

Thursday Afternoon, November 13, 2014

Scanning Probe Microscopy Focus Topic

Room: 312 - Session SP+AS+BI+NS+SS-ThA

Probing Chemical Reactions at the Nanoscale

Moderator: Carl Ventrice, Jr., University at Albany-SUNY, Jun Nogami, University of Toronto, Canada

2:20pm SP+AS+BI+NS+SS-ThA1 Surface Structures of Catalysts in Reactive Environments with Scanning Tunneling Microscopy, *Franklin (Feng) Tao, L.T. Nguyen*, University of Notre Dame **INVITED**

Structure and chemistry of catalysts under a reaction condition or during catalysis are the key factors for understanding heterogeneous catalysis. Advance in ambient pressure photoelectron spectroscopy has taken place over the last decades, which can track surface chemistry of catalysts in gas environment of Torr or even tens of Torr pressure range. Environmental TEM has been developed for studying structures of catalysts while they are in a gas or liquid phase. In terms of environmental TEM, images at a pressure up to bars have been obtained although 1-10 Torr to one bar is the typical pressure range of in-situ studies of catalysts by E-TEM. Compared to structural and chemical information of catalyst particles offered from environmental TEM, packing of adsorbed molecules on a catalyst surface and arrangement of catalyst atoms of catalyst surface are complementary for the structure information provided by environmental TEM. High pressure scanning tunneling microscopy (HP-STM) is the most appropriate technique to achieve these pieces of important information. With the HP-STM the structures of surfaces of model catalysts under a reaction condition or during catalysis can be visualized. Surface structures of catalysts only formed under a reaction condition or during catalysis can be tracked. Such information is significant for understanding catalysis performed at solid-gas interfaces.

In this talk, I will present the historical development of HP-STM. Then, I will review the pressure-dependent packing of chemisorbed molecules; one type of pressure dependence is the change of packing of adsorbates from site-specific binding in UHV or a gas phase with a low pressure to non-specific binding in a gas phase at a relatively high pressure; the other type is a switch from one specific binding site to another specific binding site along the increase of the pressure of gas phase of the reactant. In addition, restructuring of a catalyst surface is another consequence of the increase of the gas phase pressure. The threshold pressure at which a restructuring is performed depends on the original surface structure and the intrinsic electronic state of the metal. I will review the surface restructurings of metal model catalysts including different vicinal surfaces in different reactant gases. In addition, the in-situ studies of Pt(110) and Rh(110) during CO oxidation will be taken as two examples to illustrate the in-situ studies of surfaces of metal model catalysts under reaction conditions (in a gas phase of one reactant) and during catalysis (in a mixture of all reactants of a catalytic reaction).

3:00pm SP+AS+BI+NS+SS-ThA3 Numerical Analysis of Amplitude Modulation Atomic Force Microscopy in Aqueous Salt Solutions, *P. Karayaylali, Mehmet Z. Baykara*, Bilkent University, Turkey

We present a numerical analysis of amplitude modulation atomic force microscopy in aqueous salt solutions, by considering the interaction of the microscope tip with a model sample surface consisting of a hard substrate and soft biological material through Hertz and electrostatic double layer forces (P. Karayaylali and M.Z. Baykara, *Applied Surface Science*, 2014, DOI: [10.1016/j.apsusc.2014.02.016](https://doi.org/10.1016/j.apsusc.2014.02.016)). Despite the significant improvements reported in the literature concerning contact-mode atomic force microscopy measurements of biological material due to electrostatic interactions in aqueous solutions, our results reveal that only modest gains of ~15% in imaging contrast at high amplitude set-points are expected under typical experimental conditions for amplitude modulation atomic force microscopy, together with relatively unaffected sample indentation and maximum tip-sample interaction values.

3:20pm SP+AS+BI+NS+SS-ThA4 Surface Potential Investigation of AlGaAs/GaAs Heterostructures by Kelvin Force Microscopy, *S. Pouch, Nicolas Chevalier, D. Mariolle, F. Triozon, Y.M. Niquet, T. Melin, L. Borowik*, CEA, LETI, MINATEC Campus, France

The Kelvin force microscopy (KFM) provides a spatially resolved measurement of the surface potential, which is related to the energetic band structure of a material. However, it depends strongly on the physical properties of the tip, e.g. width of the apex, the geometric shape and the stiffness of the cantilever as well as the surface sample state. The goal of this work is to investigate the surface potential measured by KFM on

AlGaAs/GaAs heterostructures. For this study, we used a certified reference sample (BAM-L200), which is a cross section of GaAs and $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ epitaxially grown layers with a decreasing thickness (600 to 2 nm) and a uniform silicon doping ($5 \times 10^{17} \text{ cm}^{-3}$). The resulting stripe patterns are commonly used for length calibration and testing of spatial resolution in imaging characterization tools (ToF-SIMS, SEM, XPEEM...). The surface potential measurement is performed under ultra-high vacuum with an Omicron system by using two acquisition modes: the amplitude modulation (AM-KFM), sensitive to the electrostatic force and the frequency modulation (FM-KFM), sensitive to its gradient. Three kinds of tips have been used for this study: platinum or gold nanoparticles coated silicon tips and super sharp silicon tips.

We will present the measurements obtained with these different tips for the narrowest layers (typ. < 40 nm). The surface potential mapping reveals a contrast around 300 meV between $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ and GaAs layers. However, we observed that this contrast vanishes when layer thickness becomes thinner. This loss of contrast cannot be only explained by the resolution limit of the KFM technique. Indeed, we will discuss the effect of the band bending length scale at the AlGaAs/GaAs interface related to the dopant concentration. The contribution of band bending between the layers is evaluated by a self-consistent simulation of the electrostatic potential, accounting for the free carriers distribution inside the sample and for the surface and interface dipoles. We will show that the electric fields of the narrowest layers recover each other, resulting in the partial or total loss of the contrast between $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ and GaAs layers. The simulation results will be compared to the experimental results in order to emphasize that the surface potential contrast is not only influenced by the resolution limit.

4:00pm SP+AS+BI+NS+SS-ThA6 Probing the Quantum Nature of Hydrogen Bonds at Single Bond Limit in Interfacial Water, *Ying Jiang*, Peking University, China **INVITED**

Quantum behaviors of protons in terms of tunneling and zero-point motion have significant effects on water properties, structure, and dynamics even at room and at higher temperature. In spite of tremendous theoretical and experimental efforts, accurate and quantitative description of the quantum nuclear effects (QNEs) in water is still challenging, due to the difficulty of accessing the internal degrees of freedom of water molecules. Using a low-temperature scanning tunneling microscope (STM), we are able to resolve in real space the internal structure, that is, the O-H directionality, of individual water molecules adsorbed on a solid surface [1,2]. The key steps are decoupling electronically the water from the metal substrate by inserting an insulating NaCl layer and enhancing the molecular density of states of water around the Fermi level via tip-water coupling. These techniques allow us not only to visualize the concerted quantum tunneling of protons within the H-bonded network, but also to determine the impact of proton delocalization on the strength of hydrogen bonds by resonantly enhanced inelastic electron tunneling spectroscopy (IETS).

Key words: STM, IETS, water, QNEs, proton transfer, H-bonding strength

[1] J. Guo, X. Z. Meng, J. Chen, J. B. Peng, J. M. Sheng, X. Z. Li, L. M. Xu, J. R. Shi, E. G. Wang*, and Y. Jiang*, "Real-space imaging of interfacial water with submolecular resolution", *Nature Materials* 13, 184 (2014).

[2] J. Chen, J. Guo, X. Z. Meng, J. B. Peng, J. M. Sheng, L. M. Xu, Y. Jiang*, X. Z. Li*, E. G. Wang, "An unconventional bilayer ice structure on a NaCl(001) film", *Nature Communications* 5, 4056 (2014).

4:40pm SP+AS+BI+NS+SS-ThA8 Resonant Enhanced Spectroscopy of Molecular Rotations with the STM and Field Effect Control of Molecular Dynamics, *Fabian Natterer, F. Patthey*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *Y. Zhao, J.E. Wyrick, J.A. Stroschio*, NIST, *H. Brune*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Inelastic electron tunneling spectroscopy (IETS) with the scanning tunneling microscope (STM) has vastly fueled the study of magnetic, electronic and vibrational properties of individual atoms and molecules due to its unmatched spatial and excellent energy resolution. Recently [1,2], rotational excitations could be characterized with IETS for the first time and yielded valuable insights into surface dynamics, bond lengths, and, notably about the nuclear spin state of homonuclear molecules. In particular, the two alike nuclei induce symmetry constraints in consequence of the Pauli principle and a certain alignment of nuclear spins requires a specific set of rotational levels J . We demonstrate rotational excitation spectroscopy (RES) with the STM for hydrogen, its isotopes, and mixtures thereof, physisorbed on metal supported graphene and hexagonal boron nitride, as well as on exfoliated graphene devices. We observe excitation energies that are equivalent with rotational transitions ($\Delta J = 2$) of molecules in the gas

phase for hydrogen, hydrogen-deuteride, and deuterium, respectively. Notably, these values represent the nuclear spin isomers *para*-H₂ and *ortho*-D₂. For HD, an additional $J = 0 \rightarrow 1$ transition is discerned, which is allowed for heteronuclear diatomics. We discuss the excitation mechanism in the light of resonant enhanced tunneling [3,4], and illustrate how the dynamics of molecules could be controlled by applying an electric field using a back gating graphene device geometry [5].

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[3] F. D. Natterer, F. Patthey, H. Brune, *arXiv:1403.1312* (2014)

[4] B. N. Persson, A. Baratoff, *Phys. Rev. Lett.* **59**, 339 (1987)

[5] J. Chae *et al.*, *Phys. Rev. Lett.* **109**, 116802 (2012)

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