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- * Single bond mechanochemistry at Silicon surfaces
- * Ethane bridged Zn-Porphyrin dimmers for tert-butylamine detection using magneto-optic surface plasmon resonance gas sensing
- * Preparation of complexes of Tobacco mosaic virus and magnetic nanoparticles and investigation of their behavior in an oscillating magnetic field

* EUSKAMPUS
Campus of International Excellence of the
Basque Country University

dear readers,

Dear Readers,

Merry Christmas & Happy New Year 2013 from all the Phantoms Foundation team.



The AtMol Integrated Project (EU/ICT/FET) will establish comprehensive process flow for fabricating a molecular chip, i.e. a molecular processing unit comprising a single molecule connected to external mesoscopic electrodes with atomic scale precision and preserving the integrity of the gates down to the atomic level after the encapsulation. This E-nano Newsletter issue contains an article providing new insights on single bond mechanochemistry at silicon surfaces.

In 2011, the nanoICT project (EU/ICT/FET Coordination Action) launched its second call for exchange visits for PhD students and research personnel. The first outcome reports were published in issues 22, 23 & 25 and this edition contains two new articles providing insights in relevant fields for nanoICT.

On the scientific policy side, several Campus of International Excellence have been launched recently in Spain to promote research & technology transfer, new educational programs, etc. In this newsletter, the strategic goals of the Campus of International Excellence - CEI Euskampus - are described in detail.

We would like to thank all the authors who contributed to this issue as well as the European Commission for the financial support (ICT/FET FP7 AtMol No. 270028).

> Dr. Antonio Correia Editor - Phantoms Foundation

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Single bond mechemochemistry at Silicon surfaces

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1. Single atom extraction

The primary objective of the four year, eleven partner Atomic Scale and Single Molecule Logic Gate Technologies (AtMol) ICT project – namely, the fabrication of a molecular chip whose logic functions are derived from a *single* molecule – necessitates the imaging and control of matter at the single atom and single molecule levels [1]. Since the pioneering experiments of Don Eigler and his colleagues at IBM Almaden over twenty years ago [2], the scanning tunnelling microscope (STM) has been used to selectively position and modify individual adsorbates on a variety of substrates. Arguably the most elegant example of STM manipulation in recent years has been the assembly, and subsequent finely tuned distortion, of an artificial graphene lattice formed by CO molecules on a Cu(111) surface [3]. In a ground-breaking demonstration of the capabilities of state-of-the-art STM, Manoharan and co-workers used the tip of the tunnelling microscope to produce the precise amount of lattice distortion required to mimic the presence of very high magnetic fields (up to 60 T).

Manipulation modes other than lateral displacement of adsorbates are also, of course, possible. Earlier this year, and

building on their previous work on the electronic transport properties of atomic wires, Simmons and co-workers reported the fabrication of a single atom transistor [4]. This work is of particular relevance to the AtMol project as it exploited the hydrogen depassivation technique pioneered by Lyding et al. in the mid-nineties [5] to fabricate the devices with atomic scale precision. As reported in the previous eNano Newsletter (#25), the AtMol consortium, through the efforts of Marek Szymonski's research group at Jagiellonian University in Krakow, has fabricated pre-defined patterns of single dangling bonds (DBs) on the hydrogen-passivated Ge(100) surface via this H-desorption process (which is driven by vibrational heating arising from inelastic scattering of tunnelling electrons.)

Although the same fundamental patterning tool as that employed by Simmons et al. was used to generate the DB patterns on H:Ge(100) - i.e. extraction of H atoms using the tip of an STM - the strategy for device design and implementation differs dramatically. A concept at the core of the AtMol project is the quantum Hamiltonian computing (QHC) approach pioneered by Joachim et al. [6]¹. This represents a radically different and entirely non-classical approach to carrying out logic operations at the atomic or molecule scale where the logic operation is embedded in the Hamiltonian describing the electronic properties of a molecule or pattern of DBs (which, depending on the degree of

¹ QHC is not to be confused with quantum computing. In the QHC approach phase evolution on the time scale of the processing is not exploited and so decoherence is not an issue.

coupling between the bonds, can be thought of as a large ‘molecule’).

2. Mechanical atom manipulation

STM is of course not the only scanning probe technique available for precise control of atoms and molecules at surfaces. There has been a very rapid growth of interest in non-contact atomic force microscopy (NC-AFM) of late, due both to the introduction of the qPlus sensor geometry by Franz Giessibl (University of Regensburg) and a variety of exciting experiments which have not only demonstrated that extremely high resolution is possible using the technique [7] but that the force required to laterally displace single adsorbed atoms can be determined [8]. (“Non-contact” AFM is perhaps something of a misnomer as an increasing number of experiments are carried out in the Pauli exclusion regime of the tip-sample interaction potential, where the tip-sample separation is below the equilibrium bond length for the interacting atoms. “Dynamic force microscopy” is perhaps a more apt description. Nonetheless, the NC-AFM moniker is widely used and so, in the interests of consistency, will also be employed here).

We have recently shown [9] that the qPlus variant of NC-AFM can be used to controllably switch silicon dimers at the Si(100) surface between two stable (buckled) states, using mechanical force alone to modify the intradimer bond angle (see Fig. 1). This type of force-driven manipulation of single bonds bears many of the hallmarks of the mechanochemistry strategy proposed by Drexler a couple of decades ago [10], for which he was subsequently heavily criticised. Today, however, mechanochemistry is a nascent sub-field of scanning probe microscopy - and, more broadly, nanoscience - and within the AtMol consortium it is actively being pursued as a means to manipulate

surfaces and adsorbates which complements, and in principle has the potential to supersede, the tunnel current/field driven approaches generally used in STM manipulation.

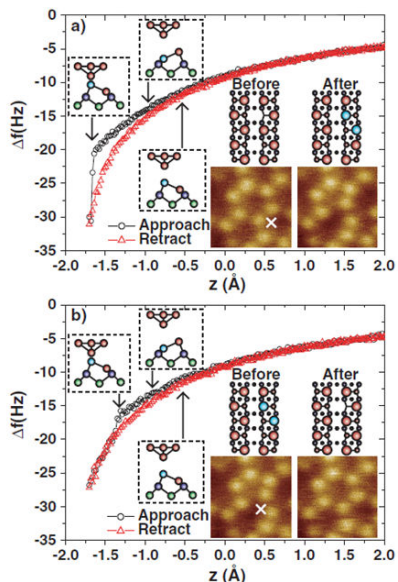


Fig. 1 > Flipping silicon dimers using chemomechanical force alone. Examples of dimer flipping showing frequency shift vs tip-sample separation curves (and corresponding before and after NC-AFM images) for (a) the creation, and (b) the removal (lower) of a two-phason state. Taken from Ref. 9./

As with any scanning probe technique, the tip state plays a crucial role in image formation, spectroscopy, and manipulation. In NC-AFM, however, the physicochemical properties and the geometry of the tip are significantly more influential than in STM due to the mixture of short-range (chemical) and long-range (van der Waals, electrostatic) forces which underpins any NC-AFM experiment. Gaining control over tip structure is therefore essential in order to understand not only the physics of image formation but to exploit the highly local nature of the

probe-sample interaction for atomic and molecular manipulation.

3. Probing the probe

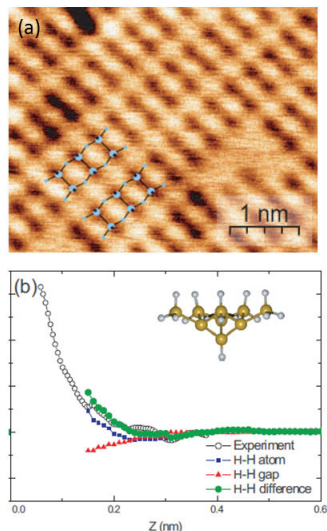


Fig. 2 > (a) A non-contact atomic force microscope image of the H:Si(100) surface taken with a qPlus sensor. The contrast is inverted such that the dark features in the image are associated with the H atoms passivating the silicon dimers. (b) A comparison of experimental and theoretical force-distance curves. Best agreement is reached when a H-passivated tip is used for the theoretical simulations. Taken from Ref. 11./

Given that, as described above, depassivation of Si(100) via hydrogen atom removal using an STM tip plays a central role in the AtMol project, we have recently focused both experimentally and theoretically on the interaction of NC-AFM tips with the H:Si(100) surface. Fig. 2(a) is a constant frequency shift NC-AFM image of H:Si(100)-(2x1) where the minima (i.e. dark spots) in the image correspond to the positions of the hydrogen atoms (see the ball-and-stick model in the inset) [11]. Thus, the image contrast is inverted compared to that we

might expect. A comparison, Fig. 2(b), of experimentally measured force-distance curves with their theoretical counterparts calculated using density functional theory (DFT) shows that the contrast inversion arises from the termination of the tip with hydrogen, resulting in a passivated, non-reactive apex. We stress that image inversion of this type is extremely common in our NC-AFM measurements of H:Si(100), most likely due to the (reactive) silicon termination of our tips [9] promoting a transfer of H from the surface to the probe. For more detailed information on the experimental and theoretical protocols please see Refs. 12 and 15. Similar regular observations of image contrast have been made by Such et al. during NC-AFM of hydrogen-passivated Ge(100) [12].

There then arises the question of the influence of the hydrogen termination of the probe on not just its imaging characteristics but on its propensity for atomic manipulation. More specifically, is hydrogen extraction from H:Si(100) possible using a H-passivated tip? If not, which particular type of tip apex is required in order to extract (or deposit) a hydrogen atom? We have addressed these questions using a series of DFT calculations involving two ‘archetypal’ H-terminated tip geometries which were studied in terms of their ability to transfer a H atom to a Si(100)-c(4x2) surface (Fig. 3 and Ref. 13). The key message resulting from these calculations is that even relatively minor modifications in the structure of the tip apex can have a major influence on the ability of NC-AFM to modify a surface at the atomic level.

With a tip apex which adopts a (111)-like symmetry, i.e. the terminating atom is back-bonded to three nearest neighbours in a so-called H₃ geometry (see Fig. 3), the H atom at the tip stubbornly refuses to transfer to the underlying Si(100) surface. Instead, the binding geometry of

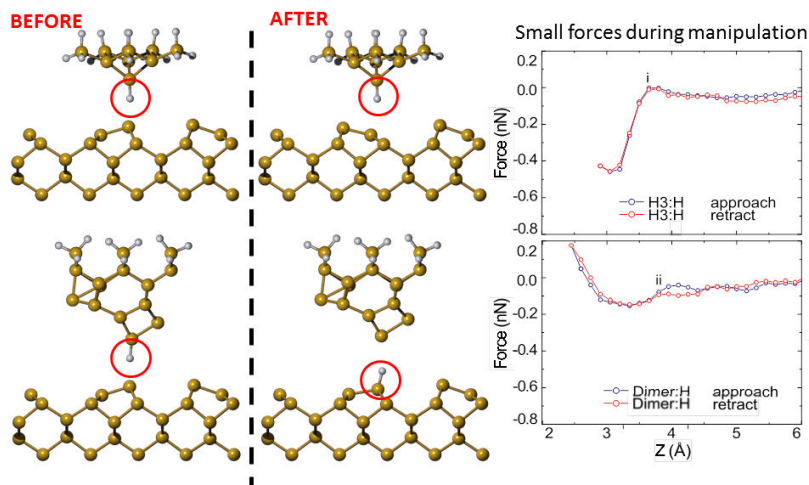


Fig. 3 > Importance of the tip apex geometry in determining which manipulation processes are possible in NC-AFM. The uppermost “before” and “after” geometries show that for a ‘H₃’-type H-terminated tip, hydrogen transfer to a Si(100)-c(4x2) surface is not possible. With a dimerised tip, however, H transfer is energetically favourable (as shown in the lowermost “before” and “after” images). The corresponding force distance curves are shown on the right. See Ref. 13 for more details.

the H atom at the tip is sufficiently stable - that is, the tip is sufficiently well-passivated - that it can be used to push (rather than pull, as is the case in Fig. 1) a silicon dimer from one buckled configuration to the other stable conformation. On the other hand, when a somewhat less rigid dimer-terminated tip is chosen, H atom transfer becomes possible. The short range chemical forces involved in the transfer are, however, remarkably small (~ 100 pN), as compared to the dimer flipping events shown in Fig. 1. Thus, a tip that gives good atomic resolution images of the H:Si(100) surface may well not be appropriate for the deposition or extraction of H - not only is an atomically sharp tip necessary but the bonding geometry of the atom terminating the apex has to be appropriate for the atomic manipulation task at hand.

4. Orienting a single molecule probe

Atomic precision mechanochemistry with NC-AFM therefore necessitates much greater control over the precise structure of the tip apex than is required for STM-actuated manipulation of atoms (which typically involves inelastic tunnelling-mediated dynamics). This begs the question as to how the structure of the tip can be monitored directly during scanning probe - and, in particular, NC-AFM - experiments. Guillaume Schull, Richard Berndt and co-workers have carried out a series of elegant experiments [14] where they have used single adatoms on metal surfaces to ascertain the orientation of a C₆₀ molecule which they have transferred to the end of an STM tip. Each adatom (and its associated atomic orbital) has a smaller effective radius of curvature than the molecule terminating the tip and so it

acts as an imaging centre, providing direct real space images of the apex of the STM probe.

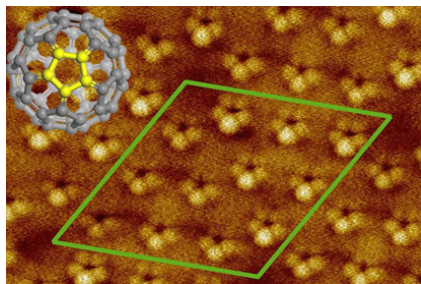


Fig. 4 > NC-AFM image of the Si(111)-(7x7) surface taken with a C₆₀-terminated tip. In this case the molecule is oriented so that a pentagonal face is facing the surface (albeit with a small tilt). Note difference in contrast between faulted and unfaulted halves of the unit cell. See Ref. 16 for more details./

We recently extended this ‘inverse imaging’ technique to NC-AFM, exploiting the dangling bond orbitals of the adatoms of the Si(111)-(7x7) surface as mini-tips (as first demonstrated by Giessibl et al. [15]) and thereby enabling atomic resolution imaging of a C₆₀ molecule terminating a qPlus sensor (Fig. 4 and Ref. 16). (Although Temirov et al. [17] have pioneered a technique they have coined scanning hydrogen tunnelling microscopy (SHTM) which enables atomic resolution imaging of the structure of adsorbed molecules, in general STM is sensitive only to molecular orbital density and therefore lacks the ability to resolve the atomic ‘framework’ of molecules).

While a variety of different molecular orientations have been resolved in our experiments, in Fig. 4 we show only an image of the ‘iconic’ pentagonal face of C₆₀. This image is noteworthy from a number of perspectives. First, the image was acquired in the attractive regime of the tip-sample interaction potential -

operation within the Pauli exclusion regime is not necessary to attain atomic resolution. This can be understood in the context of the reactive nature of the C₆₀-terminated tip with regard to the underlying Si adatoms. (Jelinek et al. [18] have similarly highlighted the central role played by tip reactivity in NC-AFM imaging of carbon nanostructures.)

Second, the precise orientation of the molecule at the end of the tip (in terms of rotation and tilt) can be determined directly from the NC-AFM image. For geometries where the molecule is adsorbed such that a double- or single-bond is facing the surface it is not possible to unequivocally distinguish between these possibilities using NC-AFM alone, for the reasons discussed in Ref. 16. In that case a comparison of the STM data with Hueckel molecular orbital calculations [19] is also required to ascertain the precise molecular orientation.

Finally, the termination of the tip with C₆₀ lends a hydrophobic functionality to the probe. This of course is of particular benefit when investigating other adsorbed molecular species as it potentially provides a route towards rudimentary chemical specificity. Of arguably more interest, however, is the possibility of terminating the probe with a molecule capable of rather more site-specific interactions such as hydrogen-bonding. This is something we are actively pursuing at the moment.

5. Automated Optimisation: Evolving the Probe

A significant amount of a scanning probe microscopist’s working time is spent coercing the tip into a state that yields atomic resolution. For NC-AFM in particular, a wide variety of different image types, each showing atomic resolution, are possible depending on the

precise structure of the apex of the probe. The same is true to a lesser extent for scanning tunnelling microscopy. Thus, not only is atomic resolution required but a very specific type/class of image is generally sought (corresponding to that where the tip is providing an accurate representation of the surface structure).

The component at the very heart of scanning probe microscopy - the probe itself - therefore represents a major bottleneck in both the imaging and manipulation processes. Over the past three years we have explored the possibility of both automating the tip preparation process and, more importantly, of establishing the possibility of 'dialling in' a particular state of the probe. In essence, our long term objective is the development of algorithms and protocols to enable the addition of two buttons to the graphical user interface of an ultrahigh vacuum scanning probe microscope controller: "Auto-Optimize Tip" and "Generate Tip State X" (where Tip State X is selected from a library of possibilities).

Our first steps towards realising these extremely challenging goals are shown in Fig. 5 (taken from Ref. 20). Here we chose the 'archetypal' tip-sample system for STM studies: a PtIr tip scanning a graphite sample. We select as a target image type either the trigonal or honeycomb structure of the graphite lattice (both types of structure are commonly observed in STM images of the highly oriented pyrolytic graphite (HOPG) surface). Our strategy for tip optimisation comprises two distinct algorithms. We first start with simple rules-based protocols very similar to those used by a human operator in deciding the quality of an STM tip. When the image quality passes a certain threshold (determined by a number of different metrics, as described in Ref. 20)

the rule-based algorithm is superseded by an evolutionary algorithm which mutates the scan parameters, compares the fitness of the image against the target, and makes a selection in parameter space based on the fitness. The gradual evolution of the fitness of the STM image is shown in Fig. 5. Note that no human operator involvement, other than the placement of the tip and sample in the microscope at the start of the experiment, was required.

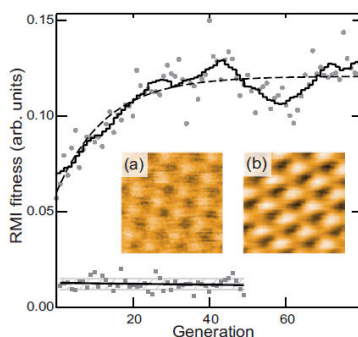


Fig. 5 > Automated probe microscopy via evolutionary strategies at the atomic scale. The figure shows the gradual increase in fitness of STM images of a graphite sample due to scan parameters selected via an evolutionary algorithm. Random selection (lower graph) produces no change in fitness. From Ref. 20./

Our future goals with regard to automated probe control include computer-controlled selection of the orientation of a tip-adsorbed molecule (such as the C_{60} molecule described in the previous section) and, of key importance for the AtMol project, the automatic generation of dangling bond patterns on H:Si(100).

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AtMol Events

Ecole de Physique des Houches AtMol Winter School

Quantum resources for single molecule-machines

Les Houches-France
January 27 - February 01, 2013

This is a winter school on surface atom and single molecule machines. We start from the basis of quantum control towards quantum and classical designs of atomic scale machineries.

The School will take place at the Ecole Physique des Houches in the French Alps at the foot of Mt. Blanc.

The courses are set up for PhD students, engineers, Post Doctoral fellows and researchers interested to enter this new field of research. New atomic scale multiple access experimental tools to/from an atomic scale machinery (nano-communications) will be detailed.

The physics of the first surface atom circuits, molecule Boolean logic gates, molecule gears (trains of gears) together with the operation of a single molecule motor will be described from theoretical and experimental viewpoints.

Registration Fee: 375 Euros including registration and full board for the week
Registration Deadline: January 10, 2013

Directors

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S.-W. Hla (Ohio University, Argonne National Laboratory, USA)

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