Tuesday Morning, October 16, 2007

Nanometer-scale Science and Technology

Room: 616 - Session NS-TuM

Imaging of Nanostructures

Moderator: N.P. Economou, Carl Zeiss SMT, S. Hasegawa, University of Tokyo, Japan

8:00am **NS-TuM1 Atomic-Scale Studies of Complex Oxide Interfaces Using Aberration-Corrected Z-Contrast Imaging and EELS**, ***R.F. Klie***, *G. Yang*, University of Illinois - Chicago **INVITED**

Interfaces in complex oxide materials have been an enduring theme in materials physics, where the interplay of the reduced dimensionality, proximity effects, as well as surface relaxation, reconstruction and segregation creates interfacial states that are distinct from their bulk counterparts. It has long been recognized that the perovskite oxides provide a unique opportunity to bring materials with diverse and even mutually exclusive properties into intimate contact, thereby creating interfaces with excellent structural and chemical compatibility that potentially can be implemented in novel electronic devices. In recent years, novel techniques have been developed in analytical scanning transmission electron microscopy (STEM) that can be used to directly study the atomic-scale structure-property relationships of interfaces in complex oxides, both at room and LN_2 temperature. In particular, by using aberration-corrected Z-contrast imaging and electron energy-loss spectroscopy (EELS), the structure, composition and bonding can all be characterized directly with a spatial and energy resolution that cannot be achieved by any other technique. Here, we will demonstrate that the combination of aberration-corrected Z-contrast imaging and EELS can be used to analyze a wide range of properties in complex oxide materials, such as CMRs, high-k dielectrics and high-temperature superconductors. In particular, I will concentrate on my recent discovery of the cooperative doping-effect in the high-T_c superconductor $YBa_2Cu_3O_{7-x}$ (YBCO), where the presence of grain boundaries causes a significant reduction in the critical current density (J_c). I will explain the atomic-level origin of the improved J_c across grain boundaries in Ca-doping YBCO, and propose a number of potential dopants to further improve the materials properties.[1] Further, I will discuss the effects of oxygen vacancy segregation on the dielectric property of ultra-thin $SrTiO_3$ on GaAs(001)[2] and conclude with our recent discovery that the Co-ion spin-state in Co-based perovskite oxides can be directly measured by EELS.

[1] Klie, R.F., J.P. Buban, M. Varela, A. Franceschetti, C. Jooss, Y. Zhu, N.D. Browning, S.T. Pantelides, and S.J. Pennycook, Nature, 2005. 435(7041): p. 475-478.
[2] Klie, R.F., Y. Zhu, E.I. Altman, and Y. Liang, Applied Physics Letters, 2005. 87(14).

8:40am **NS-TuM3 In-situ Observation of Active Electronic Devices using Electrically Biased TEM Holder**, ***D.S. Ko***, *S.D. Kim*, Seoul National University, Republic of Korea, *X.S. Li, K.S. Park, Y.K. Kim*, Samsung Advanced Institute of Technology, Republic of Korea, *C.G. Park*, National Center for Nanomaterials and Technology, Republic of Korea, *Y.W. Kim*, Seoul National University, Republic of Korea

In-situ transmission electron microscopy (TEM) became one of the major fields in physics and materials science as the advanced technologies were adopted to observe real-time changes of microstructures in a confined space of TEM.[1,2,3] We developed an in-situ TEM holder to investigate the live operation of electronic devices and we present step-by-step manufacturing procedures of nano-manipulator-electrical signal holder applied to investigate the transport of matters in Light Emitting Diode (LED) and Phase-changing Random Access Memory (PRAM). The TEM sample of active electron device was prepared by focused ion beam followed by plasma etching as reported earlier[4] to remove the Ga-contamination at the surface. The removal of surface layer with Ga was essential to remove a leakage path of current. As-FIB-prepared LED sample showed illumination only after the plasma etching process. In order to make electrical contact to the samples of electronically active device, tungsten tip was fabricated using electro-chemical polishing technique in 10% NaOH. The tip fabricated was small enough to locate the contact pad with 30-40 nm in apex diameter. The apex radius of commercially available tungsten tip was too big for probing to make electrical contact to the target device. Tungsten probe was mounted on the 4-mm diameter, quadrant piezo tube, which was linked to micrometer for the coarse movement. In-situ observation of intermixing and materials transport in commercially available GaN LED and phase-changing of calcogenide material in PRAM device, is investigated and the recorded.

[1] C.M. Grimaud and O. Lourie, In Situ Electrical Probing by TEM-STM: instrumentation and applications for nanocharacterization, Microsc. Microanal. 10(suppl 2), 1112 (2004)
[2] T. Kizuka et al, Metal-Insulator Transition in Stable One-Dimensional Arrangements of Single gold Atoms, Jpn. J. Appl. Phys. 40 L170 (2001)
[3] D. Golberg, et al, In situ electrical probing and bias-mediated manipulation of dielectric nanotubes in a high-resolution transmission electron microscope, Appl. Phys. Lett. 88 123101 (2006)
[4] D.S. Ko, et al, Effective removal of Ga residue from focused ion beam using a plasma cleaner, Ultramicroscopy 107, 368 (2007).

9:00am **NS-TuM4 Measuring Atomic Size Objects on Electrically Insulating Surfaces in Ultrahigh Vacuum**, ***S.C. Fain***, *N. Ruzycki, J. Morales, T.C. Lovejoy, E.N. Yitamben, M.A. Olmstead, F.S. Ohuchi*, University of Washington

Frequency modulation non-contact atomic force microscopy (ncAFM) provides a way to measure atomic size objects on electrically insulating surfaces in ultrahigh vacuum. Computer simulations indicate that the apparent height of clusters one atomic layer high is much less than the actual height when the lateral extent of the cluster is much less than the tip radius.[1] For example the apparent height of a 1.4 nm diameter, one-atomic-layer-high cluster of 19 atoms on a flat surface is expected to be 12% of its actual height when imaged by a typical probe tip of 20 nm radius. The apparent height of the cluster is predicted to be much closer to the real height as the cluster height increases. We have performed measurements on semiconducting surfaces with various cluster sizes by both ncAFM and scanning tunneling microscopy (STM) using various probe tips. Evidence in qualitative agreement with the computer simulations has been obtained for clusters on a surface with Cr co-deposited with Ga_2Se_3 on Si(100):(2x1)As. We acknowledge support from NSF NER-0508216, NSF DMR-0605601, and an IGERT Traineeship to TCL from NSF and NCI grant DGE-0504573.

[1] S. C. Fain, Jr., C. A. Polwarth, S. L. Tait, C. T. Campbell, and R. H. French, Nanotechnology 17, S121-127 (2006).

9:20am **NS-TuM5 Ambient Dynamic Mode AFM Non-contact Operating Regime Determination**, ***C.C. Wang***, *B. Liu, B. Leung, Y. Uritsky*, Applied Materials Inc.

Dynamic mode AFM, which uses a cantilever vibrating near its natural mechanical frequency, is the most popular AFM imaging method in the ambient. As AFM tip approaches the sample, it enters the non-contact regime first due to attractive force interactions and, as tip continues to descend, it starts to contact surface intermittently.[1] During tip descend, the vibration amplitude continuous to decrease. Therefore, using a feedback loop that maintains a constant amplitude set-point during AFM imaging, the AFM can be operated in either non-contact mode or intermittent contact mode and the set-point of former is higher than that of the latter. Non-contact mode is desirable, because it affords higher spatial resolution and longer tip life.[2] Hence, accurate determination of the non-contact amplitude operating range is needed. A unique characteristic of phase signal of cantilever is that, in non-contact regime, phase changes monotonically with tip-to-sample distance, but as soon as tip makes intermittent contact with sample, the phase signal abrupt jumps in the other direction.[1] Therefore, non-contact regime can be determined by approaching tip to surface in open-loop condition, monitoring the amplitude and phase signals at the same time and determining the amplitude corresponding to phase reversal point. However, this popular method causes tip and sample damage and inaccurate non-contact regime determination. A new method is reported here. In this method, the tip approach is stopped at the start of non-contact interaction regime and the feedback loop is turned on; the tip descend is then resumed by lowering the amplitude set-point continuously and at the same time monitoring the phase signal; as soon as the phase signal makes a sudden discontinuous reversal, the intermittent contact mode is reached. By recording the amplitude set-point at the onset of intermittent contact, the non-contact regime can be determined more precisely. It is shown that this range depends on tip material, sample material and the cantilever initial vibration amplitude. Therefore, this method can be used to image sample surface properties and to optimize non-contact operating parameters.

[1] R. Garcia and A. S. Paulo, Phys. Rev. B 60, 4961 (1999)
[2] C. Wang et al., Proceedings: the 2005 International Conference on Characterization and Metrology for ULSI Technology, 194 (2005).

9:40am **NS-TuM6 Atomic Resolution AFM with a Purely Electrical QPlus Sensor**, ***B. Uder***, *M. Maier, A. Bettac, A. Feltz*, Omicron NanoTechnology, Germany

In contrast to conventional optical detection AFM, self-sensing or purely electrical detection schemes have not yet been established as reliable and routine techniques for atomic resolution under UHV conditions. The QPlus sensor however, has successfully been used for LT STM with 5 K operation and is now intruduced for variable temperature operation with the VT STM. The QPlus sensor employs a quartz tuning fork for force detection in non-

contact AFM operation mode. One prong of the tuning fork is fixed while the SPM probe tip is mounted to the second prong. It thus acts as a quartz lever transforming it's oscillation into an electrical signal as a result of the piezo-electric effect. The feedback signal is based on frequency shift originating from tip-sample force interaction. A dedicated pre-amplification technique ensures distance control based on the vibrational signal. The main motivation for the QPlus sensor is to improve AFM resolution for short range forces by the high spring constant of the sensor (approx. 1800 N/m, cantilever typ. a few ten N/m) and small oscillation amplitudes in the range of 1nm or below (cantilever typ. 10 nm), which more precisely match the range of the involved (chemical) forces. Optimal image performance was achieved using conventionally wet-chemically etched tungsten tips, glued onto the tuning fork. This allows for highest performance in simultaneous or alternative STM/STS operation. Measurements on Si(111) 7x7 show that tunnelling current and vibrational signal are clearly separated. In addition, benchmark measurements on NaCl with a typical corrugation of approx. 10pm prove that resolution on insulation samples is competitive to best cantilever based AFM results.

10:40am **NS-TuM9 Imaging Performance Variations in Organic Solar Cells with Time-Resolved Electrostatic Force Microscopy and Photocurrent-sensitive Atomic Force Microscopy**, ***D.S. Ginger***, University of Washington **INVITED**

We study organic/organic and organic/inorganic interfaces in polymer solar cells using time-resolved Electrostatic Force Microscopy (trEFM), and photoconductive Atomic Force Microscopy (pcAFM). These techniques allow us to measure charge generation, collection, and trapping with sub-100 nm resolution so we can correlate variations in performance directly with variations in local film morphology. This talk will describe our trEFM and pcAFM studies of polymer/polymer and polymer/fullerene solar cells. In model blends of polyfluorenes we present surprising evidence that the majority of the collected photocurrent arises away from the visible domain interfaces. In polymer/fullerene cells we show that even the best devices exhibit a distribution of local quantum efficiencies and fill factors that vary on two characteristic length scales. First, we observe performance variations over tens of nanometers that we associate with vertical connectivity of the fullerene domains. Second, in these same devices we observe performance variations over several hundred nanometer length scales (much larger than the characteristic polymer or fullerene domain sizes). We explore the possibility that these larger-scale performance variations are associated with the interface between the polymer blend and the underlying indium tin oxide contact.

11:20am **NS-TuM11 Investigation of Charge Trapping in GaN Films using Scanning Kelvin Probe Microscopy and Conductive Atomic Force Microscopy**, *J.C. Moore, M.A. Reshchikov, J. Xie, H. Morkoc,* ***A.A. Baski***, Virginia Commonwealth University

A new combination of conducting atomic force microscopy (CAFM) and scanning Kelvin probe microscopy (SKPM) was used to study localized charge trapping for MBE-grown GaN films. Charge was injected into the near-surface region of a GaN film by scanning local regions using CAFM with a reverse bias applied to the sample. Time-resolved local surface potential measurements were then obtained using SKPM after charge injection, where an induced band bending caused by charging of surface/interface states was observed. In dark environments and for applied CAFM biases greater than 10 V, the density of charged states ($2x10^{12}$ cm^{-2}) doubled immediately after scanning as compared to unscanned regions. This increase in charged states resulted in an increase of surface band bending of ~3 eV that dissipated quasi-exponentially with time. Induced band bending greater than 0.5 eV was still observed up to 4 hr after charge injection, indicating that charge trapping is relatively stable in a dark environment. Initial values for band bending depend on the applied CAFM bias during injection, where nominal band bending (<0.5 eV) occurs for biases less than 8 V and a saturation value of ~3 eV occurs at biases greater than 10 V. A phenomenological model was used to model the CAFM charge injection via a tunneling mechanism, where electrons travel from the tip through a thin surface gallium oxide barrier and become trapped at the oxide/GaN interface. Saturation occurs due to the existence of a finite density of chargeable interface states. After charging occurs via CAFM, the decrease in induced band bending with time was found to be consistent with a thermionic model of charge transfer from the interface to the bulk. As expected, charged interface states could be rapidly neutralized (<1 s) via photovoltage caused by illumination with UV light. Funding provided by NSF and AFOSR.

11:40am **NS-TuM12 Sinc or Sine? The Band Excitation Method and Energy Dissipation Measurements by SPM**, ***S. Jesse***, *S.V. Kalinin*, Oak Ridge National Laboratory

Mapping energy transformation pathways and energy dissipation on the nanometer scale and understanding the role of local structure on dissipative behavior is a grand challenge for nanoscale imaging in areas ranging from electronics and information technologies to efficient energy production and use. To date, dissipation measurements are invariably based on either phase and amplitude detection in constant frequency mode, or as amplitude detection in frequency-tracking mode. Sampling of a single frequency in the Fourier domain of the system allows only two out of three parameters (amplitude, resonance, and Q) to be determined independently. The analysis in both cases implicitly assumes that amplitude is inversely proportional to the Q-factor and is not applicable when the driving force is position dependent, as is the case for virtually all SPM measurements. Here, we developed and implemented a new approach for SPM detection based on the excitation and detection of a signal having a finite amplitude over a selected region in the Fourier domain. The detected signal is Fourier transformed and fitted by appropriate model. This data acquisition scheme substitutes standard lock-in or PLL detection. This band excitation (BE) SPM allows very rapid acquisition of the full frequency response at each point in an image and in particular enables the direct measurement of energy dissipation through the determination of the Q-factor of the cantilever-sample system. This band excitation method allows acquisition of the local spectral response at a ~10ms/pixel rate, compatible with fast imaging. We demonstrate this technique with electromechanical imaging, the investigation of dissipative defects in magnetic force microscopy, and force-distance spectroscopy. The BE method thus represents a new paradigm in SPM, beyond traditional single-frequency excitation and is applicable as an extension to many existing SPM techniques. Research was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

12:00pm **NS-TuM13 Electromechanical Imaging, Polarization Switching, and Intermittent-Contact PFM in a Liquid Environment**, ***B.J. Rodriguez***, *S. Jesse, A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Electromechanical activity is a universal feature of molecular and biological systems, ranging from piezoelectricity in calcified tissues to voltage-controlled ion channels and the functionality of cardiac miocytes and cells for auditory signal transduction. Here, we study the mechanisms of electromechanical imaging by Piezoresponse Force Microscopy (PFM) in liquid environments using model ferroelectric systems. The effects of the conductive properties of the liquid on the localization of the dc electric field are studied from the polarization patterns created by the voltage pulses applied to the tip. Under ambient conditions, the biased tip establishes a highly-localized electric field that decays rapidly with distance from the tip-surface junction, resulting in small, well-defined domains. For solvents with intermediate conductivities, the electric field is localized, but the characteristic length scale is significantly larger than the tip size and is mediated by pulse length via the mobile ion diffusion length. The switching in this case results in the formation of irregular fractal domains. In conductive solvents, the solution is uniformly biased, resulting in a homogeneous electric field across the film thickness and partial or complete uniform switching. Notably, high resolution imaging is possible even in polar solvents because of the high excitation frequencies, minimization of the diffusion paths, and high localization of the strain that transmit predominantly through the mechanical (rather than electrical) contact. The same screening effect in solution enables a mechanically modulated approach for intermittent-contact PFM in solution. In air, this mode is dominated by electrostatic forces, which are screened in solution, allowing the electromechanical signal to dominate. These results elucidate a strategy for high resolution imaging of electromechanical activity in biological and molecular systems in liquid environments.

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