

Tuesday Afternoon, October 30, 2012

Scanning Probe Microscopy Focus Topic

Room: 16 - Session SP+AS+BI+ET+MI+NS-TuA

Advances in Scanning Probe Imaging

Moderator: S. Allen, The University of Nottingham, UK, Z. Gai, Oak Ridge National Laboratory

2:00pm **SP+AS+BI+ET+MI+NS-TuA1 Molecules Investigated with Atomic Resolution using Scanning Probe Microscopy with Functionalized Tips**, L. Gross, F. Mohn, N. Moll, G. Meyer, IBM Research - Zurich, Switzerland **INVITED**

Single organic molecules were investigated using scanning tunnelling microscopy (STM), noncontact atomic force microscopy (NC-AFM), and Kelvin probe force microscopy (KPFM). With all of these techniques submolecular resolution was obtained due to tip functionalization by atomic manipulation. The techniques yield complementary information regarding the molecular structural and electronic properties.

Using NC-AFM with CO terminated tips, atomic resolution on molecules has been demonstrated and the contrast mechanism was assigned to the Pauli repulsion [1]. On the other hand, by using STM the molecular frontier orbitals, i.e., the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), were mapped [2]. Using a CO terminated tip for orbital imaging with the STM, the resolution can be increased and the images correspond to the gradient of the molecular orbitals due to the p -wave character of the tip states [3]. Finally, KPFM reveals information about the distribution of charges within molecules by measuring the z -component of the electrostatic field above the molecule, as demonstrated on the hydrogen tautomerization switch naphthalocyanine [4].

References :

- [1] L. Gross *et al.* *Science* **325**, 1110 (2009).
- [2] J. Repp *et al.* *Phys. Rev. Lett.* **94**, 026803 (2005).
- [3] L. Gross *et al.* *Phys. Rev. Lett.* **107**, 086101 (2011).
- [4] F. Mohn *et al.* *Nature Nanotechnol.* **7**, 227 (2012).

2:40pm **SP+AS+BI+ET+MI+NS-TuA3 Functional Imaging of Jahn-Teller Dynamics at the Single-molecule Scale**, J. Lee, S.M. Perdue, A. Rodriguez Perez, P.Z. El-Khoury, V.A. Apkarian, University of California, Irvine

Taking advantage of both elastic and inelastic tunneling processes of a molecule isolated at the double-barrier tunneling junction of a scanning tunneling microscope, both static and dynamic parts of the Hamiltonian can be visualized with submolecular resolution. This is illustrated by imaging Jahn-Teller (JT) driven vibronic dynamics within Zn-etio porphyrin (ZnEtio), in its various reduced forms, in what may be regarded as nature's choice of a molecule as a controllable current switch. Unique interpretations are afforded through simultaneously recorded functional images, such as maps of: a) energy resolved differential current, b) spectrally resolved electroluminescence, c) conduction bistability, d) reduction/oxidation potentials (maps of charging and discharging). We focus on the radical anion, ZnEtio⁻, which is reduced by injecting an electron to a single ZnEtio molecule adsorbed on a thin aluminum oxide film grown on NiAl(110). In contrast with the neutral, the saddle-shaped radical anion lies flat on the surface of the oxide. The discharge map directly shows that the excess electron is localized in the ²p_x orbital of the entire porphyrin macrocycle, as a result of the JT active rectangular (B_{1g}) distortion of the molecule. The static JT potential leads to conduction bistability, with reversed switching polarity depending on whether tunneling electrons are injected in the occupied ²p_x orbital or the diamond (B_{2g}) coordinate which serves as a transition state that connects the p_x and p_y orbitals at the two B_{1g} minima. In addition to the JT switching, the dynamic JT states are directly imaged through electroluminescence spectra, induced by injection of a second electron in the anion. The spectra consist of a continuum due to radiative ionization of the dianion, and sharp Fano resonances of the vibronic progression of the JT active modes. A detailed analysis of the spectra yields the vibronic couplings and the wavefunctions. Vibronic structure is inherent in STM topographic images, and has hitherto not been fully recognized.

3:00pm **SP+AS+BI+ET+MI+NS-TuA4 Atomic and Chemical Resolution of Heterogeneous 1-D Metallic Chains on Si(100) by Means of nc-AFM and DFT**, M. Setvin, M. Ondracek, P. Mutombo, Z. Majzik, P. Jelinek, Institute of Physics of ASCR, Czech Republic

Scanning Probe techniques are widely used to image atomic and electronic structure of surfaces and nanostructures. However atomic and chemical

resolution of complex nanostructures (e.g. molecules, nanoparticles or nanowires) is still the large challenge. Several methods (see e.g. [1-3]) have been already proposed to achieve the single-atom chemical resolution. In the work [3] it was showed that the single-atom chemical identification can be achieved via force-site spectroscopy measurements using Frequency Modulation Atomic Force Microscopy (FM-AFM). The validity of the method was demonstrated on semiconductor surface alloy composed of isovalent species (Si, Sn and Pb). In this particular case, the valence electrons of surface atoms possess very similar electronic structure close to sp³ hybridization with characteristic dangling bond state. Hence the maximum short-range force is mainly driven by the position of the dangling bond state with respect to the Fermi level.

In this work, we investigated atomic and chemical structure of heterogeneous 1-D chains made of III and IV group metals grown on Si(100) surface [4] by means of room-temperature (RT) FM-AFM measurements combined with DFT simulations. Here 1D chains consist of heterogeneous buckled-dimer structures with unknown chemical ordering. What more, the presence of buckled dimers composed by chemical species of different valence makes this system very challenging for true atomic and chemical resolution by means of SPM.

In this contribution, we will show first that FM-AFM technique even at RT is able to achieve atomic resolution of individual atoms forming dimers, much superior to the contrast obtained by the traditional STM technique. Secondly, we will demonstrate that the single-atom chemical identification is still possible combining the force-site spectroscopy at RT with DFT simulations even in such complex systems as the heterogeneous 1D metallic chains.

- [1] M. Schmid, H. Stadler, P. Varga *Phys. Rev. Lett.*, **70**, p. 1441 (1993)
- [2] L. Gross *et al.* *Science* **325**, 5944 (2009).
- [3] A. Foster *et al.* *Phys. Rev. Lett.* **102**, 256103 (2009).
- [4] Y. Sugimoto, P. Pou, M. Abe, P. Jelinek, R. Perez, S. Morita, O. Custance, *Nature* **446**, 64 (2007)
- [5] L. Magaud, A. Pasturel, and J.-Y. Veuillen, *Phys. Rev. B* **65**, 245306 (2002).

4:00pm **SP+AS+BI+ET+MI+NS-TuA7 Simple Routes to High Speed and Super Resolution AFM**, J.K. Hobbs, University of Sheffield, UK **INVITED**

Over the past two decades atomic force microscopy has developed to become the workhorse of molecular nanotechnology. However, despite this success, it has failed to deliver consistently in two areas where it arguably has most potential, namely sub-molecular resolution imaging and the following of processes in real time. Here our work to tackle these challenges will be discussed.

We have developed a new approach to reaching high resolution within a conventional AFM, based on torsionally driven T-shaped cantilevers, dubbed "torsional tapping AFM". The use of torsional oscillations gives improved dynamics (high Q-factor, high frequency), without excessively increasing the spring constant. The small offset of the tip from the axis of rotation gives improved lever sensitivity. Combined, these result in an approximately 12 fold improvement in sensitivity when compared to the same AFM with a conventional tapping cantilever. This improved sensitivity allows ultra-sharp whisker tips to be used in a routine manner, giving true molecular resolution even on soft materials presenting surfaces with tens of nanometres of topography. For example, individual polyethylene chains both in the crystalline phase, and at the interface with the amorphous phase, can be clearly imaged in a conventionally processed sample of plastic, with polymer chain-to-chain resolution down to 0.37 nm [1]. Data from semi-crystalline polymers to naturally occurring protein crystals will be presented.

High speed AFM requires methods for scanning rapidly, for maintaining tip-sample contact ("feedback"), and for constructing the topography image. We have shown that resonant scanners [2] give a robust method for rapid scanning. In a conventional AFM the feedback and the topographic image are inextricably linked. However, this places a limit on scan speed as it demands that the tip has reached equilibrium at each point on the image if the height is going to be accurately obtained. We have adopted a different approach, in which the height of the tip is directly measured using an interferometric approach, freeing the feedback loop to minimising tip-sample forces. This allows topographic images with height traceable to the wavelength of the interferometric laser to be obtained at imaging rates greater than one frame a second. Coupled with resonant scanners, giving scan areas up to 40x40 μm² an AFM platform capable of in-line industrial applications is obtained.

1. Mullin, N.; Hobbs, J. K., *Phys Rev Lett* **2011**,107
2. Humphris, A. D. L.; Miles, M. J.; Hobbs, J. K *Appl Phys Lett* **2005**,86 (3)

4:40pm SP+AS+BI+ET+MI+NS-TuA9 A Scanning Probe Microscopy Study of Trimesic Acid Self-Assembly on Highly Oriented Pyrolytic Graphite. V. Korolkov, S. Allen, C.J. Roberts, S.J.B. Tendler, The University of Nottingham, UK

We have investigated trimesic acid (1,3,5-benzenetricarboxylic acid, TMA) adsorption on highly oriented pyrolytic graphite (HOPG) surfaces from aqueous medium at room temperature. Both atomic force (Peak Force Tapping mode) and scanning tunnelling microscopy were utilized to follow the adsorption dynamics and molecular arrangements. A chicken-wire arrangement for adsorbed molecules with an average pore size of 11 ± 1 Å was established and observed using both scanning techniques. We found that this structure forms a monolayer within ~ 100 seconds of exposure of the HOPG surface to 50 μ M TMA solution in H₂O. The monolayer structure was found to be stable for at least 48h under ambient conditions. STM was observed to lead to some desorption of TMA from a dynamically formed TMA film, and was only able to image the monolayer of TMA molecules in intimate contact with the HOPG. AFM revealed that TMA films formed using higher concentrations or longer adsorption times formed multilayers with similar molecular spacings and displayed an island growth morphology.

We have achieved an excellent resolution on an ambient running AFM. We have demonstrated that the combination of STM and AFM is essential, if not a must, to look at ultimate monolayers in the ambient conditions. Overall a facile green chemistry method for TMA monolayer fabrication from aqueous media on a HOPG surface has been established.

5:00pm SP+AS+BI+ET+MI+NS-TuA10 Understanding the Role of the Probe in SPM Imaging of Metal Oxides: New Opportunities for In-Depth Surface Analysis. H. Mönig, Univ. of Münster, Germany, M. Todorovic, Univ. Autónoma de Madrid, Spain, M.Z. Baykara, Yale Univ., T.C. Schwendemann, Southern Connecticut State Univ., J. Götzten, Ö. Ünverdi, E.I. Altman, Yale Univ., R. Perez, Univ. Autonoma de Madrid, Spain, U.D. Schwarz, Yale Univ.

Metal oxide surfaces play an indispensable role in a number of catalytic processes of technological and scientific importance. A fundamental understanding of the role that metal oxide surfaces play in such applications requires an experimental technique that allows analyzing chemical and electronic surface properties down to the atomic scale. The powerful method of three-dimensional atomic force microscopy (3D-AFM) in combination with scanning tunneling microscopy (STM) can be used towards this goal with great success. However the interpretation of results is not straightforward, particularly because the structure and chemistry of the probe tip employed in the experiments influences the measured data.

In this talk, using a combination of experimental STM data and density functional theory (DFT) calculations, we will study the effect of changing the tip structure and chemistry, as well as imaging parameters such as tip-sample distance and bias voltage on STM images obtained on the model surface of Cu(100)-O, a surface oxide layer consisting of nearly co-planar copper (Cu) and oxygen (O) atoms. We observe that STM image contrasts and atomic species with highest tunneling probability vary greatly with changing tip properties and imaging parameters. Reasonable matches between calculated and experimentally recorded STM images are observed, allowing the determination of particular tip models used in the experiments. Additionally, the effect of rotating the model tip structures with respect to the sample surface results in asymmetric features in simulated STM images, reproducing certain peculiar patterns observed experimentally. To sum up, the results presented here underline the significant role that the tip plays in SPM measurements and describe potential routes to optimize the gathered information through deliberate manipulation of tip properties as well as imaging parameters.

5:20pm SP+AS+BI+ET+MI+NS-TuA11 Characterizing the Best Tips for NC-AFM Imaging on Metal Oxides with Force Spectroscopy and Theoretical Simulations. D. Fernandez-Torre, Universidad Autónoma de Madrid, Spain, A. Yurtsever, Osaka University, Japan, P. Pou, Universidad Autónoma de Madrid, Spain, Y. Sugimoto, M. Abe, S. Morita, Osaka University, Japan, R. Perez, Universidad Autónoma de Madrid, Spain

Metal oxides play a key role in a wide range of technological applications. To optimize their performance, it is essential to understand their surface properties and chemistry in detail. Noncontact atomic force microscopy (nc-AFM) provides a natural tool for atomic-scale imaging of these insulating materials. Some of these materials, including ceria (CeO₂), and particularly titania (TiO₂), have been extensively studied with nc-AFM in the last few years. Experiments on the rutile TiO₂(110) surface show, at variance with STM, that a variety of different contrasts can be obtained, and frequent changes among different imaging modes are observed during scanning. The

two most common contrasts are the “protrusion” and the “hole” mode imaging modes, that correspond, to imaging bright the positive or the negative surface ions respectively, but other contrasts like the “neutral” mode and the “all-inclusive” mode—where all the different chemical species and defects are imaged simultaneously—have been also identified.

Understanding the image contrast mechanisms and characterizing the associated tip structures is crucial to extract quantitative information from nc-AFM measurements and to identify the nature of the observed defects. While in many cases the same nc-AFM image can be explained by different models, and even different underlying tip-sample interactions, we show here that the combination of force spectroscopy (FS) measurements and first-principles simulations can provide an unambiguous identification of the tip structure and the image contrast mechanism. In particular, we show that the best tips to explain the protrusion and hole mode forces are TiO_x-based clusters differing in just one H atom at the tip apex, discarding previously proposed Ti-terminated tips that would lead to forces much larger than the ones observed in the experiments. The less frequent neutral and all-inclusive images are associated to Si tips where contamination is limited to just an O atom or OH group at the apex. These models provide a natural explanation for the observed contrast reversals by means of H transfer to/from the tip, an event that we indeed observe in our simulations. As tip contamination by surface material is common while imaging oxides, we expect these tips and imaging mechanisms to be valid for other oxides. Our results for the imaging of CeO₂ surfaces and of metal atoms (K, Pt) adsorbed on TiO₂ support this conclusion.

5:40pm SP+AS+BI+ET+MI+NS-TuA12 Direct Probe of Interplay between Local Structure and Superconductivity in FeTe_{0.55}Se_{0.45}. M.H. Pan, W.Z. Lin, Q. Li, B.C. Sales, S. Jesse, A.S. Sefat, S.V. Kalinin, Oak Ridge National Laboratory

A key challenge in high-temperature superconductivity is to determine the role of local crystallographic structure and chemical effects on the superconducting critical temperature, T_c . Iron chalcogenide superconductors (‘11’) are ideal model systems for deciphering the role of local effects on the superconductivity, primarily because they cleave leaving non-polar surfaces unlike other families of iron arsenide superconductors (‘1111’ or ‘122’) and cuprates. Here, we explore the interplay between local crystallographic structure, composition and local electronic and superconductive properties. Direct structural analysis of scanning tunneling microscopy (STM) data allows local lattice distortions and structural defects across a FeTe_{0.55}Se_{0.45} surface to be explored on a single unit-cell level. Concurrent superconducting gap (SG) mapping reveals suppression of the SG at well-defined structural defects, identified as a local structural distortion (Guinier-Preston zone). The strong structural distortion is related to the vanishing of the superconducting state. This study provides insight into the origins of superconductivity in iron chalcogenides by providing an example of atomic-level studies of the structure-property relationship.

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