Wednesday Afternoon, October 31, 2012

Scanning Probe Microscopy Focus Topic
Room: 16 - Session SP+AS+BI+ET+MI+TF-WeA

Emerging Instrument Formats
Moderator: A. Belu, Medtronic, Inc.

2:00pm SP+AS+BI+ET+MI+TF-WeA1 Electrochemical Strain Microscopy: Nanoscale Imaging of Solid State Ionics, *S. Jesse*, Oak Ridge National Laboratory **INVITED**
Electrochemical reactions in solids underpin multiple applications ranging from electroresistive non-volatile memory and neuromorphic logic devices memories, to chemical sensors and electrochemical gas pumps, to energy storage and conversion systems including metal-air batteries and fuel cells. Understanding the functionality in these systems requires probing reversible (oxygen reduction/evolution reaction) and irreversible (cathode degradation and activation, formation of conductive filaments) electrochemical processes. Traditionally, these effects are studied only on the macroscopically averaged level. In this talk, I summarize recent advances in probing and controlling these transformations locally on nanometer level using scanning probe microscopy. The localized tip concentrates an electric field in a nanometer scale volume of material, inducing local ion transport. Measured simultaneously, the electromechanical response (piezo response) or current (conductive AFM) provides the information on bias-induced changes in a material. Here, I illustrate how these methods can be extended to study local electrochemical transformations, including vacancy dynamics in oxides such as titanates, LaxSr1-xCoO3, BiFeO3, and YxZr1-xO2. The formation of electromechanical hysteresis loops indistinguishable from those in ferroelectric materials illustrate the role ionic dynamics can play in piezoresponse force microscopy and similar measurements. In materials such as lanthanum-strontium cobaltite, mapping both reversible vacancy motion and vacancy ordering and static deformation is possible, and can be corroborated by post mortem STEM/EELS studies. The possible strategies for elucidation ionic motion at the electroactive interfaces in oxides using high-resolution electron microscopy and combined ex-situ and in-situ STEM-SPM studies are discussed. Finally, the future possibilities for probing electrochemical phenomena on in-situ grown surfaces with atomic resolution are discussed. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

2:40pm SP+AS+BI+ET+MI+TF-WeA3 Probing Electrochemical Phenomena in Reactive Environments at High Temperature: *In Situ* **Characterization of Interfaces in Fuel Cells**, *S.S. Nonnenmann, R. Kungas, J.M. Vohs, D.A. Bonnell*, University of Pennsylvania
Many strategies for advances in energy related processes involve high temperatures and reactive environments. Fuel cell operation, chemical catalysis, and certain approaches to energy harvesting are examples. Scanning probe microscopy provides a large toolbox of local and often atomic resolution measurements of phenomena at a scale that enables understanding of complex processes involved in many systems. Inherent challenges exist, however, in applying these techniques to the realistic conditions under which these processes operate. To overcome some of these challenges, we have designed a system that allows SPM at temperatures to 850° C in reactive gas environments. This is demonstrated with the characterization of an operating fuel cell. Solid oxide fuel cells (SOFCs) offer the highest conversion efficiencies with operating temperatures ranging from 400° C - 1000° C; and operate under variable gaseous fuel environments – H_2-based environments (anode side) and O_2-based environments (cathode side). Topography and the temperature dependence of surface potential are compared to impedance. While not (yet) at atomic levels of spatial resolution, these probes are at the scale to examine local interface properties.

3:00pm SP+AS+BI+ET+MI+TF-WeA4 High-Resolution Scanning Local Capacitance Measurements, *M. Brukman*, University of Pennsylvania, *S. Nanayakkara*, National Renewable Energy Laboratory, *D.A. Bonnell*, University of Pennsylvania
Spatial variation of dielectric properties often dictates the behavior of devices ranging from field effect transistors to memory devices to organic electronics, yet dielectric properties are rarely characterized locally. We present methods of analyzing 2nd harmonic-based local capacitance measurements achieved through non-contact atomic force microscopy. Unlike contact-based methods, this technique preserves tip shape and allows the same probe to realize high-resolution topographic imaging and scanning surface potential imaging. We present an improved analysis of the electrical fields between tip and sample, yielding high sensitivity to the capacitance-induced frequency shift.

The techniques are applied to thin-film ceramics (SrTiO2 and HfO2), metals (Pt and Ti), and mixed-phase self-

assembled monolayers to illustrate application over all orders of dielectric constant. Conversion from frequency shift signal to dielectric constant κ is demonstrated, with sub-5 nm spatial resolution and dielectric constant resolution between 0.25 and 1.

4:00pm SP+AS+BI+ET+MI+TF-WeA7 Experimental Calibration of the Higher Flexural Modes of Microcantilever Sensors, *J.D. Parkin, G. Hähner*, University of St Andrews, UK
Microcantilevers are widely employed as probes not only in atomic force microscopy [1], but also as sensors for mass [2], surface stress [3], chemical identification [3], or in measuring viscoelastic properties of cells [4].

Use of the higher flexural modes of microcantilever sensors is an area of current interest due to their higher Q-factors and greater sensitivity to some of the properties probed [2]. A pre-requirement for their exploitation, however, is knowledge of their spring constants [5]. None of the existing cantilever calibration techniques can calibrate the higher flexural modes easily.

We present a method that allows for the determination of the spring constants of all flexural modes. A flow of gas from a microchannel interacts with the microcantilever causing a measurable shift in the resonance frequencies of all flexural modes [6]. The method is non-invasive and does not risk damage to the microcantilever. From the magnitude of the frequency shifts the spring constants can be determined with high accuracy and precision. Experimental data for the response of the first four flexural modes of microcantilever beams used in AFM with spring constants in the range of ~0.03-90 N/m will be presented.

The spring constants of the first mode determined using our method are compared to those obtained with the Sader method [7]. Finite element analysis computational fluid dynamics (CFD) simulations of the experimental setup are used to provide an insight into the interaction of the flow with the microcantilever.

References

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4:20pm SP+AS+BI+ET+MI+TF-WeA8 Atomic Imaging with Peak Force Tapping, *B. Pittenger, Y. Hu, C. Su, S.C. Minne*, Bruker AFM, *I. Armstrong*, Bruker Nano Surfaces Division
As its name implies, Atomic Force Microscopy (AFM) has long been used to acquire images at the atomic scale. However these images usually only show the lattice of atoms in the crystal and do not show individual atomic defects. In order to achieve atomic resolution, researchers have typically had to design their systems for the ultimate in noise performance, sacrificing ease of use, flexibility, and scan size. Recently we have demonstrated that, by using Peak Force Tapping, our large sample platforms (Dimension Icon, Dimension FastScan) are capable of obtaining atomic resolution imaging along with maps of the tip-sample interaction. Unlike standard TappingMode, or FM-AFM, Peak Force Tapping uses instantaneous force control, allowing the system to be insensitive to long range forces while maintaining piconewton level control of the force at the point in the tapping cycle that provides the highest resolution – the peak force. Since the modulation frequency is far from resonance, the technique is less sensitive to the cantilever thermal noise (Brownian motion). In addition to topography, this technique can provide maps of the interaction between the tip and the sample. This is possible since Peak Force Tapping has access to the instantaneous force between tip and sample at any point in the modulation cycle. To study the details of a tip-sample interaction, Atomic Peak Force Capture can acquire the entire force distance curve used to create the interaction maps. These curves can be exported for easy analysis with models of tip-sample interaction. In this talk we will discuss the latest atomic resolution results using Peak Force Tapping and the

implications of this with regard to studies of dissolution, crystallization, ordered liquids, and corrosion.

4:40pm SP+AS+BI+ET+MI+TF-WeA9 Nanoscale Chemical Composition Mapping with AFM-based Infrared Spectroscopy, *C.B. Prater, M. Lo, Q. Hu,* Anasys Instruments, *C. Marcott,* Light Light Solutions, *B. Chase,* University of Delaware, *R. Shetty, K. Kjoller,* **E. Dillon**, Anasys Instruments **INVITED**
The ability to identify material under an AFM tip has been identified as one of the "Holy Grails" of probe microscopy. While AFM can measure mechanical, electrical, magnetic and thermal properties of materials, until recently it has lacked the robust ability to chemically characterize unknown materials. Infrared spectroscopy can characterize and identify materials via vibrational resonances of chemical bonds and is a very widely used analytical technique. We have successfully integrated AFM with IR spectroscopy (AFM-IR) to obtain high quality infrared absorption spectra at arbitrary points in an AFM image, thus providing nanoscale chemical characterization on the sub-100 nm length scale. Employing the AFM-IR technique, we have mapped nanoscale chemical, structural and mechanical variations in multilayer thin films, nanocomposites, polymer blends, organic photovoltaics, and biological materials including hair, skin, and bacterial and mammalian cells. Light from a pulsed infrared laser is directed at a sample, causing rapid thermal expansion of the sample surface at absorbing wavelengths. The rapid thermal expansion creates an impulse force at the tip, resulting in resonant oscillations of the AFM cantilever. The amplitude of the cantilever oscillation is directly related to the infrared absorption properties of the samples, enabling measurements of IR absorption spectra far below the conventional diffraction limit. AFM-IR can be used both to obtain point spectra at arbitrary points and to spatially map IR absorption at selected wavelengths. Simultaneous measurement of the cantilever's contact resonance frequency as excited by the IR absorption provides a complimentary measurement of relative mechanical properties. We have used these techniques to chemically identify individual chemical components in polymer nanocomposites and multilayer films and performed subcellular spectroscopy and chemical imaging on biological cells. Using self-heating probes we have been able to locally modify the state of a semicrystalline polymer and observe the resulting change in absorption spectra on the nanoscale. Using polarization sensitive AFM-IR, we have mapped spatial variations in molecular orientation in electrospun fibers.

5:20pm SP+AS+BI+ET+MI+TF-WeA11 Quantifying Nanomechanical Properties with Simultaneous AM-FM and tanδ Imaging, *T. Mehr, A. Moshar, R. Proksch, I. Revenko, N. Geisse, S. Hohlbauch, D. Walters, J. Cleveland, J. Bemis, C. Callahan, D. Beck*, Asylum Research
Frequency-Modulated (FM) is a powerful, quantitative technique for mapping interaction forces between an oscillating tip and sample. Since FM-AFM typically requires the use of three feedback loops, one ongoing challenge has been stable and cross-talk free operation. Amplitude-modulated Atomic Force Microscopy (AM-AFM), also known as tapping mode, is a proven, reliable and gentle imaging method with wide spread applications. Recently, the phase signal of the first resonant mode has been recast in terms of the tip-sample loss tangent.[1] This allows quantitative imaging of a response term that includes both the dissipated and stored energy of the tip sample interaction. Combining AM and FM imaging allows reaping the benefits of both techniques.[2] Because the feedback loops are decoupled, operation is more robust and simple than conventional FM imaging. In this mode, the topographic feedback is based on the AM signal of the first cantilever resonance while the second resonance drive is frequency modulated. The FM image returns a quantitative value of the frequency shift that in turn depends on the sample stiffness and can be applied to a variety of physical models. We will present results on a wide variety of materials as well as discussing quantitative separation of the elastic and dissipative components of the tip-sample interactions.[3]

References

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5:40pm SP+AS+BI+ET+MI+TF-WeA12 Simultaneous Scanning Tunneling and Atomic Force Microscopy with Subatomic Spatial Resolution, *FJ. Giessibl*, University of Regensburg, Germany
Frequency-modulation AFM can be combined with scanning tunneling microscopy, yielding a simultaneous data set for current and average force gradient. Ternes et al. [1] have shown that for some metallic contacts, force

and current are proportional. The interaction of a tungsten tip with a CO molecule adsorbed on Cu(111), however, yields a much different symmetry and distance dependence of tunneling current and force [2]. The tunneling current yields a gaussian dip over the CO molecule, while the forces show a strong angular dependence with force fields that vary strongly by distance and angle within the extent of the single front atom, displaying subatomic variations. While the simultaneous acquisition of current and force can reveal new information about the atomic and electronic structure of matter, the tunneling current can modify the atomic forces. This "phantom force" [3,4], a modification of the electrostatic attraction between tip and sample, originates in an alteration of the effective potential difference between tip and sample caused by strongly localized voltage drop induced by the tunneling current. The talk discusses the potential of combined STM/AFM as well as the challenges, in particular with respect to tip preparation and characterization.

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