanofabrication for Electronics and Life Science, Marseille, France, 26-30 June, 2006

Corrugated membranes for improved pattern definition with micro/nanostencil lithography, M.A.F. van den Boogaart, M. Lishchynska, L. M. Doeswijk, J. C. Greer and J. Brugger, Sensors and Actuators A: Physical, **130-131**, 568-574 (2006)

Mechanical properties of the domains of titin in a Go-like model, M. Cieplak, A. Pastore, and T.X. Hoang, Journal of Chemical Physics, **122**, 054906 (2005)

Modelling competitive guest binding to beta-cyclodextrin molecular printboards, D. Thompson and J. A. Larsson, Journal of Physical Chemistry B, in press (2006)

Conclusions

The NaPa project has now passed the halfway of the project. The midterm evaluation was extremely positive, proving the justification for the integration of the R&D activities in the field of emerging nanopatterning methods. The project has produced a substantial record of journal and conference papers and conference presentations. In addition the collaboration between the partners from academia and SMEs and industrial partners has been very successful. It is obvious that when the research and business activity in the field related to new nanopatterning methods increases, the partners manufacturing tools and materials can exploit the results and benefit from the project, not only from the innovations but also from the market established in Europe and the visibility of the project itself.

More information about the project can be found from *www.napaip.org*

NaPa
Emerging Nanopatterning Methods

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

Post-doctoral Position: "Pi-Conjugated Supramolecular Liquid Crystals for (Supra)Molecular Electronics" (CEA-LETI, Grenoble, France)

This CEA-Grenoble/LETI post-doctoral position for chemist is a part of a 4 years research program (sponsored through the "Carnot Label" grant of CEA-LETI) in between three French research
laboratories: Laboratoire d'Intégration Mémoires et Nanodispositifs (LIMN) of CEAGrenoble/DRT/LETI/DIHS, UMR5819 (CEA-CNRS-UJF)-Structures et Propriétés d'Architectures Moléculaires (SPrAM), and UMR7610(CNRS-UPMC)-Laboratoire de Chimie des Polymères.
This program entitles "Molecular junctions & interconnects: Pi-conjugated self-assembled nanowires & supramolecular architectures" aims at studying and evaluating the intrinsic and ultimate
(opto)electronic transport properties of tailored-made single Pi-conjugated nanowires & supramolecular LC architectures for the emerging fields of molecular, supramolecular, and
organic/plastic electronics.
The selected post-doctoral fellow will focus on the synthesis and chemical/structural/thermal characterizations of pi-conjugated Supramolecular Liquid Crystals (oligomers & dendrimers) within the UMR5819(CEA-CNRS-UJF)-SPrAM laboratory, Grenoble (France).

Application should include a letter in which the applicant state her/his interests and experiences relevant to this project, a detailed CV with a list of publications, and two recommendation letters or contacts of two referees. Moreover, proper consideration will be given to candidate who will propose a short (one page maximum) research proposal. This LETI post-doctoral position (1 year +1) will be located in Grenoble (France) and will officially start in November-December 2006.
Contact: Dr. P. RANNOU (*patrice.rannou@cea.fr*)

Post-doctoral Position: "Pi-Conjugated Liquid Crystalline Polymers for (Supra)Molecular Electronics" (CEA-LETI, Paris, France)

This CEA-Grenoble/LETI [1] post-doctoral position for chemist is a part of a 4 years research program (sponsored through the "Carnot Label" grant of CEA-LETI) in between three French research
laboratories: Laboratoire d'Intégration Mémoires et Nanodispositifs (LIMN) of CEAGrenoble/DRT/LETI/DIHS, UMR7610(CNRS-UPMC)-Laboratoire de Chimie des Polymères, and UMR5819(CEA-CNRS-UJF)-Structures et Propriétés d'Architectures Moléculaires (SPrAM).

Neither a PhD nor a previous post-doctoral position done within a CEA Research centre. The selected postdoctoral fellow will focus on the synthesis and chemical/structural/thermal characterizations of pi-conjugated Liquid Crystalline Polymers within the UMR7610(CNRS-UPMC)-"Laboratoire de Chimie des Polymères" laboratory, Paris (France). Electronic transport measurements and nanofabrication issues (related to micro/nano-FETs (Field-Effect Transistors)) will be developed in close collaboration with post-docs and researchers of the two other laboratories associated with this CEA-Grenoble/LETI 4 years program: CEA-Grenoble/DSM/DRFMC/UMR5819(CEA-CNRS-UJF)-SPrAM & CEA-Grenoble/DRT/LETI/DIHS/LIMN

The candidate (She/He) should have a solid experience in organic and macromolecular chemistry associated with liquid crystalline polymers. A particular attention will be given to applications submitted by skillful chemists specialized in the synthesis of pi-conjugated materials (organic semiconductors).
Hands-on knowledge of conventional (NMR, FTIR and UV-Vis spectroscopes & LCrelated characterization (DSC-POM-XRD) / purification techniques are a must. Excellent communication skills in English are required.

Application should include a letter in which the applicant state her/his interests and experiences relevant to this project, a detailed CV with a list of publications, and two recommendation letters or contacts of two referees. Moreover, proper consideration will be given to candidate who will propose a short (one page maximum) research proposal. This LETI post-doctoral position (1 year +1) will be located in Paris (France) and will officially start in November-December 2006.
Contacts: Prof. A.J. ATTIAS (*attias@ccr-jussieur.fr*) and Dr. F. MATHEVET (*fabrice.mathevet@cea.fr*).

Post-doctoral Position: "Synthesis and grafting of molecules on surfaces and nano-objects" (CEA-LITEN, Grenoble, France)

A post-doctoral position is available at CEA-Grenoble (www.cea.fr) in the LITEN laboratory for hybrid components (Direction de la Recherche Technologique), in close relationship with CEA optronic department LETI-DOPT.
The subject is part of the CHIMTRONIQUE Program which aims to develop chemistry for future electronic devices.
This project focuses on the synthesis and grafting of molecules on surfaces and nano-objects. The goal is to realize molecular based photodiodes.
The contract is available for 2 years (1 year renewable, Carnot program fundings) - Starting date: November/December 2006
The candidates who wish to apply should submit their application letter via e-mail, together with a CV and two letters of recommendation to *jean-pierre.simonato@cea.fr*

PhD Positions (13) : "Nano Engineered Superconductors for Power Applications, NESPA " (Several European cities)

Leading experts from 13 European universities, research centres and industrial companies will establish NESPA, a Marie Curie Research and Training Network funded within the EU´s 6th framework programme and coordinated by the IFW Dresden. The Research and Training Network NESPA will focus on the research topic of the development of high temperature superconductor (HTS) materials for power applications.
Within the NESPA program 13 PhD student positions in different research fields are available. The PhD candidates benefit from a network of leading experts from research and industry all over Europe working interdisciplinary on the development of high temperature superconductor cables and devices for power applications. The activities will comprise experimental work, analysis and characterization as well as topics as design, simulation and calculation.
Candidates should send an application which should include a CV, a certificate with the disciplines of the university degree and corresponding marks, and a short statement of research interest. A list of 3 referees will be welcome.
Deadline: 20 September 2006 by e-mail or mail to:

Dr. Teresa Puig / Prof. Xavier Obradors
Dep. Materials magnètics i superconductors - Institut de Ciència de Materials de Barcelona
CSIC - Campus UAB - 08193 Bellaterra - SPAIN
e-mail: *Teresa.Puig@icmab.es* / *Xavier.Obradors@icmab.es*

PhD Position: "Characterization of multicomponent oxides for transparent flexible electronics" (UB, Barcelona, Spain)

Profile: Physicist, physics engineer, materials engineer
Job description: Optical, electrical and morphological characterization of multicomponent oxides suitable for TTFT devices. Determination of stability and static and dynamic electrical characteristics of nanodevices fabricated with these materials.

PhD Position: "Electron microscopy techniques applied to multicomponent oxides for transparent flexible electronics" (UB, Barcelona, Spain)

Profile: Physicist, physics engineer, materials engineer
Job description: Structural, chemical and morphological characterization by using TEM-HREM, SEM and FIB of multicomponent oxides suitable for TTFTs. Application of FIB for fabrication of nanodevices based on these materials.

PhD Position: "Nanolithography of multicomponent oxides for transparent flexible electronics" (UB, Barcelona, Spain)

Profile: Physicist, physics engineer, materials engineer
Job description: Design, nanolithography (by NIL, HEL, FIB, EBL, …), nanocharacterization (by AFM, optical microscopies, …) and assembly of nanodevices for transparent flexible electronics based on multicomponent oxides.

Contact: Anna Vilà.
Department of Electronics – UB
Phone: +34 93 4039170 / Fax: +34 93 4021148
e-mail: *anna@el.ub.es*

Post-doctoral Position: "Ultra High Density recording technique" (CEA-LETI, Grenoble, France)

In the Optronics Department on the French Atomic Energy Commission laboratory: (CEA/LETI/DOPT/SIONA), research programs on recording technologies cover several area from next generation of DVD (BluRay format) to advanced Ultra High Density recording by micro probes. The Ultra High Density recording technique consists in writing/reading data in a media at nanometer scale - using micro tips similar to the ones used in Atomic Force Microscopy.
The Postdoctoral candidate will specifically address this later topic that can bring alternative solutions for very compact memories for nomadic systems (PDAs, telephones...), and for massive memories for archiving applications.

Work will focus on:
- the explanation of the physical phenomena with such nanostructures
- the design of a tip/media demo
- the implementation of technological processes existing at the CEA-LETI for tests
- the characterization of expected effects by means of an atomic force microscope.

Contact: Serge Gidon - (*serge.gidon@cea.fr)*

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

(October 2006)

6th International Conference on Materials for Microelectronics and Nanoengineering
October 29-31, 2006. Cranfield (UK)
http://www.mfmn2006.euspen.com/

Nanoelectronics, NEMS & MEMS, NanoFabrication

VII Portuguese/Spanish Conference on Controlled Drug Delivery
October 22 - 24, 2006. Pamplona (Spain)
http://www.splc-crs.org/congress2006/

Nanomaterials / Nanomedicine

Frontiers In Scanning Probe Microscopy Workshop
October 4 - 6, 2006. Birck Nanotechnology Center - Purdue University (USA)
http://www.inac.purdue.edu/workshops/spm06/

SPM

Nanotec Forum 2006 Conference & Exhibition
October 4 - 6, 2006. Stockholm, Sweden
http://www.nanotec.se

Nanotechnologies / Nanotechnology Business

(November 2006)

nano solutions 2006
November 28 - 30 2006. Cologne, Germany
http://www.nanosolutions-cologne.com/

Nanotechnology Business

Nanofair 2006
November 21-22, 2006. Dresden, Germany
http://www.nanofair.com/

Nanomaterials / Nanoelectronics / Nanotechnology Business

nano '06: nanostructured materials for functional, structural and bio-applications
November 13 - 15, 2006. Brno, Czech Republic
http://csnmt.fme.vutbr.cz/to.en/nano06

Nanomaterials / Nanobiotechnology / Nanotechnologies

Nanotechnology Aerospace Applications - 2006.
Bordeaux (France), November 09-10, 2006
http://www.nanospain.org/files/conferences/LS_AVT-129.pdf

Nanotechnology Business, Nanotechnologies

(December 2006)

6th ANQUE International Congress of Chemistry
December 05 - 07, 2006. Puerto de la Cruz, Tenerife (Spain)
http://www.anque2006.org/

Nanochemistry

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

Peptide nanotubes lead to coaxial nanocables (August 15, 2006)

http://www.nanotechweb.org/articles/news/5/8/7/1

Researchers at Tel Aviv University and the Hebrew University of Jerusalem (Israel) have made coaxial metal nanocables by using self-assembled peptide nanotubes as a template.

Keywords: Nanotubes / Molecular Electronics

IBM Researchers look beyond silicon technology and investigate molecules for the future of information processing (August 04, 2006)

http://www.ibm.com/news/no/no/2006/08/nanotechnology.html

Scientists at the IBM Zurich Research Laboratory have demonstrated how a single molecule can be switched between two distinct conductive states, which allows it to store data.

Keywords: Molecular Electronics

Purdue engineers lay groundwork for 'vertically oriented nanoelectronics' (August 01, 2006)

http://www.purdue.edu/UNS/html4ever/2006/060801.Fisher.vertical.html

Engineers at Purdue University have developed a technique to grow individual carbon nanotubes vertically on top of a silicon wafer, a step toward making advanced electronics.

Keywords: Nanoelectronics, Nanotubes

Organic transistors act as sensors (August 01, 2006)

http://www.nanotechweb.org/articles/news/5/7/14/1

US researchers have developed a new type of organic molecular transistor that can sense and respond to its chemical environment.

Keywords: Molecular Electronics, Nanotubes

Scientists build 'magnetic semiconductors' one atom at a time (August 01, 2006)

http://www.princeton.edu/main/news/archive/S15/37/72E21/

US researchers have turned semiconductors into magnets by the precise placement of metal atoms within a material from which chips are made.

Keywords: Nanomagnetism, Nanoprobes

Report from the Consultation Meeting on 'Atomic Scale Technologies', Brussels, May 29-30, 2006

David Guedj
European Commission
David.Guedj@cec.eu.int

Foreword
The aim of the meeting was to define the area, the research topics and the rationale at the European dimension for atomic scale technologies, identifying grand challenges and promising research directions in ICT.

It is hoped that this report can provide the foundation for an initiative in the coming FP7 programme.

"One atom more or one atom less makes a difference..."

Challenge
Control the functionality of a single object at the atomic scale and develop new ways of exploiting the physical resources of this single object to acquire, store and process classical information. By a single object or 'molecule of matter', it is understood a restricted number of atoms that can serve as a building block for the implementation of a device or a machine.

Rationale
Manipulation and control at the atomic scale offer the ultimate engineering capability in terms of size of the building blocks and the possibility to design and assemble at the atomic scale a device or a machine able to perform computations, mechanical motion or signal transduction.

The aim is to exploit recent advances in physics, chemistry and biology to put at work a single atom or molecule, control its functionality on an atomic scale.

The detailed control of processes at the atomic scale will enable new information processing paradigms and technologies, exploring for example new methods to process the information at the atomic-scale compared to the sole charged carrier transport in existing microelectronic technologies; e.g. transfer of excitons, plasmons, or chemical (mechanical) information inside a single molecule or between molecules,

- The use of the inherent precision of atoms and molecules as sensors, measurement devices and standards.

- The use of single atom technologies to functionalize artificial (bio) molecules.

- The use of a common platforms (nanometer scale devices) combining (bridging) from biomolecules to coherent atom manipulation, from molecular electronics to semiconductors.

The range of research spans from single atom control in vacuum up to single molecule and biomolecular activity in embedded systems. The initiative therefore requires innovative and multidisciplinary approaches merging key areas such as molecular electronics, single molecule biophysics, coherent atom manipulation and surface chemistry.

Research Focus & Challenges
The three major challenges are:
To develop enabling technologies for the control at the single atom/molecule scale. The tools to be used could be: optical traps, electro-magnetic fields, scanning probe techniques, surface techniques, single atom/molecule source, methods for nanostructuring of atomic/molecular beams and surfaces at the single particle level, new single particle detection systems.
To explore new ways to acquire, store and process information in single atom/molecule based systems.
To develop an understanding of the fundamental processes and the theoretical tools and models, adapted to describe the atomic-scale functionality.

Detailed challenges include:

To determine, control and design the electronic, magnetic and optical properties & states, the structure and the shape of a single (isolated) object at the atomic/molecular scale.

To reliably interface a single object to another (i.e. addressing, reading, and controlling).

To take advantage of the inherent precision of atoms & molecules (e.g. energy states)

To overcome noise, fluctuations, structural disorder and uncontrolled dissipation.

To optimize decoherence processes for achieving classical behavior of logical degrees of freedom in single atoms/molecules.

To reliably interface a single atom/molecule to the macroscopic world (i.e. addressing, reading, and controlling).

To develop prototypes for molecular machines, controlled at the atomic level.

To develop techniques to obtain full readout capabilities for individual atomic/molecular states.

To develop new "nanosorters" beyond the established methods in biology and physical chemistry, that enable to separate and purify particles on the atomic and molecular scale according to their physical properties.

Why now?
The opportunity is now given to pool and exploit recent and upcoming advances in physics, chemistry and biology to control the functionality of a single atom or molecule in a system.

Present technologies are approaching fundamental limits (scaling, power,...), which calls for alternative technologies and processes.

Atom-scaled technologies will provide the ability to use atomic-scale precision to take advantage of the complexity of atoms and molecules for future information processing systems.

It is important to bring together leading scientific expertise in Europe, across various disciplines, in atomic-scale technologies to gain a leadership in science and engineering in this emerging field.

Expected Impact
Inter-disciplinary, collaborative research on synergetic approaches to single atom/molecule manipulation in order to achieve functionality and information processing (e.g. quantum gases and surface science, modeling tools, feedback control techniques at the single atom level)

A few examples of emerging technologies to be expected from this initiative could be:

Ultimate precision/control of a single atom or molecule functionality, control of the connectivity and of addressability of a single atom/molecule. Control of state and conformation, where the conformation is connected to the function.

An appropriate technology to exchange energy, data and instructions within a single atom or molecule and between different atoms or molecules.

Control and synthesis down to the sub-nano scale, constructing the system one-by-one from atomic and molecular building blocks.

Control and design of a biomolecule functionality (mechanics & electronics of molecular machines, biochemical processes, enzymatic activities,..) at the single atom level (no thermodynamics). Understanding and control of a biological process molecule per molecule.

Molecule based computers.

Atomic clocks.

Atoms and Molecules as sensors: use the inherent precision in atomic and molecular physics to build ultra sensitive and/or ultra precise devices.

Interfacing between single atomic/molecular systems and the macro world. The interface has to allow the detailed (atom by atom, one makes a difference) control of the atomic/molecular system

Expected Benefits

Atomic scale technologies are generic for the Emerging Nano and QIPC initiatives in IST.

Atom scale technologies are most promising for:

Developing new ways to acquire information and perform first processing steps. This will yield dramatically faster and more efficient computation for many technological applications.

Developing faster and “colder” computers because of shorter signal pathways and a dramatically reduced number of switching elements.

New and unexpected system properties may emerge, once we have full control over atomic and nanoscale systems.

Motivation &Vision

There are a lot of classical, semi-classical and quantum resources in a single atom/molecule that can be used to design, synthesize and operate a large variety of atom/molecule-based machines. A large effort is required to explore the technologies that will give access to these resources and to produce these atom /molecule-based machines.

EUROPEAN COMMISSION
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Emerging Technologies and Infrastructures
Future and Emerging Technologies

Theory and numerical simulations for the Pico-Inside project

Xavier Bouju and Christian Joachim
The NanoSciences Group, CEMES-CNRS, Toulouse (France)

The Pico-Inside project aims to develop the architecture, the atomic scale technology and the chemistry to explore and quantify intramolecular resources for integrating much more than a single logic gate inside a single molecule. To reach this goal, five units structure the network [1]. As molecules are the corner-stones, two units are dedicated to the design and the synthesis of large multi-functional molecules [1,2]. These molecules have to exhibit particular functionalisations not only to be able to produce a logic gate but also to be anchored on a surface [2]. The other unit is thus focussing on theoretical aspects by looking for the chemical board able to transform an input information to an output signal [1]. In other words, the involved partners want to theoretically demonstrate that intramolecular quantum evolution based on the non-stationary mixing of large molecule quantum states can perform digital operations. Two other units are dedicated to the interconnection technology at the atomic scale. In fact, a single molecule has to be deposited on a surface and connected to nano-electrodes and then to atomic wires in order to exchange information. The geometry adopted is planar and a maximum of five steps of interconnection are necessary to reach the macroscopic world starting from the atomic scale level [3-6]. Experimental tools are low temperature UHV STM and UHV NC-AFM, providing information about elastic and inelastic intramolecular effects and about the adsorption of large organic molecules [7,8] on a surface together with the stability of metallic wires [3-5]. Specific moulding molecules will help in stabilising atomic metallic wire [4,9] in complement with atomic manipulation for creating those wires. A special attention will be focused on the metallurgy of nanoscopic mesa pads and on the mesoscale interconnect with the nano-stencil technique. All these experimental efforts are sustained by Omicron.

Finally, one unit is exploring the theoretical problem related to the adsorption of large molecules on perfect and hybrid (metal-insulator and metal-semiconductor) crystal surfaces such as their energetic on the surface including diffusion, stable adsorption sites, electronic and vibrational structures. Actually, this atomic scale technology requires a lot of modelisation. At the root of the Pico-Inside modelisation activity is the fact that we are going to deal with large molecules adsorbed on an insulating surface or at least on a large gap semi-conducting surface, where metallic electrodes will be in electronic interaction with a few chemical groups of those molecules. This requires a large effort in term of the understanding of the adsorption site and geometry of large conjugated molecules on semiconductors and insulators. A second topic concerns STM and NC-AFM image calculation, associated to simulations of molecular manipulations.

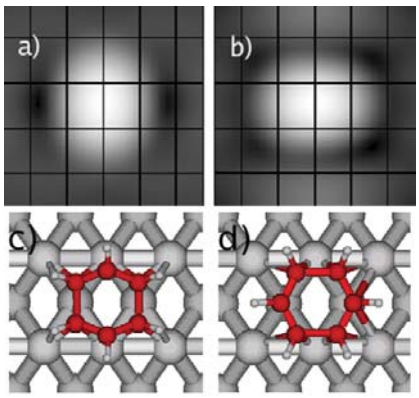

Fig. 1. a) and b) STM images of a single benzene molecule adsorbed on Cu(110) calculated with the ESQC code. c) and d) Two different conformations obtained with ASED+ code and used for the simulated images.

Theory of adsorption of large molecules on surfaces

Since the molecules targeted in Pico-Inside are quite large, mainly different molecular mechanics (MM) methods are under testing. The development of hybrid (embedding) electronic structure methods is undertaken, combining high quality quantum mechanical calculation of a finite part of the system (the cluster) with molecular mechanics calculations for the rest of the surface system. The papers of Alex Shluger and Lev Kantorovich in this issue explain the strategies followed by the UCL and KCL partners. In Toulouse, we are developing an embedding method based on a semi-empirical electronic structure technique and using the atom superposition and electron delocalization (ASED) scheme. Compared to the initial ASED code, a supplementary term has been added in order to take into account three-body interactions (ASED+). This new code can be seen as compromise between standard MM codes and DFT methods. In fact, MM codes using standard force-fields (MM4, UFF...) are fast and very well adapted for physisorbed systems and, of course, for intramolecular deformations. DFT calculations give a good description of the chemisorption but need huge computational costs for large molecules on a surface. On the other hand, ASED+ is faster than DFT and only few parameters (Slater exponents and ionization potentials) are necessary. As a benchmark, the case of a benzene molecule chemisorbed on Cu(110) has been studied (Fig. 1). Very good agreements have been found with experimental and DFT results [10]. As an important concern in Pico-Inside is the structure and mobility of large molecules on crystal surface, it is important to use an efficient and reliable technique. Figure 2 shows a series of calculations with ASED+ of polyacenes on Cu(110) starting from benzene to pentacene. The key point is that theses molecules can diffuse more easily along the [1-10], as experimentally observed [11]. Due to a large size of the molecules involved, there will be a number of stable adsorption sites and orientations of the molecules. We shall study their diffusion between theses conformations, that is important for

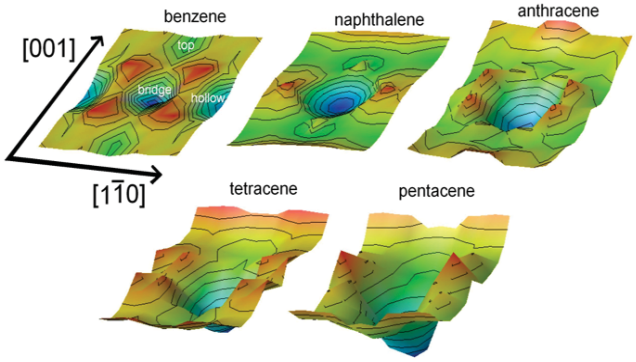

Fig. 2. Minimal potential energy surface maps of five polyacene molecules adsorbed on Cu(110) calculated with the ASED+ code. The diffusion of polyacene molecule is more favorable in the [1-10] direction

understanding molecules stability and mobility at various temperatures. These calculations are not trivial since translational and rotational degrees of freedom of any molecules during their diffusion are combined and will often be accompanied by bond breaking and bond forming events.

STM and AFM image calculations

Once the adsorption site and molecular conformation of the adsorbate is found, theoretical interpretation of experimentally acquired STM and NC-AFM images of adsorbed molecules has to be tackled. For ten years, the EHMO-ESQC method (extended Hückel molecular orbital - elastic scattering quantum chemistry) has demonstrated its efficiency to interpret experimental STM images with a very good degree of confidence. At least, some forty papers have already been published where ESQC was used with various adsorbates (atoms, small and large molecules) on metallic and semiconducting substrates and on thin insulating films as well (Fig. 3). Thus, the efforts have now to be focused to an improvement of ESQC code to speed up the computation time. This stage is very well tackled by our Fujitsu partner. By reducing the image computation time, it may become possible to perform the optimisation between experimental and numerical results leaving the computer to follow the convergence automatically.

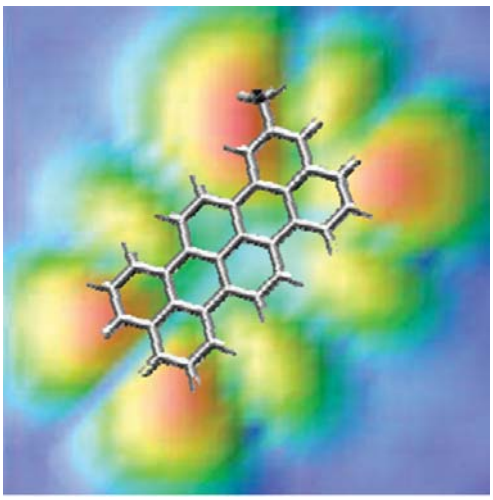

Fig. 3. ESQC-STM image calculation of a single methylterrylene molecule adsorbed on two monolayers of NaCl(100) deposited on Cu(111) surface. The thin insulating film allows the decoupling of the electronic structure of the molecule from the metallic substrate. The structure of molecular orbitals can then be well resolved.

NC-AFM is not only able to obtain accurate images of various substrates, it is also efficient to get dissipation information of adsorbates. This dissipation signal indicates what are the efficient channels of a molecule. Such an identification of molecular soft phonons could be used to induce mechanical functions With the help of a virtual NC-AFM, imaging and dissipation signals can be calculated once a specific force-field mesh is introduced as a data set. The improvement of our numerical code will consists in the introduction of the different noises of the experimental setup.

STM or NC-AFM manipulations of single adsorbates is an important topic in Pico-Inside. A virtual STM already exists [12] allowing the direct comparison between experimental manipulation signatures and theoretical ones. The precise mechanical behaviour can then be identified. The use of this numerical code will be applied for the manipulation of large molecules.

Acknowledgements

We would like to thank our collaborators (Stéphane Ami, Francesco Ample, Ivan Duchemin, Mohamed Hliwa, Sladjana Stojkovi?, Carlos Villagómez Ojeda, Nouza Jlida) of the NanoSciences group in Toulouse with whom we are sharing the work to address these theoretical and simulations topics. We also want to acknowledge our Pico-Inside partners of Fujitsu (Pierre Lagier, Jean Latour) for the active collaboration in Pico-Inside.

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Imaging and Manipulating Molecules On Reactive Surfaces

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An ability to image and manipulate organic molecules with an Atomic Force Microscopy (AFM) tip after their deposition on insulating, semiconducting or metallic surfaces is an important part of the PICO-inside project. Indeed, in AFM an atomically sharp tip is oscillated at resonance above the surface with constant amplitude and frequency, which is achieved by simultaneously changing the excitation amplitude and the tip-sample distance. The latter results in topography, while the former – in dissipation images, both show from atomic to molecular resolutions. Since in AFM the mechanical interaction between the tip and surface plays the major role, AFM is a universal imaging tool, whereas Scanning Tunnelling Microscopy (STM) is only limited to conducting surfaces. In addition, if with STM in most cases it is difficult to obtain submolecular resolution necessary to characterise the adsorbed species on the surfaces in detail, AFM may provide some hope as dissipation images should be more sensitive to various molecular groups that may have several possible configurations (e.g. CH3, NH2, etc.).

There are several questions we shall try to raise here: (i) is it possible to obtain a submolecular resolution of adsorbed molecules and, at the same time, an atomic resolution of the surface to place the molecule in correctly, (ii) what may be the mechanism of manipulation of molecules on surfaces with AFM and (iii) the role played by the tip. Theoretical ab initio methods are indispensable tools in addressing these issues, and, as an example of our approach, we shall consider one system which has been studied recently in great detail, namely, a C60 molecule on the Si(001) surface.

We shall start by pointing out that using a Si tip terminated with a dangling bond it is possible to obtain an atomic resolution of the Si(001) surface in AFM topography images [1,2]. As it well known, the surface consists of rows of dimers and their buckling within and between rows results in several reconstructions of the surface. Shown in Fig. 1 calculated AFM images demonstrate that one can clearly recognise the upper dimmer atoms in the images and, by doing so, the particular surface reconstruction.

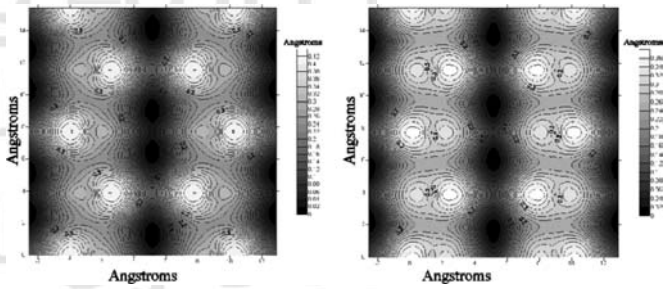

Fig. 1. Calculated AFM images of the c(4x2) (left) and p(2x1) (right) reconstructions of the Si(001) surface [1].

Similarly, one can obtain the topography AFM image of the C60 molecule on the same surface. C60 can adopt a large number of adsorption configurations [3-5], in which it forms covalent bonds with 3-4 Si atoms, either on the row or in the trough (between rows). In most cases the molecule is oriented either with two hexagons or with a hexagon and adjacent pentagon to the AFM tip. It is seen from the images in Fig. 2, calculated using the same Si tip [6], that both these orientations can be clearly recognised. More importantly, in this particular case, both images of the surface and of the molecule can be obtained using the same experimental conditions (such as the frequency shift). This means that it must be possible to image both the surface and the molecule during the same scan. Consequently, it should be possible to identify the adsorption configuration almost uniquely by checking with all possibilities [5].

Thus, theory predicts for this particular case that submolecular resolution with AFM should be possible. The crucial point is the reactive Si tip we have used in our calculations. If not for this particular tip, it would not have been possible to achieve this resolution. The same applies to the surface as well. Since the tip structure is never known in the actual AFM experiments, it is important to emphasize that our calculations indicate on the possibility of successful imaging. However, this rises a question of the tip preparation and control in AFM experiments, which is still an unsolved problem.

Finally, we have also studied repulsive manipulation of the C60 molecule with a number of different tips on the Si(001) surface [5,7]. We find that the molecule rolls rather than slides on the surface, i.e. the manipulation mechanism proceeds via pivoting of the C60 over its front “legs” from one stable site to the other, see Fig. 3. This allows breaking of only two bonds rather than all four, which leads to lower energy barriers. Diffusion of this molecule should be based on the same mechanism as well.

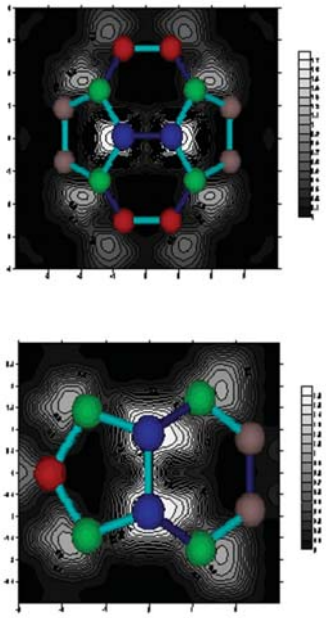

Fig. 2. Calculated AFM images of the C60 molecules adsorbed in two configurations on the Si(001) surface with either two hexagons or with a hexagon and a pentagon facing up the tip.

Finally, we have also studied repulsive manipulation of the C60 molecule with a number of different tips on the Si(001) surface [5,7]. We find that the molecule rolls rather than slides on the surface, i.e. the manipulation mechanism proceeds via pivoting of the C60 over its front “legs” from one stable site to the other, see Fig. 3. This allows breaking of only two bonds rather than all four, which leads to lower energy barriers. Diffusion of this molecule should be based on the same mechanism as well.

Still, more work need to be done in order to understand whether the same conclusions can be drawn for other types of molecules and surfaces. We should also investigate how crucial the tip structure is for successful imaging and manipulation of molecules of interest. We should also consider other possible manipulation possibilities, such as pulling (attractive mode), vertical lifting, etc. Finally, we should make the dissipation image calculation of surfaces and molecules on them a routine task.

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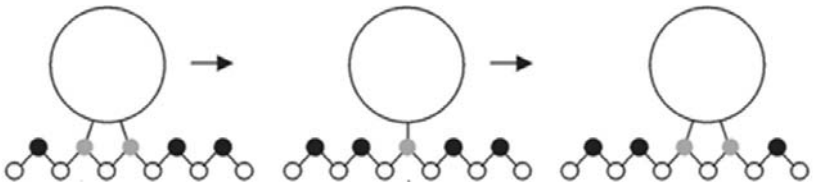

Fig. 3. Pivoting mechanism of C60 manipulation/diffusion on the Si(001) surface [5,7].

How to make organic molecules to stick to oxide surfaces?

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There has been significant progress in recent years in the deposition, and then the subsequent imaging with non-contact Atomic Force Microscopy (NC-AFM), of a variety of organic molecules on insulating substrates. The control and utilisation of individual adsorbed molecules could have profound technological implications, specifically in the area of molecular electronics - which promises to dramatically increase the power and decrease the size of information technology. The Pico-Inside project, which is a collaboration between many groups in European union, aims to demonstrate that a single molecule is capable of performing a logical operation through an evolution of quantum states.

One of the architectures to be explored by the project is that of an isolated molecule adsorbed on an insulating surface and connected to macroscopic electrodes, which can then exchange information with the molecule. In order to achieve this it is essential to understand in detail the interaction of the molecule with the surface. Specifically it is important to know how the molecule will bind and diffuse on the surface and how the interaction with the surface will modify its electronic structure. It will also be important to understand mechanisms of controlled manipulation with a scanning probe microscope tip, since it may be required to move the molecule into a specific position in order to connect it to the electrodes.

As part of our contribution to the Pico-Inside project, we are investigating the adsorption, diffusion and manipulation of organic molecules on the oxide surfaces MgO (001) and TiO_2 (011). These surfaces are well characterised using various surface science methods including SPM and are good candidates for a potential substrate. MgO is a good insulator whereas TiO_2 is a wide gap semiconductor and can be imaged using both STM and AFM. The remainder of this article will describe the modelling that we are performing on these systems and how this can be used to aid the experimental efforts of the Pico-Inside project.

Ab-initio calculations

To accurately model both the molecule, the surface and their interaction it is essential to perform high quality electronic structure calculations. To study the adsorption of an isolated molecule, which is a non-periodic system, we employ an embedded cluster code developed in our group called Gaussian Used for Embedded System Studies (GUESS) [1]. In this method the molecule and a small region of the surface directly below it (the quantum region) are treated from first principles using localised basis sets and the B3LYP hybrid functional with the Gaussian package [2], and are free to move. This cluster is then surrounded by a region of classical polarisable ions treated using the shell model [3], that are also relaxed. Finally, this system is embedded in a large array of fixed point charges (see Figure 1).

This set-up allows us to treat the molecule and its interaction with the surface to a high level of accuracy and detail, while also having a realistic representation of the electrostatic field generated by the surface over a large area. In a typical calculation, a single organic molecule (such as that shown in Fig. 1) is positioned on the surface and then the total energy of the system is minimised with respect to the coordinates of all free atoms. We can then determine quantities such as adsorption energies and equilibrium configurations as well as important information about the electronic structure, such as molecular orbital levels, electronic polarisation and charge transfer.

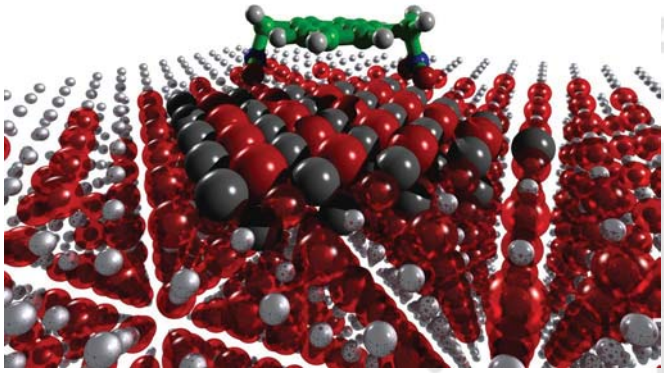

Figure 1: Illustration of the system configuration in an embedded cluster calculation.

We have performed extensive calculations using this method, studying the adsorption of various organic molecules (which consist of aromatic systems with various chemical groups) on the MgO (001) surface. It has been found that there is virtually no transfer of charge between the molecule and the surface and the electronic structure of the adsorbed molecule is relatively un-perturbed from that in isolation. The interaction is therefore purely electrostatic and non-polar molecular groups such as benzene and methyl groups have very little binding to the surface. As a result of this, part of our efforts have been to investigate chemical groups and their configurations that will bind strongly to the surface and prevent too rapid diffusion of the molecule.

We are currently investigating the interaction of certain molecules with defect sites on the MgO surface, such as monolayer step edges, corners and vacancies. We are particularly interested in how molecules can be anchored to vacancies in the surface and how the charge state of the vacancy can modify the electronic structure of the adsorbed molecule. It has recently been demonstrated that the charge state of individual oxygen vacancies (F-centres) in the MgO (001) surface can be modified with an SPM tip [4].

Generating inter-atomic force-fields

The embedded cluster method allows us to accurately model the electronic structure of the molecule and the surface, however these calculations are very computationally expensive and are, therefore, limited to geometry optimisations on small molecules. If we wish to study in detail the dynamics, diffusion and manipulation of larger molecules a classical force-field must be used to describe the inter-atomic interactions. Reliable force-fields exist for the isolated surface and the isolated molecule, however there are no reliable force-fields to describe the interaction of the molecule with the surface.

To address this problem we have developed a systematic approach to deriving force-fields for the surface-molecule interaction from the *ab initio* calculations [5]. The interactions inside the molecule are described with an intra-molecular force-field (e.g. MM4, CHARM), and inside the surface with a separate appropriate force-field. Each atom in the molecule then interacts with each atom in the surface via pair-potentials which have been parameterised to fit *ab initio* data. To make the high level calculations feasible the force-field was parameterised

using small molecules to simulate the functional groups making up the full molecule, e.g. methyl groups where parameterised from the interactions of methane with the surface. It was then shown by comparing calculations of larger molecules, composed of several functional groups, that the interactions where indeed additive to a good approximation and that the "molecular Lego" approach allows us to derive force-fields for almost arbitrary molecule-surface interactions (Figure 2).

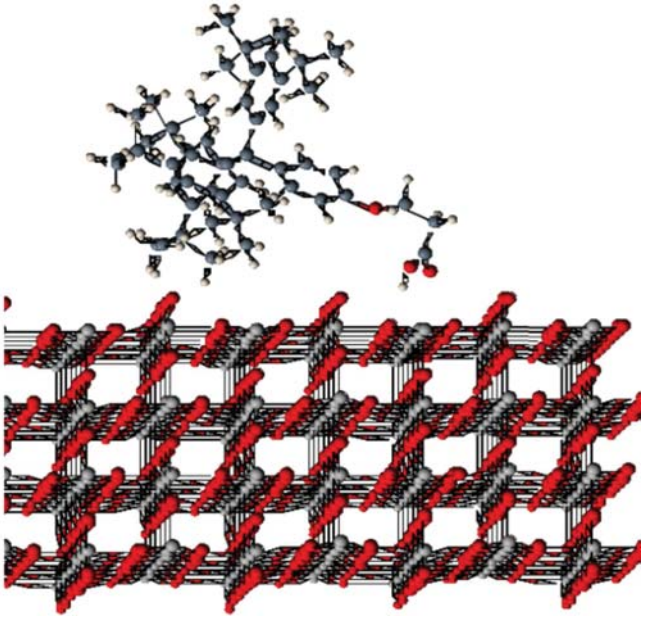

Figure 2. A large organic molecule anchored to a TiO_2 surface via a carboxyilic acid group. The molecule is composed of several units - four phenyl rings, aliphatic carbon atoms and a CO_2H tail. The force-field for the interaction of each group with the surface was determined separately, then the total molecule put together like a lego kit.

We have used this approach to develop potentials for organic molecules interacting with the TiO_2 (110) surface, where it has been demonstrated that they reproduce adsorption energies and configurations to a high degree of accuracy. We are currently in the process of applying the same procedure for organic molecules on the MgO (001) surface.

Diffusion on TiO_2

With a reliable force-field for the interaction of the molecule with the surface, it is possible to study a wide range of processes in detail. For instance, the imaging of adsorbed molecules with an atomic force microscope (AFM), which necessitates using empirical potentials due to the large numbers of calculations required to generate an image [6]. We examined in detail the AFM imaging of large and small molecules on MgO and TiO_2 [7], and discussed the problems with achieving simultaneous atomic resolution on both adsorbate and substrate. We are presently investigating the diffusion of several model molecules (see Fig. 3) on the TiO_2 surface.

One major problem to making practical use of the properties of molecules on insulators is to balance the adsorption and diffusion energies on the surface of interest. Should the molecules not stick strongly enough or be too mobile they will either desorb or migrate to step edges of other defects. Conversely if the energy to diffuse is too large many interesting phenomena such as self assembly/aggregation or the ability to manipulate the molecules with an atomic force microscope will not be possible. With the development of reliable force-fields it is possible to screen a wide variety of molecules and tune their mechanical properties before carrying out expensive/time consuming experiments, much as the pharmaceuticals industry checks the likelihood of a drug binding to the correct receptors before any actual synthesis is undertaken. As a simple example, the binding of molecules to the TiO_2 surface is found to be extremely sensitive to the degree of freedom that the legs that bind the molecule to the surface have, with very rigid groups forcing the molecule to compromise geometries and thereby lowering the adsorption energy. The rigidity of the whole molecule is also a factor if it makes multiple attachments to the surface, and understanding the mechanism of diffusion for these types of molecules is currently being pursued. Figure 3 shows the diffusion of a small molecule bound to the rutile surface by two CO_2H groups, the flexibility of the legs is such that each of the anchoring groups can move independently, allowing the molecule to "walk" along the rows of titanium atoms on the surface.

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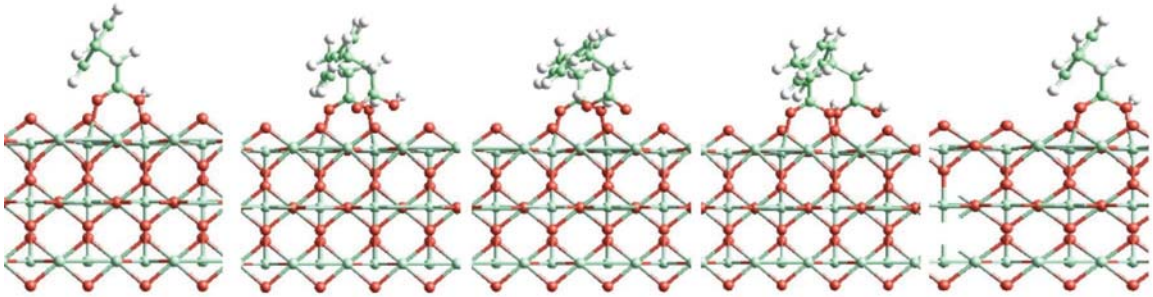

Figure 3: Illustration of a prototype 'walker' molecule on the TiO_2 surface.

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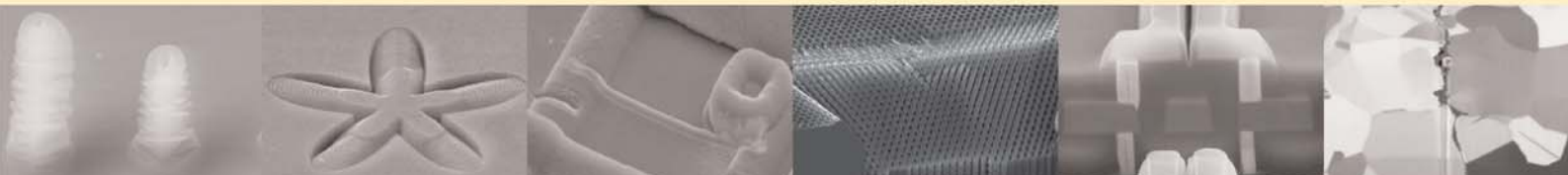
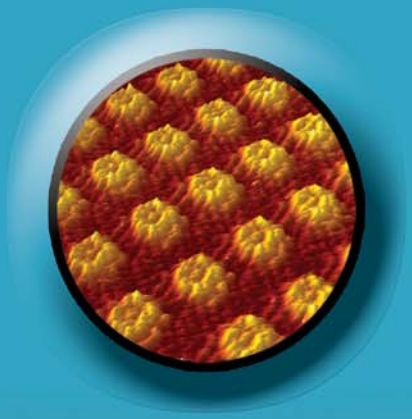


SURFACE ANALYSIS



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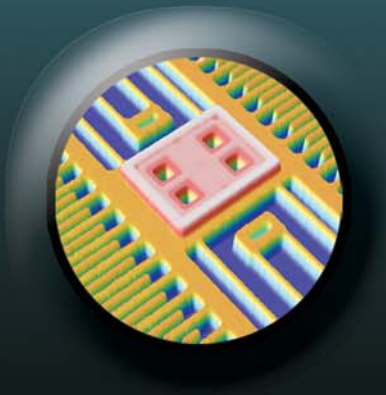

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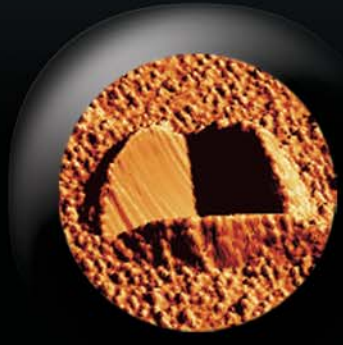

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