Monday Morning, October 18, 2010

Nanometer-scale Science and Technology
Room: La Cienega - Session NS-MoM

Oxide Based Nanoelectronics
Moderator: C. Nakakura, Sandia National Laboratories

8:40am **NS-MoM2 Oxidation Kinetics of Electron Beam Evaporated Nano Copper Thin Films by Kelvin Probe Measurements**, ***A. Subrahmanyam***, IIT Madras, India

Copper is a very good interconnect in microelectronics because it has a high thermal and electrical conductivities and low electromigration resistance. However, the formation of an oxide layer on Cu (even at room temperature) induces trap states at the Cu/Cu oxide interface that can ultimately cause a decrease in its thermal and electrical conductivities, as well as a significant degradation in its interconnection capabilities. These effects become more and more critical when the copper is in nano form for use in ULSI. The partial oxides of copper can also be a very good candidate for plasmonic structures.

Copper exhibits two valences. The size effects and partial oxidation of copper bring significant changes in the electrical resistivity. Thus the surface oxidation kinetics of nano copper are important. In the present communication, pure copper thin films have been prepared by electron beam evaporation technique on cleaned glass substrates at 500 K. The thickness is varied in the range : 20 nm to 300 nm. The electrical resistivity of these films ranges from $5.201*10^{-6}\ \Omega$ cm to $9.206*10^{-6}\ \Omega$ cm. The carrier concentration and electron mobility have been evaluated by Hall measurements. In order to follow the surface oxidation kinetics of copper thin films with varying grain sizes exposed to the ambient at 300K, the contact potential (cpd) / work function measurements by Kelvin probe technique have been performed. The increase in the contact potential difference (cpd) indicates the oxidation kinetics of these films.

9:00am **NS-MoM3 Hot-wire Chemical Vapor Deposition of Tungsten Oxide Nanoparticles for Use in Energy Applications**, ***C.-P. Li***, *C.A. Wolden*, Colorado School of Mines, *R. Tenent, A.C. Dillon*, National Renewable Energy Laboratory

Crystalline tungsten oxide nanoparticles were synthesized by hot-wire chemical vapor deposition (HWCVD). These materials are being examined for use in numerous energy related applications including electrochromic windows and fuel cells. It is possible to tune the particle morphology by changing key synthesis parameters including filament temperature, substrate temperature, and oxygen partial pressure. The resulting nanostructures are characterized by a number of techniques including transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. The dependence of nanoparticle size and morphology will be described both as a function of HWCVD synthesis conditions as well as post-deposition annealing treatments. The resulting nanoparticles are suspended in solution and used to form thin films on transparent conducting oxide coated glass substrates using an ultrasonic spray deposition process. Ultrasonic spray coating is a cost effective, scalable deposition process that offers an excellent route to achieve large-scale implementation of electrochromic films. Important ultrasonic spray variables include substrate temperature, precursor concentration, carrier solvent and other parameters related to solution atomization. The electrochromic properties of these films were characterized by performing cyclic voltammetry in registry with *in situ* measurements of optical transmission. Particular attention is paid to optimizing performance metrics such as coloration efficiency and cycling stability. Using the measurements described above, we will evaluate the important process-structure-performance relationships in these systems.

9:20am **NS-MoM4 Monitoring Charge Storage Processes in Nanoscale Oxides using Electrochemical Scanning Probe Microscopy**, ***K.R. Zavadil***, *J. Huang, P. Lu*, Sandia National Laboratories

Advances in electrochemical energy storage science require the development of new or the refinement of existing *in situ* probes that can be used to establish structure – activity relationships for technologically relevant materials. The drive to develop reversible, high capacity electrodes from nanoscale building blocks creates an additional requirement for high spatial resolution probes to yield information of local structural, compositional, and electronic property changes as a function of the storage state of a material. In this paper, we describe a method for deconstructing a lithium ion battery positive electrode into its basic constituents of ion insertion host particles and a carbon current collector. This model system is then probed in an electrochemical environment using a combination of atomic force microscopy and tunneling spectroscopy to correlate local activity with morphological and electronic configurational changes. Cubic spinel $Li_{1+x}Mn_{2-x}O_4$ nanoparticles are grown on graphite surfaces using vacuum deposition methods. The structure and composition of these particles are determined using transmission electron microscopy and Auger microprobe analysis. The response of these particles to initial de-lithiation, along with subsequent electrochemical cycling, is tracked using scanning probe microscopy techniques in polar aprotic electrolytes (lithium hexafluorophosphate in ethylene carbonate:diethylcarbonate). The relationship between nanoparticle size and reversible ion insertion activity will be a specific focus of this paper.

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9:40am **NS-MoM5 Tuning Superconductivity at the $LaAlO_3/SrTiO_3$ Interface**, ***A.D. Caviglia***, *S. Gariglio, N. Reyren, C. Cancellieri, A. Fête*, University of Geneva, Switzerland, *M. Gabay*, University of Paris-Sud, France, *J.-M. Triscone*, University of Geneva, Switzerland **INVITED**

Electronic states with unusual properties can be promoted at interfaces between complex oxides [1]. A striking example is the interface between the band insulators $LaAlO_3$ and $SrTiO_3$, which displays conductivity with high mobility and 2D superconductivity [2,3]. We will discuss recent experiments that revealed the sensitivity of the normal and superconducting state to external electric fields. Using the electrostatic field effect, the phase diagram of the system has been mapped out, revealing a quantum phase transition between a superconducting state and an insulating state [4]. We will also lay out an example of an electronic property arising from the interfacial breaking of inversion symmetry, namely a large spin-orbit interaction, whose magnitude can be modulated by the application of an external electric field [5].

[1] E. Dagotto, *Science* **318**, 1076 (2007)

[2] A. Ohtomo, H. Y. Hwang *Nature* **427**, 423 (2004)

[3] N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M Gabay, D. A. Muller, J.-M Triscone, J Mannhart *Science* **317**, 1196 (2007).

[4] A. D. Caviglia, S. Gariglio, N. Reyren, D. Jaccard, T. Schneider, M Gabay, S. Thiel, G. Hammerl, J. Mannhart, J.-M Triscone *Nature* **456**, 624 (2008).

[5] A. D. Caviglia, M Gabay, S. Gariglio, N. Reyren, C. Cancellieri, J.-M Triscone *Phys. Rev. Lett.* **104**, 126803 (2010).

10:40am **NS-MoM8 Fabrication and Characterization of Ferroelectric $BiFeO_3$ Nanocapacitors for Next Generation FeRAMS**, ***L.E. Ocola***, *S. Hong, R. Nath Premnath, W. Li*, Argonne National Laboratory, *S. Jackson*, Illinois Mathematics and Science Academy, *R. Katiyar*, University of Puerto Rico, *O.H. Auciello*, Argonne National Laboratory

11:00am **NS-MoM9 Polarization-Dependent Electron Transport in Thin Films of Uni- and Multiaxial Ferroelectrics**, ***P. Maksymovych***, Oak Ridge National Laboratory, *J. Seidel*, University of California, Berkeley, *S. Jesse*, Oak Ridge National Laboratory, *P. Yu, Y.-H. Chu*, University of California, Berkeley, *A.P. Baddorf*, Oak Ridge National Laboratory, *R. Ramesh*, University of California, Berkeley, *S.V. Kalinin*, Oak Ridge National Laboratory

The intrinsic coupling of soft-phonon order parameters and electron transport in ferroic materials can usher a wide range of novel physical phenomena with potential for new applications in information technology, energy harvesting and quantum computing. In this talk we will present local conductivity and piezoresposne measurements on the surfaces of uniaxial ($Pb(Zr_{0.2}Ti_{0.8})O_3$) and multiaxial ($BiFeO_3$) perovskite ferroelectrics, with film thicknesses ranging from 30 nm to 100 nm. Conductive atomic force microscopy revealed that most of these films possesses highly non-linear, and often hysteretic current-voltage characteristics, and in many cases the hystereses could be correlated to local polarization switching induced by the electric field of the AFM tip. In lead zirconate titanate, the large spontaneous polarization produced up to 500-fold enhancement of local conductivity, and the film remained sufficiently conducting in the bias-region significantly smaller than the switching voltage. As a result, this effect can be used for a non-destructive and resistive read-out of the polarization state on length-scales down to 10 nm, implementing a prototypical memory function. Extending the I-V measurements to low-temperatures revealed a strong exponential dependence of the conductivity.

We developed a novel analysis scheme, which enabled identifying trap-assisted Fowler-Nordheim tunneling and Poole-Frenkel hopping as two dominant mechanisms behind non-linear I-V curves. Curiously, we have been able to separate the contributions due to interface- and bulk-limited conduction, as well as to visualize spatially-resolved variations due to each transport regime.

We will further discuss the peculiarities of local electron transport through $BiFeO_3$, and in particular the mechanism behind local conductivity of 109^o ferroelastic domain walls. Based on a statistical analysis of I-V curves and simultaneous measurements of local transport and piezoresponse, we suggest that the domain wall is not a static conducting object under a biased tip, but instead that a transient, local and microscopically reversible topological distortion of polarization structure at the wall contributes to enhanced electron transport. In particular, it produces a seminal example of ferroic memristive functionality.

The measurements were conducted at the Center for Nanophase Materials Sciences sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. DOE.

[1] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, S. V. Kalinin,

Science 324 (2009) 1421.

[2] P. Maksymovych, J. Seidel et. al, submitted (2010)

11:20am **NS-MoM10 Observation of Unintentionally Incorporated Nitrogen Complexes in Vapor-Liquid-Solid Grown ZnO and GaN Nanowires**, *A. Soudi, **Y. Gu***, Washington State University

Semiconductor nanowires have been intensively explored as building blocks for the next-generation electronic and opto-electronic devices. Further advances towards real-world applications require a reliable and precise control of material properties, which, to a large extent, are determined by impurities. Controlled incorporation of functional impurities enables an impurity-engineering approach, whereby novel material properties can be engineered based on the interactions between impurities and the one-dimensional material host. On the other hand, unintentional impurity incorporation can be significant in determining nanowire electronic properties. Therefore, efforts towards identifying impurity species, especially those incorporated unintentionally, as well as understanding their microscopic structures and effects on material properties, are critical to advancing nanowire-based device technologies.

To this end, Raman scattering spectroscopy provides an effective approach to probing impurity incorporation in various materials. When complemented by mass spectrometry studies, this technique can enable unambiguous identifications of impurity species by their vibrational frequencies (i.e. impurity vibrational modes). As impurity vibrational characteristics are sensitive to the surrounding environment, the lattice locations of these impurity atoms can also be determined. Furthermore, the nanoscale spatial resolution of Raman scattering spectroscopy can provide insightful information on the possible routes of impurity incorporation, shedding light on the relationship between nanowire synthesis conditions and material properties.

In this work, using Raman scattering spectroscopy complemented by mass-selected time-of-flight particle emission techniques, we show the presence of unintentionally incorporated nitrogen complexes (most likely interstitial nitrogen molecules) in ZnO and GaN nanowires grown via the vapor-liquid-solid (VLS) process. Spatially resolved Raman scattering spectra obtained at various locations on single nanowires suggest a possible route of nitrogen incorporations via metal nanocatalysts during the growth. As nitrogen impurities have profound effects on electronic properties of ZnO and GaN, these results have significant implications for current efforts on realizing high-performance opto-electronic device applications based on these nanomaterials. In addition, with the VLS process as one of the most common growth modes for synthesizing semiconductor nanowires, these experimental findings might be relevant for many nanowire systems, signifying the necessity of more studies on unintentional impurity incorporation in these nanomaterials.

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