

# Thursday Morning, November 12, 2009

## Nanometer-scale Science and Technology

Room: L - Session NS-ThM

### Characterization and Imaging at the Nanoscale

Moderator: C. Nakakura, Sandia National Laboratories

8:00am **NS-ThM1 Depth Resolved Luminescence from ZnO Nanowires**, *R.A. Rosenberg, S. Vijayalakshmi, M. Abu Haija*, Argonne National Laboratory, *J. Zhou, J. Liu, S. Xu, Z.L. Wang*, Georgia Institute of Technology

Nanodevices based on wide bandgap semiconductors have great potential in applications running from photon detectors to gas sensors. Critical to their successful implementation is knowledge of the surface and interfacial properties. In the present work we have utilized the limited penetration depth of soft x-rays (550-1000 eV) to study the near surface properties of vertically aligned ZnO nanowires. For a grazing angle of 5 degrees the penetration depth of these x-rays varies between 11 and 65 nm. Thus by obtaining optical luminescence spectra as a function of energy it is possible to probe the near surface region with nm-scale resolution. We will present energy dependent optical luminescence data from ZnO nanowire samples with diameters of 350 nm, 390 nm and 720 nm. In each case the ratio of the oxygen vacancy luminescence to the near band edge luminescence intensity peaks at an energy corresponding to ~17 nm x-ray penetration. This shows that the nanowires of three different diameters have a near surface defect region with a width of ~20 nm, which agrees with the conclusions from previous photoluminescence and cathodoluminescence studies [1-3]. Applications of this technique to other systems will also be discussed.

This work was performed at the Advanced Photon Source and was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357.

#### REFERENCES

- [1] N. Pan et al., *J. Phys. Chem. C* 111, 17265 (2007).
- [2] I. Shalish, H. Temkin, and V. Narayanamurti, *Phys. Rev. B* 69, 245401 (2004).
- [3] J. D. Ye et al., *App. Phys. Lett.* 92, 131914 (2008).

8:20am **NS-ThM2 Scanning Chemical Microscopy of Nanoscale Roughness Formation in Photoresist Materials**, *R. Ramos, I. Riisness, M. Gordon*, University of California Santa Barbara

Developing a molecular-level understanding of surface chemistry is of critical importance for advancements in the fields of surface science, materials research and catalysis. In particular, the ability to characterize, interrogate and image the chemical composition of surfaces at high spatial resolution would provide greater insight into surface reaction mechanisms and dynamics. For this purpose, optical spectroscopy, when combined with scanning probe microscopy, is a powerful tool for simultaneous chemical identification and imaging of surfaces at the nanoscale. Over the past few years, enhancement of optical fields through plasmonic coupling of light with metal nanostructures has been used for near-field vibrational spectroscopy (e.g., surface- and tip-enhanced Raman spectroscopy – SERS/TERS). However, these techniques have not seen widespread use for surface nanocharacterization because of poor quality field enhancers (i.e., reproducible tips) and difficulties in interpreting spectroscopic data.

In this work, we will show how careful design of the plasmonic properties of the tip and scanning configuration can turn TERS into a robust chemical analysis technique. Our experimental setup combines a tuning fork/cantilever-based scanning probe microscope with in-situ Raman and reflectance spectroscopy; the system also allows simultaneous mechanical and electrical surface interrogation at the nanoscale. In this talk, we will demonstrate that spatially correlating topography with chemical fingerprinting can provide insight into mechanisms of photoresist roughening. This issue is critical in the microelectronics industry as the size of device structures is reduced; specifically, roughness generated during the lithography and plasma etching steps in device fabrication is ultimately transferred into the active parts of the device, leading to lower performance. By combining near-field optical and chemical interrogation with traditional far-field vibrational spectroscopy and X-ray photoelectron spectroscopy, we will highlight the chemical processes involved in roughness formation in advanced photoresist polymers and investigate how they are affected by plasma exposure.

8:40am **NS-ThM3 In Situ Nanoscale Characterization of Gas Fluxes of Organic Membranes by Flux-Lateral Force Microscopy**, *L.S. Kocherlakota, D.B. Knorr, R.M. Overney*, University of Washington

Characterization studies of polymeric membranes for enhancing the gas transport rates are highly significant in current separation technologies. However transport property analyses like gas permeability measurements are bulk scale methods with limited access to local transport properties in multiphase systems such as nanocomposites membranes. In this context our group has developed a flux-lateral force microscopy (F-LFM) technique<sup>1</sup> for the in situ nanoscale characterization of the membranes, by monitoring the gas fluxes through them on a nanoscale. This technique, which is based on atomic force microscopy (AFM) utilizes the lubricating effect and the mechanical property changes in the membrane to determine fluxes. It was demonstrated by this technique that lateral force vs. pressure curves offered a direct measure of local gas permeabilities. In this paper we present the nanoflux analysis in Poly(trimethyl silyl propyne) (PTMSP), a glassy polymer with highest gas permeability of all known synthetic polymeric systems as well as high organic vapor/permanent-gas selectivity. The local fluxes in PTMSP films measured by F-LFM are compared to global fluxes obtained from conventional integrated methods. The sensitivity of F-LFM technique is demonstrated by presenting the reverse selective transport rates of He and CO<sub>2</sub> in PTMSP membranes as detected by the technique. The paper will also address the impact of aging, and flux dependence on film thickness.

#### Reference:

- <sup>1</sup> J.H. Wei, M. He, and R.M. Overney, *Direct measurement of Nanofluxes and Structural Relaxations of Perfluorinated Ionomer Membranes by Scanning Probe Microscopy*, *J. Membrane Sci.* **279**, 608-14 (2006)

9:00am **NS-ThM4 Nanoscale Electrodes by Conducting Atomic Force Microscopy at Elevated Temperatures**, *M. Louie*, California Institute of Technology, *A. Hightower*, Occidental College, *S. Haile*, California Institute of Technology

The combination of conducting atomic force microscopy (AFM) and electrical measurements (AC impedance spectroscopy and cyclic voltammetry) offers many advantages for measuring fuel cell electrode kinetics. The use of a conducting AFM probe as a nanoelectrode enables isolation and characterization of a single electrode-electrolyte interface without the need for a reference electrode. Furthermore, this technique permits studies of the spatial dependence of mechanistic phenomena while providing controllable electrode-electrolyte contact areas. The feasibility of using a nanoscale probe as a fuel cell electrode has been examined for the polymer electrolyte membrane system at room temperature (1-2). Higher temperature capabilities would make this technique useful for a wide variety of material systems, including low-to-intermediate temperature solid electrolytes.

Here, we demonstrate the viability of conducting AFM under controlled environments and at temperatures relevant to proton conducting solid acid compounds. Solid acid compounds have been demonstrated as viable proton conducting electrolytes for fuel cells (3-4), with peak power densities of ~400 mW/cm<sup>2</sup> at ~240 °C (5). Such fuel cells provide several advantages over polymer membrane fuel cells, including improved kinetics due to higher operating temperatures, impermeability of the membrane to fuels, and elimination of the need for complex water management systems. However, activation overpotential losses, particularly at the cathode, limit the performance (6), and electrode kinetics are not yet well understood.

We select cesium hydrogen sulfate, CsHSO<sub>4</sub>, as a representative solid acid electrolyte for the study of oxygen electroreduction. Experiments are performed with a platinum-coated probe in contact with CsHSO<sub>4</sub>. The Pt-based counter electrode, which covers the entire opposing area of the electrolyte, is effectively reversible and contributes negligible overpotential to the measurements. We discuss the experimental challenges associated with high impedance systems and mitigation strategies to extract meaningful information. We also present impedance spectra and cyclic voltammograms for Pt|CsHSO<sub>4</sub>.

1. R. O'Hayre, M. Lee, F. B. Prinz, *J Appl Phys* **95**(12), 8382-8392 (2004)
2. D. A. Bussian, J. R. O'Dea, H. Metiu, S. K. Buratto, *Nano Lett* **7**(2), 227-232 (2007)
3. D. A. Boysen, T. Uda, C. R. I. Chisholm, S. M. Haile, *Science* **303**, 68-70 (2004)
4. S. M. Haile, D. A. Boysen, C. R. I. Chisholm, R. B. Merle, *Nature* **410**, 910-913 (2001)
5. T. Uda and S. M. Haile, *Electrochem Solid State Lett* **8**(5), A245-A246 (2005)

9:20am **NS-ThM5 Unraveling Atomic Structures on CeO<sub>2</sub>(111) by Dynamic Force Microscopy**, *M. Reichling*, Universität Osnabrück, Germany **INVITED**

Cerium dioxide (ceria) is a material that is widely used for catalytic applications. It is, for instance, an essential part of the 3-way catalytic converter known from automotive technology and holds substantial promise in other diverse research areas like solid-fuel cell technology for the production of hydrogen. In this context, ceria acts as an oxygen buffer as well as promoting noble-metal catalytic activity. The capability for storing and releasing oxygen is believed to be the result of the rapid formation and elimination of oxygen vacancy defects. Therefore, defects at slightly and strongly reduced CeO<sub>2</sub>, specifically on the thermodynamically most stable (111) surfaces are of great interest as they may be the key to understanding surface chemistry on ceria.

To reveal and identify surface and sub-surface defects on CeO<sub>2</sub>(111), we apply dynamic scanning force microscopy (NC-AFM) providing highest resolution images of the surface structure and its irregularities. For the identification of defects, the detailed atomic structures of features found in experiments is related to predictions from DFT calculations on relevant surface defects. In this way, we are able to identify surface and sub-surface vacancies, surface hydroxide and Ce<sup>3+</sup> ions. Furthermore, we demonstrate that water readily adsorbs at the surface at room temperature but may diffuse and cluster on terraces as well as step edges. Individual water molecules can also be laterally manipulated by the tip of the force microscope with atomic precision.

10:40am **NS-ThM9 High-Resolution Atomic Force Microscopy in Three Dimensions**, *U.D. Schwarz, M.Z. Baykara, T.C. Schwendemann, B.J. Albers, N. Pilet, E.I. Altman*, Yale University

With the recent introduction of three-dimensional atomic force microscopy (3D-AFM), the recording of dense three-dimensional surface force and energy fields with atomic resolution have become possible for the first time [1]. The main obstacles for producing high-quality 3D force maps are long acquisition times that lead to data sets distorted by drift, and tip changes. Both problems are reduced but not eliminated by low-temperature operation.

As we will show, key for the successful realization of 3D-AFM is the application of novel data acquisition and analysis procedures. In particular, an image-by-image data acquisition scheme cuts measurement times by avoiding repeated recording of redundant information, while allowing post-acquisition drift correction. All steps are illustrated with measurements performed on highly oriented pyrolytic graphite in ultrahigh vacuum at a temperature of 6 K. The area covered spans several unit cells laterally and vertically from the attractive region to where no force could be measured. The resulting fine data mesh maps piconewton forces with 6.8 pm lateral and 2 pm vertical resolution. From this 3D data set, two-dimensional cuts along any plane can be plotted. Cuts in a plane parallel to the sample surface show atomic resolution, while cuts along the surface normal visualize how the attractive atomic force fields extend into vacuum. At the same time, maps of the tip-sample potential energy, the lateral tip-sample forces, as well as the energy dissipated during cantilever oscillation can be produced with identical resolution (pN resolution for forces, meV for energies, pm for x, y, and z). Room temperature operation might be possible due to the unique post-acquisition drift correction ability. Applications in the areas of chemical imaging, surface catalysis, nanotribology, thin film growth, and device fabrication are envisioned.

[1] B. J. Albers *et al.*, *Nature Nanotechnology* **4**, 307 (2009).

11:00am **NS-ThM10 Looking Deeper: Multifunctional Scanning Probe Microscopy**, *I. Riisness, R. Ramos, C. Carach, M. Gordon*, University of California Santa Barbara

Scanning probe microscopy (SPM) has truly revolutionized the morphological and electrical characterization of surfaces at the nanoscale; however, it is still impossible to identify and image the chemical functionality of a surface at similar resolutions. For the latter, one desires a hybrid probe system which combines traditional SPM functionality with spatially-correlated spectroscopic (chemical) data at length scales <10 nm.

To this end, we will highlight multifunctional surface imaging of chemistry, morphology, and elastic/electrical properties for several material systems using our hybrid SPM instrument. In this system, a plasmonically-active metallic tip is used to locally enhance EM fields in the tip-surface gap, enabling near-field chemical imaging via Raman spectroscopy. In this talk, we will discuss instrument design, tip preparation/characterization, and initial imaging results on polythiophene-based photovoltaic films, phase-segregated diblock co-polymers, and adsorbates on metallic nanoparticles.

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