

Monday Afternoon, October 29, 2012

Graphene and Related Materials Focus Topic
Room: 13 - Session GR+EM+ET+NS+TF-MoA

Electronic Properties and Charge Transport
Moderator: T.W. Michely, Universität zu Köln, Germany

2:00pm **GR+EM+ET+NS+TF-MoA1 Influence of Substrate Offcut on Electrical and Morphological Properties of Epitaxial Graphene, R.L. Myers-Ward, V.D. Wheeler, L.O. Nyakiti, T.J. Anderson, F.J. Bezares, J.D. Caldwell, A. Nath, N. Nepal, C.R. Eddy, Jr., D.K. Gaskill, U.S. Naval Research Laboratory**

The promise of graphene-based device technologies is critically dependent on uniform wafer-scale graphene films and is most directly met through epitaxial graphene (EG) growth on silicon carbide (SiC) substrates. An essential parameter which influences this uniformity is the substrate offcut, as any deviation will result in a local change in the terrace width, impacting the growth rate and step-bunched heights observed after EG formation. For nominally on-axis SiC substrates, typical offcuts can range from $\sim 0^\circ$ to $\sim 1^\circ$ off-axis toward the [11-20] direction. Offcuts approaching 0° produce wide terraces with short step-bunched heights which offers the possibility of reduced anisotropy of transport properties [M. Yakes, et al., Nano Lett. **10**(5), 1559 (2010)] and improved EG layer uniformity. Thus, it is of interest to understand the influence of substrate offcut on carrier mobility, surface morphology, step heights, and graphene growth rate. This study investigates EG grown on a unique single 3-inch substrate possessing a large variation in offcut, from $+0.1$ to -1° toward the [11-20] direction, enhancing the information obtained on offcut influence while eliminating other substrate influences. X-ray diffraction rocking curve and peak position maps of the (0012) reflection were performed prior to growth to evaluate the crystalline quality and local offcut, respectively. Electron mobilities of EG films were determined by van der Pauw Hall measurements. Surface morphology of the EG was investigated with scanning electron microscopy, while the step heights and terrace widths were measured using atomic force microscopy.

For a given set of conditions (1620°C for 30 min in 10 slm Ar), the EG morphology is dominated by straight steps that become wavy in character as the offcut decreases to zero degrees. Close to zero degrees, the step direction rotates from [11-20] to the [1-100] direction and the steps become further distorted. The step bunch heights generally decreased (from 8 to 3 nm) as the offcut decreased and the terrace widths increased (from 0.3 to ~ 3 μm); however, for the latter, the trend is interrupted near zero degrees offcut. In addition to such morphological assessments, the impact of growth parameters, where the growth temperatures investigated were 1540, 1580 and 1620 °C and growth times were 15, 30 and 45 min, on the electrical and structural properties of EG grown on this unique substrate will be reported. For example, samples grown at 1540 °C for 30 min on witness substrates with offcuts ranging from ~ 0.4 to 0.9° had large area mobilities ranging from 780 to 1100 cm^2/Vs , where larger offcuts led to lower mobilities.

2:20pm **GR+EM+ET+NS+TF-MoA2 Direct Determination of Dominant Scatterer in Graphene on SiO₂, J. Katoch, D. Le, T.S. Rahman, M. Ishigami, University of Central Florida**

Freely suspended graphene sheets display high-field effect mobility, reaching 2×10^5 cm^2/V s. Yet, suspended graphene sheets are fragile and impractical for most experiments and applications. Graphene sheets on SiO₂ are easier to handle but possess low-carrier mobilities, which can vary by an order of magnitude from sample to sample. Poor and unpredictable transport properties reduce the utility of SiO₂-bound graphene sheets for both fundamental and applied sciences. Therefore, understanding the impact of substrates is crucial for graphene science and technology.

We have measured the impact of atomic hydrogen with kinetic energy less than 250 meV on the transport property of graphene sheets as a function of hydrogen coverage and initial, pre-hydrogenation field-effect mobility. The saturation coverages for different devices are found to be proportional to their initial mobility, indicating that the number of native scatterers is proportional to the saturation coverage of hydrogen. In order to understand this correlation between the field effect mobility and the apparent affinity of atomic hydrogen to graphene, we have performed a detailed temperature programmed desorption study on hydrogen-dosed graphene sheets. Atomic hydrogen is found to physisorb on graphene with activation energy for desorption of 60 ± 10 meV, consistent with our theoretical calculations. The associated charge transfer expected for such small desorption energy indicates that atomic-scale defects and ripples are not responsible for

determining the mobility of graphene on SiO₂ and that charged impurities in substrates define the transport property of graphene on SiO₂.

1. J. Katoch, J.H. Chen, R. Tsuchikawa, C. W. Smith, E. R. Mucciolo, and M. Ishigami, Physical Review B Rapid Communications, **82**, 081417 (2010).

2:40pm **GR+EM+ET+NS+TF-MoA3 Tuning Electronic Properties of Graphene by Controlling its Environment, K.I. Bolotin, Vanderbilt University**
INVITED

Every atom of graphene, a monolayer of graphite, belongs to the surface. Therefore, the environment of graphene -- the substrate onto which graphene is deposited and any coating on top of graphene -- intimately affects the properties of graphene. In this talk, we demonstrate that both the mechanical and electrical properties of graphene can be tuned by varying its environment.

First, we discuss the dependence of electrical transport in graphene on the dielectric constant (k) of graphene's environment. For graphene in vacuum ($k=1$) we observe very strong electron-electron interactions leading to robust fractional quantum Hall effect at temperatures up to 15K. By suspending graphene in liquids, we explore the regime of dielectric constants between ~ 1.5 and ~ 30 . We observe the dependence of carrier scattering in graphene on k and demonstrate large values for room temperature mobility ($>60,000$ cm^2/Vs) in ion-free liquids with high k . We also explore the rich interplay between the motion of ions inside liquids and transport of electrons in graphene. We observe signatures due to streaming potentials and Coulomb drag between ions in the liquid and electrons in graphene.

We also briefly address the mechanical properties of graphene and their dependence on graphene's environment. We demonstrate that the built-in strain, the substrate adhesion force and even the thermal expansion coefficient of graphene depend on the substrate supporting graphene.

3:40pm **GR+EM+ET+NS+TF-MoA6 Study of Impurity-Induced Inelastic Scattering on Suspended Graphene by Scanning Confocal Micro-Raman Spectroscopy, L.W. Huang, C.S. Chang, Academia Sinica, Taiwan, Republic of China**

We utilized a polymer-based procedure to transfer the CVD-grown graphene onto a TEM copper grid. The heat treatment was performed on the graphene membrane in an argon/hydrogen (Ar/H₂) atmosphere at 400 °C. After the transfer and heat treatment, TEM images, acquired by an ultra-high-vacuum transmission electron microscopy (UHV-TEM), demonstrated areas with distinguishable impurity distribution on the suspended graphene membrane. These areal impurity distributions can also be mapped by the scanning Raman spectroscopy correspondingly, indicating the influence of impurity-induced inelastic scattering. The results of this experiment show that the intensity ratio of Raman spectra 2D band over G band (I_{2D}/I_G) is proportional to minus fourth power of the inelastic scattering rate.

4:00pm **GR+EM+ET+NS+TF-MoA7 The Adsorption of Molecules with Large Intrinsic Electrostatic Dipoles on Graphene, L. Kong, Univ. of Nebraska-Lincoln, G.J. Perez Medina, Univ. of Nebraska-Lincoln, Univ. of Puerto Rico, J. Colón Santana, Univ. of Nebraska-Lincoln, L. Rosa, Univ. of Nebraska-Lincoln, Univ. of Puerto Rico, L. Routaboul, P. Braunstein, Maître de conférences de l'Université de Strasbourg, France, B. Doudin, Institut de Physique et Chimie des Matériaux de Strasbourg, France, C.-M. Lee, J. Choi, Kyung Hee Univ., Korea, P.A. Dowben, Univ. of Nebraska-Lincoln**

Both gold and graphene are excellent conductors, and one might expect that both conductors would fully screen the photoemission and inverse photoemission final states of a molecular adsorbate, but in fact this is not the case. The comparison of the electronic structure of p-quinonoid zwitterionic type molecules with a large intrinsic dipole of 10 Debyes adsorbed on both gold and graphene on copper substrates, shows that the interaction between the adsorbate molecules and graphene is very weak, confirming that graphene is chemically inert. We find that the photoemission and inverse photoemission final states are well screened for p-quinonoid zwitterionic dipolar molecules on gold. This is not observed in the case of this quinonoid zwitterion adsorbed on graphene on copper. This weaker screening is evident in a larger highest occupied molecular orbital to lowest unoccupied molecular orbital gap for the molecules on graphene. The larger highest occupied molecular orbital to lowest unoccupied

molecular orbital gap for the molecules on graphene indicates that a much weaker screening on the photoemission and inverse photoemission final states for these dipolar molecules on graphene than that on gold. This work is reviewed in the context of other studies of molecular adsorption on graphene.

4:20pm **GR+EM+ET+NS+TF-MoA8 Growth of and Interactions in Epitaxial Graphene Layers**, *A. Bostwick*, Lawrence Berkeley National Laboratory, *A. Walter*, *Th. Seyller*, Lawrence Livermore National Laboratory, *K. Horn*, *E. Rotenberg*, Lawrence Berkeley National Laboratory

INVITED

The electronic properties of graphene has been investigated using angle-resolved photoemission spectroscopy at the MAESTRO* facility of the ALS** synchrotron in Berkeley, California. This laboratory is unique in its ability to grow sophisticated samples for *in situ* study using angle-resolved photoemission spectroscopy, and to subtly alter their properties by engineering their surfaces by chemical doping or thickness control. In this talk I will discuss the electronic properties of graphene, focusing on the role of dopants to control the charge density and as defects to disrupt the metallic conduction. By measuring the spectrum of “plasmaronic” quasiparticle excitations, we can demonstrate the scale-free nature of the Coulomb interaction in Dirac systems. Such effects are readily observed on quasi-free standing graphene samples doped with long-range scatterers. Doping with short-range scatterers, on the other hand, results in a loss of conduction which we interpret as a manifestation of strong (Anderson) localization.

*Microscopic and Electronic Structure Observatory

**Advanced Light Source

5:00pm **GR+EM+ET+NS+TF-MoA10 Squeezing of the Graphene Dirac Cone Observed by Scanning Tunneling Spectroscopy**, *J. Chae*, *S. Jung*, *Y. Zhao*, *N.B. Zhitenev*, *J.A. Stroscio*, Center for Nanoscale Science and Technology / NIST, *A. Young*, *C. Dean*, *L. Wang*, *Y. Gao*, *J.C. Hone*, *K.L. Shepard*, *P. Kim*, Columbia University

The single-particle spectrum of graphene is described by massless Dirac quasiparticles with a linear energy-momentum dispersion relation. In this talk I examine the effect of electron interactions on the graphene energy dispersion as a function of both excitation energy E away from the Fermi energy and density n . To analyze the dispersion, we measure the Landau levels (LLs) in graphene on a hexagonal boron nitride (hBN) insulator in low magnetic fields by scanning tunneling spectroscopy. The experiments were performed in a custom designed cryogenic scanning tunneling microscope system operating at 4 K with applied magnetic fields from 0 T to 8 T. The graphene devices were fabricated by the method detailed in Dean *et al.* [1]. The disorder in graphene on hBN is reduced in comparison with the previous measurements in graphene on SiO₂ [2] allowing us to observe the LLs in fields as low as 0.5 T. By fitting the LL energies obtained at constant density, we find that the energy dispersion remains linear, characterized by a momentum-independent renormalized velocity. However, the renormalized velocity is density dependent, showing a strong increase as the charge neutrality point is approached. The overall spectrum renormalization can be described as a *squeezing* of the Dirac cone angle due to electron-electron interactions at low densities. Interestingly, we also find that the renormalization of the dispersion velocity is affected by the local disorder potential and magnetic field, which is not described by current theory.

[1]. C. Dean, A. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, and J. Hone, *Nature Nanotech.* 5, 722–726 (2010).

[2]. S. Jung, G. M. Rutter, N. N. Klimov, D. B. Newell, I. Calizo, A. R. Hight-Walker, N. B. Zhitenev, and J. A. Stroscio, *Nature Phys.* 7, 245–251 (2011).

5:20pm **GR+EM+ET+NS+TF-MoA11 Interfacial Interaction of Graphene and Metal Surfaces Investigated by Resonant Inelastic X-ray Scattering**, *L. Zhang*, University of Science and Technology of China, Advanced Light Source, *J.H. Guo*, Advance Light Source, *J.F. Zhu*, University of Science and Technology of China

The synthesis of graphene on metal surfaces by chemical vapor deposition (CVD) is the most promising method to prepare single-layer and large-area graphene, which is a prerequisite for the fabrication of graphene-based electronic devices. Therefore, the graphene/metal interfaces have attracted much attention due to their importance in graphene synthesis by CVD processes. In this presentation, we report our recent studies on the electronic structure and band dispersion of graphene on different metal surfaces (Cu, Ir and Ni) by the means of X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS). The XAS spectra for graphene on metal surfaces show strong π^*

and σ^* resonant features, indicating that the single-layer graphene films preserve the intrinsic symmetry of graphite. The resonant XES spectra of graphene on different metal surfaces change dramatically, especially for the features of π^* resonances, which can be directly related to the different strength of hybridization between graphene and metal substrates. These significant spectra changes have been proved to be an effective measure for the bonding strength of graphene on different substrates: strong band dispersion can be observed when the interaction between graphene and metal substrate is weak (such as Cu), while the band dispersion is seriously disturbed when a strong hybridization between graphene and metal substrate (such as Ni) exists. These results provide basic understanding of graphene/metal interfacial interaction, which helps to develop graphene-based electronic devices with high performances.

Tuesday Afternoon, October 30, 2012

In Situ Microscopy and Spectroscopy Focus Topic

Room: 7 - Session IS+AS+BI+ET+GR+NS-TuA

In Situ Studies of Organic and Soft Materials and In Situ Microscopy

Moderator: K. Artyushkova, The University of New Mexico, J.A. Eastman, Argonne National Laboratory

2:00pm **IS+AS+BI+ET+GR+NS-TuA1 Micronutrient Detection and Quantification from Data Obtained from Plasma Pencil Atmospheric Mass Spectrometry, M.J. Stein, E. Lo, C. Waterton, D.G. Castner, B.D. Ratner, University of Washington**

The analysis of micronutrient quantities is one component in the strategy to reduce the global burden of malnutrition-related disease. Accessibility of the proper equipment and equipment complexity impede nutrient testing in the areas that might benefit most from these studies. In this work, we present an analysis of micronutrients in a physiological range from blood plasma using plasma pencil atmospheric mass spectrometry (PPAMS), a method for sampling a sample's surface at ambient temperature and pressure conditions. The effectiveness of our PPAMS system is demonstrated using characteristic and tandem mass spectra on raw nutrient controls. Key micronutrient peaks and fragmentation patterns are observed. Next, we analyze a sample matrix of micronutrients in porcine plasma in which the nutrient concentrations are varied. Principal component analysis (PCA) is then employed on the spectra. The resulting PCA scores showed that these nutrients are separable at different nutrient concentrations to 95% confidence. The loadings peaks are shown to contain several of the key peaks observed in the raw nutrient powders as principal separators. The PPAMS technique is compared to several traditional techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrospray ionization mass spectrometry (ESI-MS). Separation of the nutrients at concentrations relevant for human blood-based nutrient detection is possible in both ESI-MS and PPAMS. However, ToF-SIMS is found to require 5x to 1000x higher concentrations than PPAMS for folate, vitamin A, and iodine in order to achieve similar separation of the micronutrients. In addition to the qualitative information obtained from the PCA results, quantitative predictive values are obtained by the application of a Bayesian wavelet-based functional mixed model. Since the mass spectra are modeled as functions in this model, peak detection methods are not required and the final results utilized the full spectral response. The final predicted values are compared to the known concentration values and the mean standard error of prediction (MSEP) is calculated. The accuracy of the predictive model was found to be dependent on the ionization potential of the individual nutrients. Metallic-nutrients were hypothesized to be more sensitive to outside cationization effects than their larger organic counterparts. In addition to quantitation, the physical properties of the ionization process were explored. Using XPS and ellipsometry in conjunction with carefully timed exposures and concurrent fragment PCA, it is determined that the PPAMS ionization is a softer form of ionization than most vacuum-based techniques.

2:20pm **IS+AS+BI+ET+GR+NS-TuA2 In Situ Real Time Examination of the Thin Film Growth of Pentacene on Polymeric Dielectrics Using X-Ray Synchrotron Radiation: Unexpected Changes in the Evolution of Surface Morphology with Substrate, T.V. Desai, A.R. Woll, J.R. Engstrom, Cornell University**

We have examined the thin film growth of pentacene on SiO₂ and on three different polymeric dielectrics using *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy (AFM). The polymeric dielectrics investigated spanned the range from a low surface energy hydrophobic surface (polystyrene, PS), to a medium surface energy hydrophobic surface (polymethylmethacrylate, PMMA), to a high surface energy hydrophilic surface [poly(ethylene imine), PEI]. We have also compared these results to pentacene growth on clean SiO₂. On all surfaces, pentacene forms a polycrystalline thin film, whose structure is that of the previously identified "thin film" phase. From *in situ* real-time x-ray scattering, we find that pentacene exhibits layer-by-layer (LbL) growth on all surfaces investigated, but the extent of LbL growth is a strong function of the underlying substrate. This result is unexpected as the transition to more 3D-like growth occurs for thicknesses where the underlying substrate is effectively almost entirely covered by the growing pentacene thin film. Layer-by-layer growth is significantly more prolonged on PEI (up to ~6 MLs), followed by SiO₂ and PMMA (up to ~4 MLs) and finally PS (up to ~3 MLs). This trend is also seen in the variation of both the roughness and the in-plane feature sizes of ~10 ML thick films, where the films are the smoothest, and the

feature sizes are the largest for growth on PEI, whereas on PS, the films are roughest, and the feature sizes are the smallest. Concerning possible reasons for this behavior, we can exclude the effects of the structure of the crystalline thin film (they were the same in all cases), and the roughness of the polymeric dielectric (rms roughness differed by < 0.1 nm) as major contributing factors. Surface energy of the polymeric thin films, however, provided the best explanation for the observed behavior, suggesting that thermodynamic driving forces play an important role in the evolution of thin film structure. In terms of molecular scale phenomena, interlayer transport and step-edge crossing events may be influenced by the mobility of the near-surface polymeric layers in the underlying substrate, which can be quite different for the ultrathin PEI layers vs. the much thicker PMMA and PS thin films.

2:40pm **IS+AS+BI+ET+GR+NS-TuA3 In Situ, Real-Time Diagnostics of Colon Cancer and Inflammatory Bowel Diseases by Direct Combination of Endoscopy and Rapid Evaporative Ionization Mass Spectrometry, Z. Takats, Imperial College, UK, L.A. Sasi-Szabo, University of Debrecen, Hungary, J. Kinross, Imperial College, UK, J. Balog, Medimass Ltd., L. Muirhead, K.C. Schafer, C. Guallar-Hoyas, Imperial College, UK**

INVITED

Rapid identification of biological tissues is a long-standing problem on various fields of interventional medicine, with special regard to cancer diagnostics and cancer surgery. While histological techniques provide the ultimate solution for the cellular-level identification of cancer cells, the approach is extremely complex and time consuming. Nevertheless, accelerated version of histopathology (so-called 'frozen section' method) is widely used for the intraoperative characterization of tissue samples removed from the surgical area. Since frozen section histology is less reliable than the traditional approaches, and the accelerated procedure still takes approx. 30 minutes for a single sample, there has been ongoing research for the development of more accurate and faster methods.

Molecular spectroscopy techniques including IR, Raman, solid state NMR and mass spectrometry have been used for the characterization of intact biological tissues and showed enormous potential for the differentiation of tissues with various histologies, including multiple different types of cancer.

Rapid Evaporative Ionization Mass Spectrometry is based on the observation that electrosurgical dissection of vital tissues involves the ionization of various tissue constituents, with special emphasis on membrane lipids. Electrosurgical methods employ electric current for the rapid heating and evaporation of tissue material and they are widely used both for dissection and coagulation on practically all fields of surgery. Hence, the direct combination of electrosurgery with mass spectrometry provides a tissue identification methodology, where the tissue manipulation part is already widely used by surgeons and fully approved from regulatory point of view. Electrosurgical methods are also employed on the field of endoscopy, both for coagulation and dissection. Combination of endoscopy with *in-situ* mass spectrometric tissue identification resulted in a diagnostic device which can potentially identify lesions in body cavities *in-situ*, in real-time.

Electrosurgical electrode assembly and ion transfer device were embedded into working channel of commercially available colonoscope. The device was coupled with a linear ion trap mass spectrometer, and the system was utilized during diagnostic colonoscopic interventions. Adenomae, adenocarcinomae and mucosal areas affected by inflammatory bowel diseases were successfully identified, in complete agreement with histopathological examination.

4:00pm **IS+AS+BI+ET+GR+NS-TuA7 Nanocrystal Phase Transformations in ZBLAN Glass Ceramics, J.A. Johnson, University of Tennessee Space Institute, C. Alvarez, Northwestern University, Y. Lui, Argonne National Laboratory, C.E. Johnson, University of Tennessee Space Institute, A. Petford-Long, Argonne National Laboratory**

In-situ and *ex-situ* TEM investigations of fluorochlorozirconate (FCZ) glass have led to the discovery of previously unreported BaF₂ in the face-centered-cubic (FCC) and orthorhombic phases. These FCZ glasses are a class of material based on ZBLAN glasses, which are being developed for uses in advance mammography systems. The FCZs of interest have been doped with Eu (II) for use as either a scintillator or a storage phosphor material but need to be partially crystalline to show good optical properties. The photo-stimulated luminescence of this material, for use as storage phosphor, is attributed to the characteristic 5d-4f emission of Eu²⁺ present in the BaCl₂ nanocrystals. The crystals formed are known from XRD experiments to be hexagonal and orthorhombic BaCl₂ depending on the annealing temperature, 265 and 295°C respectively. *In-situ* and *ex-situ* TEM heating experiments were used to study the nucleation and growth process

of the nanocrystals at the EMC. The nanocrystals nucleate and grow through-out the glass matrix when annealing FCZ glasses, therein producing a nanocomposite glass-ceramic system. The traditional BaCl₂ orthogonal phase in addition to the unreported FCC and orthogonal BaF₂ phase have been found in multiple ZBLAN compositions in which the content of Cl and F has been varied. This indicates that annealing FCZ glasses produces polymorphic crystals of both BaCl₂ and BaF₂, which vary in size from 10 nm to 100 nm.

Mössbauer Spectroscopy has also given indisputable evidence that the divalent Europium enters the nanocrystals.

4:20pm IS+AS+BI+ET+GR+NS-TuA8 *In Situ* Microscopy of Organic Film Growth: Zn-Phthalocyanine on Ag(100), A. Al-Mahboob, J.T. Sadowski, Brookhaven National Laboratory

Metal phthalocyanines are attracting significant attention, owing to their potential for applications in chemical sensors, solar cells and organic magnets. As the electronic properties of molecular films are related to their crystallinity and molecular packing, the optimization of film quality is important for improving the performance of organic devices.

In this work, we studied the dynamics of nucleation and structural evolution of zinc-phthalocyanine (ZnPc) films on Ag(100) surface, employing real-time low-energy electron microscope (LEEM) complemented by DFT calculations. We have observed two different modes of ZnPc nucleation, depending on the growth temperature. At lower temperatures ZnPc nucleates in a double domain structure, with bulk-like square lattice similar to one reported by Dou et al. [2]. LEED patterns recorded in LEEM experiment show that ZnPc monolayer (ML) grows epitaxially, having a square lattice with $(4/3)\sqrt{13} \times (4/3)\sqrt{13} R33.69^\circ$ unit cell (denoted R33.69) with respect to the substrate lattice. At temperatures of 170°C or above, nucleation of less dense epitaxial ZnPc, having single domain orientation, was observed, with square lattice parameters exactly 5 times larger (5x5) than the Ag(100) substrate.

Utilizing LEEM to observe the ZnPc nucleation at varying substrate temperatures – from room temperature (RT) to 225°C – we have observed that the nominal ZnPc coverage required for the onset of nucleation has strong temperature dependence. The nucleation commences at about 0.2 ML at RT, while 0.7 ML is required at 190°C. At the same time the completion of 1st layer occurs at constant nominal coverage of ZnPc, independent of substrate temperature. Based on that observation, the delay in onset of nucleation could be understood as a result of increased equilibrium concentration of diffusing ZnPc molecules at higher temperatures. This is in contrast to a delay in nucleation and giant island growth observed during vacuum deposition of anisotropic molecules like pentacene (Pn), in which case the energy barrier for the reorientation of the molecule from diffusing state into its crystalline orientation plays a critical role [3]. Real-time tracking of the evolution of ZnPc island area at varying deposition conditions combined with DFT analysis revealed that the 5x5 structure has both, a detachment barrier with respect to attachment, and a pre-factor (or attempt frequency), lower than those for bulk-like structures, allowing for controlling of the resulting ZnPc structure.

[1] E. Bauer, Rep. Prog. Phys. **57**, 895 (1994).

[2] W. Dou et al, J. Chem. Phys. **133**, 144704 (2010).

[3] Al-Mahboob et al, Phys. Rev. **B 82**, 235421 (2010).

4:40pm IS+AS+BI+ET+GR+NS-TuA9 *In Situ* Sub-Micrometer Scale Chemical Imaging with Scanning Transmission X-ray Microscopy, S.T. Kelly, P. Nigge, Lawrence Berkeley National Laboratory, A. Laskin, B. Wang, Pacific Northwest National Laboratory, A. Tivanski, S. Ghorai, University of Iowa, T. Tyliczszak, M.K. Gilles, Lawrence Berkeley National Laboratory

Spatially resolved chemical information on length scales shorter than 50 nm has become crucial in many areas of science and engineering -- from analyzing the chemistry of geological and environmental samples to quantifying the detailed chemical structure of novel materials engineered on the nanoscale. Scanning transmission x-ray microscopy (STXM) allows collection of specific chemical speciation data on these length scales through the acquisition and analysis of near-edge x-ray absorption fine structure (NEXAFS) spectra at each image pixel. However, the full usefulness of the STXM instrument may ultimately be realized in the *in situ* analysis of chemical transformations by controlling the local sample environment.

In situ STXM/NEXAFS measurements have been made in several ways thus far, ranging from simple to very complex. Introducing gases directly into the microscope chamber is effective, yet the presence of the gas along the entire optical path of the x-rays reduces signal at the detector. Furthermore, gas choice with this configuration is limited to those compatible with the microscope components. Separate *in situ* reactor cells circumvent these limitations by confining the gaseous environment to a

small region immediately around the sample. Several groups have used reactor cells to this end, with reactors ranging widely in complexity -- from simple cells with limited capability to complex systems which require substantial instrument reconfiguration.

Ideally, an *in situ* reactor for STXM should be capable, flexible, easy to install and configure, and easily fabricated. We have developed a gas phase STXM reactor cell to meet many of these requirements. The reactor mounts directly to the standard STXM sample mount (making installation relatively simple) and contains an integrated sensor to actively measure relative humidity inside the cell for experiments using water vapor. We present here recent results using the reactor cell to examine two different systems. In the first system, we observed the hygroscopic properties of mixed organic/inorganic aerosol particles at increasing levels of relative humidity. In the second system, we monitored carbon dioxide sorption in metal organic framework materials. The advantages afforded by this reactor (and future improvements to it) will enable new scientific discoveries across a wide range of fields.

5:40pm IS+AS+BI+ET+GR+NS-TuA12 *In Situ* SEM and ToF-SIMS Imaging of Liquids for Biological Applications, L. Yang, X.-Y. Yu, Z. Zhu, S. Thevuthasan, Pacific Northwest National Laboratory, J. Cowin, Cowin In-Situ Science, L. L. C.

A vacuum compatible microfluidic interface was developed to enable surface analysis of liquids. The unique feature of the liquid flow cell is that the detection window is open to the vacuum allowing direct probing of the liquid surface. The flow cell is composed of a silicon nitride membrane and polydimethylsiloxane; and it is fully compatible with vacuum operations for surface analysis. The aperture can be drilled through the 100 nm silicon nitride membrane by using the focused ion beam/scanning electron microscope (FIB/SEM). Alternatively the primary Bi⁺ ions in ToF-SIMS can be used to fabricate the aperture window in real-time. New results using this vacuum interface and recent development will be presented in this paper. Several aqueous solutions containing conjugated IgG gold nanoparticles and representative biological solutions were studied *in situ* using scanning electron microscope (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Characteristic signals of the conjugated gold nanoparticles were successfully observed through the aperture by both energy-dispersive X-ray spectroscopy (EDX) in SEM and ToF-SIMS. Comparisons were also made among wet and dry samples and liquid sample in the flow cell using SEM/EDX. Stronger gold signal can be observed in our novel portable device by SEM/EDX compared with the wet or dry samples, respectively. Our results indicate that analyses of the nanoparticle conjugated antibodies are better made in their native liquid environment. Our unique microfluidic flow cell permits *in situ* liquid observations. In addition, a variety of aqueous solutions relevant to biological systems were analyzed. Our results indicate that chemical imaging by SEM and ToF-SIMS is applicable in analyzing more complicated aqueous solutions when coupled with our novel portable microfluidic platform.

Scanning Probe Microscopy Focus Topic

Room: 16 - Session SP+AS+BI+ET+MI+NS-TuA

Advances in Scanning Probe Imaging

Moderator: S. Allen, The University of Nottingham, UK, Z. Gai, Oak Ridge National Laboratory

2:00pm SP+AS+BI+ET+MI+NS-TuA1 Molecules Investigated with Atomic Resolution using Scanning Probe Microscopy with Functionalized Tips, L. Gross, F. Mohn, N. Moll, G. Meyer, IBM Research - Zurich, Switzerland

INVITED

Single organic molecules were investigated using scanning tunnelling microscopy (STM), noncontact atomic force microscopy (NC-AFM), and Kelvin probe force microscopy (KPFM). With all of these techniques submolecular resolution was obtained due to tip functionalization by atomic manipulation. The techniques yield complementary information regarding the molecular structural and electronic properties.

Using NC-AFM with CO terminated tips, atomic resolution on molecules has been demonstrated and the contrast mechanism was assigned to the Pauli repulsion [1]. On the other hand, by using STM the molecular frontier orbitals, i.e., the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), were mapped [2]. Using a CO terminated tip for orbital imaging with the STM, the resolution can be increased and the images correspond to the gradient of the molecular orbitals due to the *p*-wave character of the tip states [3]. Finally, KPFM reveals information about the distribution of charges within molecules by measuring the *z*-

component of the electrostatic field above the molecule, as demonstrated on the hydrogen tautomerization switch naphthalocyanine [4].

References :

- [1] L. Gross *et al. Science* **325**, 1110 (2009).
- [2] J. Repp *et al. Phys. Rev. Lett.* **94**, 026803 (2005).
- [3] L. Gross *et al. Phys. Rev. Lett.* **107**, 086101 (2011).
- [4] F. Mohn *et al. Nature Nanotechnol.* **7**, 227 (2012).

2:40pm SP+AS+BI+ET+MI+NS-TuA3 Functional Imaging of Jahn-Teller Dynamics at the Single-molecule Scale. *J. Lee, S.M. Perdue, A. Rodriguez Perez, P.Z. El-Khoury, V.A. Apkarian*, University of California, Irvine

Taking advantage of both elastic and inelastic tunneling processes of a molecule isolated at the double-barrier tunneling junction of a scanning tunneling microscope, both static and dynamic parts of the Hamiltonian can be visualized with submolecular resolution. This is illustrated by imaging Jahn-Teller (JT) driven vibronic dynamics within Zn-etioporphyrin (ZnEtio), in its various reduced forms, in what may be regarded as nature's choice of a molecule as a controllable current switch. Unique interpretations are afforded through simultaneously recorded functional images, such as maps of: a) energy resolved differential current, b) spectrally resolved electroluminescence, c) conduction bistability, d) reduction/oxidation potentials (maps of charging and discharging). We focus on the radical anion, ZnEtio⁻, which is reduced by injecting an electron to a single ZnEtio molecule adsorbed on a thin aluminum oxide film grown on NiAl(110). In contrast with the neutral, the saddle-shaped radical anion lies flat on the surface of the oxide. The discharge map directly shows that the excess electron is localized in the ²p_x orbital of the entire porphyrin macrocycle, as a result of the JT active rectangular (B_{1g}) distortion of the molecule. The static JT potential leads to conduction bistability, with reversed switching polarity depending on whether tunneling electrons are injected in the occupied ²p_x orbital or the diamond (B_{2g}) coordinate which serves as a transition state that connects the p_x and p_y orbitals at the two B_{1g} minima. In addition to the JT switching, the dynamic JT states are directly imaged through electroluminescence spectra, induced by injection of a second electron in the anion. The spectra consist of a continuum due to radiative ionization of the dianion, and sharp Fano resonances of the vibronic progression of the JT active modes. A detailed analysis of the spectra yields the vibronic couplings and the wavefunctions. Vibronic structure is inherent in STM topographic images, and has hitherto not been fully recognized.

3:00pm SP+AS+BI+ET+MI+NS-TuA4 Atomic and Chemical Resolution of Heterogeneous 1-D Metallic Chains on Si(100) by Means of nc-AFM and DFT. *M. Sevin, M. Ondracek, P. Mutombo, Z. Majzik, P. Jelinek*, Institute of Physics of ASCR, Czech Republic

Scanning Probe techniques are widely used to image atomic and electronic structure of surfaces and nanostructures. However atomic and chemical resolution of complex nanostructures (e.g. molecules, nanoparticles or nanowires) is still the large challenge. Several methods (see e.g. [1-3]) have been already proposed to achieve the single-atom chemical resolution. In the work [3] it was showed that the single-atom chemical identification can be achieved via force-site spectroscopy measurements using Frequency Modulation Atomic Force Microscopy (FM-AFM). The validity of the method was demonstrated on semiconductor surface alloy composed of isovalent species (Si, Sn and Pb). In this particular case, the valence electrons of surface atoms possess very similar electronic structure close to sp³ hybridization with characteristic dangling bond state. Hence the maximum short-range force is mainly driven by the position of the dangling bond state with respect to the Fermi level.

In this work, we investigated atomic and chemical structure of heterogeneous 1-D chains made of III and IV group metals grown on Si(100) surface [4] by means of room-temperature (RT) FM-AFM measurements combined with DFT simulations. Here 1D chains consist of heterogeneous buckled-dimer structures with unknown chemical ordering. What more, the presence of buckled dimers composed by chemical species of different valence makes this system very challenging for true atomic and chemical resolution by means of SPM.

In this contribution, we will show first that FM-AFM technique even at RT is able to achieve atomic resolution of individual atoms forming dimers, much superior to the contrast obtained by the traditional STM technique. Secondly, we will demonstrate that the single-atom chemical identification is still possible combining the force-site spectroscopy at RT with DFT simulations even in such complex systems as the heterogeneous 1D metallic chains.

- [1] M. Schmid, H. Stadler, P. Varga *Phys. Rev. Lett.*, **70**, p. 1441 (1993)
- [2] L. Gross *et al. Science* **325**, 5944 (2009).
- [3] A. Foster *et al. Phys. Rev. Lett.* **102**, 256103 (2009).

[4] Y. Sugimoto, P. Pou, M. Abe, P. Jelinek, R. Perez, S. Morita, O. Custance, *Nature* **446**, 64 (2007)

[5] L. Magaud, A. Pasturel, and J.-Y. Veuillen, *Phys. Rev. B* **65**, 245306 (2002).

4:00pm SP+AS+BI+ET+MI+NS-TuA7 Simple Routes to High Speed and Super Resolution AFM. *J.K. Hobbs*, University of Sheffield, UK
INVITED

Over the past two decades atomic force microscopy has developed to become the workhorse of molecular nanotechnology. However, despite this success, it has failed to deliver consistently in two areas where it arguably has most potential, namely sub-molecular resolution imaging and the following of processes in real time. Here our work to tackle these challenges will be discussed.

We have developed a new approach to reaching high resolution within a conventional AFM, based on torsionally driven T-shaped cantilevers, dubbed "torsional tapping AFM". The use of torsional oscillations gives improved dynamics (high Q-factor, high frequency), without excessively increasing the spring constant. The small offset of the tip from the axis of rotation gives improved lever sensitivity. Combined, these result in an approximately 12 fold improvement in sensitivity when compared to the same AFM with a conventional tapping cantilever. This improved sensitivity allows ultra-sharp whisker tips to be used in a routine manner, giving true molecular resolution even on soft materials presenting surfaces with tens of nanometres of topography. For example, individual polyethylene chains both in the crystalline phase, and at the interface with the amorphous phase, can be clearly imaged in a conventionally processed sample of plastic, with polymer chain-to-chain resolution down to 0.37 nm [1]. Data from semi-crystalline polymers to naturally occurring protein crystals will be presented.

High speed AFM requires methods for scanning rapidly, for maintaining tip-sample contact ("feedback"), and for constructing the topography image. We have shown that resonant scanners [2] give a robust method for rapid scanning. In a conventional AFM the feedback and the topographic image are inextricably linked. However, this places a limit on scan speed as it demands that the tip has reached equilibrium at each point on the image if the height is going to be accurately obtained. We have adopted a different approach, in which the height of the tip is directly measured using an interferometric approach, freeing the feedback loop to minimising tip-sample forces. This allows topographic images with height traceable to the wavelength of the interferometric laser to be obtained at imaging rates greater than one frame a second. Coupled with resonant scanners, giving scan areas up to 40x40 μm² an AFM platform capable of in-line industrial applications is obtained.

1. Mullin, N.; Hobbs, J. K., *Phys Rev Lett* **2011**,107

2. Humphris, A. D. L.; Miles, M. J.; Hobbs, J. K *Appl Phys Lett* **2005**,86 (3)

4:40pm SP+AS+BI+ET+MI+NS-TuA9 A Scanning Probe Microscopy Study of Trimesic Acid Self-Assembly on Highly Oriented Pyrolytic Graphite. *V. Korolkov, S. Allen, C.J. Roberts, S.J.B. Tandler*, The University of Nottingham, UK

We have investigated trimesic acid (1,3,5-benzenetricarboxylic acid, TMA) adsorption on highly oriented pyrolytic graphite (HOPG) surfaces from aqueous medium at room temperature. Both atomic force (Peak Force Tapping mode) and scanning tunnelling microscopy were utilized to follow the adsorption dynamics and molecular arrangements. A chicken-wire arrangement for adsorbed molecules with an average pore size of 11 ± 1 Å was established and observed using both scanning techniques. We found that this structure forms a monolayer within ~ 100 seconds of exposure of the HOPG surface to 50 μM TMA solution in H₂O. The monolayer structure was found to be stable for at least 48h under ambient conditions. STM was observed to lead to some desorption of TMA from a dynamically formed TMA film, and was only able to image the monolayer of TMA molecules in intimate contact with the HOPG. AFM revealed that TMA films formed using higher concentrations or longer adsorption times formed multilayers with similar molecular spacings and displayed an island growth morphology.

We have achieved an excellent resolution on an ambient running AFM. We have demonstrated that the combination of STM and AFM is essential, if not a must, to look at ultimate monolayers in the ambient conditions. Overall a facile green chemistry method for TMA monolayer fabrication from aqueous media on a HOPG surface has been established.

5:00pm **SP+AS+BI+ET+MI+NS-TuA10 Understanding the Role of the Probe in SPM Imaging of Metal Oxides: New Opportunities for In-Depth Surface Analysis**, *H. Mönig*, Univ. of Münster, Germany, *M. Todorovic*, Univ. Autónoma de Madrid, Spain, *M.Z. Baykara*, Yale Univ., *T.C. Schwendemann*, Southern Connecticut State Univ., *J. Götzén*, *Ö. Ünverdi*, *E.I. Altman*, Yale Univ., *R. Perez*, Univ. Autónoma de Madrid, Spain, *U.D. Schwarz*, Yale Univ.

Metal oxide surfaces play an indispensable role in a number of catalytic processes of technological and scientific importance. A fundamental understanding of the role that metal oxide surfaces play in such applications requires an experimental technique that allows analyzing chemical and electronic surface properties down to the atomic scale. The powerful method of three-dimensional atomic force microscopy (3D-AFM) in combination with scanning tunneling microscopy (STM) can be used towards this goal with great success. However the interpretation of results is not straightforward, particularly because the structure and chemistry of the probe tip employed in the experiments influences the measured data.

In this talk, using a combination of experimental STM data and density functional theory (DFT) calculations, we will study the effect of changing the tip structure and chemistry, as well as imaging parameters such as tip-sample distance and bias voltage on STM images obtained on the model surface of Cu(100)-O, a surface oxide layer consisting of nearly co-planar copper (Cu) and oxygen (O) atoms. We observe that STM image contrasts and atomic species with highest tunneling probability vary greatly with changing tip properties and imaging parameters. Reasonable matches between calculated and experimentally recorded STM images are observed, allowing the determination of particular tip models used in the experiments. Additionally, the effect of rotating the model tip structures with respect to the sample surface results in asymmetric features in simulated STM images, reproducing certain peculiar patterns observed experimentally. To sum up, the results presented here underline the significant role that the tip plays in SPM measurements and describe potential routes to optimize the gathered information through deliberate manipulation of tip properties as well as imaging parameters.

5:20pm **SP+AS+BI+ET+MI+NS-TuA11 Characterizing the Best Tips for NC-AFM Imaging on Metal Oxides with Force Spectroscopy and Theoretical Simulations**, *D. Fernandez-Torre*, Universidad Autónoma de Madrid, Spain, *A. Yurtsever*, Osaka University, Japan, *P. Pou*, Universidad Autónoma de Madrid, Spain, *Y. Sugimoto*, *M. Abe*, *S. Morita*, Osaka University, Japan, *R. Perez*, Universidad Autónoma de Madrid, Spain

Metal oxides play a key role in a wide range of technological applications. To optimize their performance, it is essential to understand their surface properties and chemistry in detail. Noncontact atomic force microscopy (nc-AFM) provides a natural tool for atomic-scale imaging of these insulating materials. Some of these materials, including ceria (CeO₂), and particularly titania (TiO₂), have been extensively studied with nc-AFM in the last few years. Experiments on the rutile TiO₂(110) surface show, at variance with STM, that a variety of different contrasts can be obtained, and frequent changes among different imaging modes are observed during scanning. The two most common contrasts are the “protrusion” and the “hole” mode imaging modes, that correspond, to imaging bright the positive or the negative surface ions respectively, but other contrasts like the “neutral” mode and the “all-inclusive” mode—where all the different chemical species and defects are imaged simultaneously—have been also identified.

Understanding the image contrast mechanisms and characterizing the associated tip structures is crucial to extract quantitative information from nc-AFM measurements and to identify the nature of the observed defects. While in many cases the same nc-AFM image can be explained by different models, and even different underlying tip-sample interactions, we show here that the combination of force spectroscopy (FS) measurements and first-principles simulations can provide an unambiguous identification of the tip structure and the image contrast mechanism. In particular, we show that the best tips to explain the protrusion and hole mode forces are TiO_x-based clusters differing in just one H atom at the tip apex, discarding previously proposed Ti-terminated tips that would lead to forces much larger than the ones observed in the experiments. The less frequent neutral and all-inclusive images are associated to Si tips where contamination is limited to just an O atom or OH group at the apex. These models provide a natural explanation for the observed contrast reversals by means of H transfer to/from the tip, an event that we indeed observe in our simulations. As tip contamination by surface material is common while imaging oxides, we expect these tips and imaging mechanisms to be valid for other oxides. Our results for the imaging of CeO₂ surfaces and of metal atoms (K, Pt) adsorbed on TiO₂ support this conclusion.

5:40pm **SP+AS+BI+ET+MI+NS-TuA12 Direct Probe of Interplay between Local Structure and Superconductivity in FeTe_{0.55}Se_{0.45}**, *M.H. Pan*, *W.Z. Lin*, *Q. Li*, *B.C. Sales*, *S. Jesse*, *A.S. Sefat*, *S.V. Kalinin*, Oak Ridge National Laboratory

A key challenge in high-temperature superconductivity is to determine the role of local crystallographic structure and chemical effects on the superconducting critical temperature, T_c . Iron chalcogenide superconductors (‘11’) are ideal model systems for deciphering the role of local effects on the superconductivity, primarily because they cleave leaving non-polar surfaces unlike other families of iron arsenide superconductors (‘1111’ or ‘122’) and cuprates. **Here, we explore the interplay between local crystallographic structure, composition and local electronic and superconductive properties. Direct structural analysis of scanning tunneling microscopy (STM) data allows local lattice distortions and structural defects across a FeTe_{0.55}Se_{0.45} surface to be explored on a single unit-cell level. Concurrent superconducting gap (SG) mapping reveals suppression of the SG at well-defined structural defects, identified as a local structural distortion (Guinier-Preston zone). The strong structural distortion is related to the vanishing of the superconducting state. This study provides insight into the origins of superconductivity in iron chalcogenides by providing an example of atomic-level studies of the structure-property relationship.**

Wednesday Morning, October 31, 2012

In Situ Microscopy and Spectroscopy Focus Topic

Room: 7 - Session IS+AS+OX+ET-WeM

In Situ Characterization of Solids: Film Growth, Defects, and Interfaces

Moderator: P.W. Sutter, Brookhaven National Laboratory

8:00am **IS+AS+OX+ET-WeM1 Revealing Gas-Surface Radical Reaction Mechanisms of Self-Assembled Monolayers by Scanning Tunneling Microscopy**, *D.Y. Lee, M.M. Jobbins, S.A. Kandel*, University of Notre Dame

Scanning Tunneling Microscopy (STM) in ultra-high-vacuum is used *in situ* to investigate the surface changes of the octanethiolate self-assembled monolayer (SAM) on Au(111) upon reaction with atomic hydrogen and with atomic chlorine. For both reactions, the surface structure heavily influences the rate of monolayer degradation, but the effect of surface defects on reactivity is completely opposite when comparing the two systems. Monolayer reactivity increases with increasing hydrogen-atom exposure while decreases with further reaction with atomic chlorine. The monolayer-versus-exposure data are examined by kinetic Monte Carlo simulations and reveal that, for H-atom exposure, molecules located near surface defect sites are potentially over 500 times more reactive than close-packed areas. For Cl-atom interactions, however, the opposite occurs: close-packed regions are at least 100 times more reactive than defect sites. These observations result directly from the alkyl hydrogen abstraction and sulfur-gold bond cleavage mechanisms of SAM upon gas-phase radical bombardment.

8:20am **IS+AS+OX+ET-WeM2 In Situ Imaging of the Nucleation and Growth of Epitaxial Anatase TiO₂(001) Films on SrTiO₃(001)**, *Y.G. Du, D.J. Kim, T.C. Kaspar*, Pacific Northwest National Laboratory, *S.E. Chamberlin*, University of Wisconsin Milwaukee, *I. Lyubintsky, S.A. Chambers*, Pacific Northwest National Laboratory

TiO₂ has attracted much attention because of its potential utility in hydrogen production via water splitting, environmental remediation, and dye-sensitized solar cell fabrication. Heteroepitaxial growth of anatase is a powerful and unique way to fabricate model surfaces of the less stable anatase polymorph for fundamental surface science studies. In this work, the growth of TiO₂ anatase films on Nb doped SrTiO₃(001) by molecular beam epitaxy has been studied *in-situ* by scanning tunneling microscopy. We show that the initial growth follows the Stranski-Krastanov mode, where islands form on top of a wetting layer consisting of two monolayers (ML) of TiO₂. Well-defined (4x1) and (1x4) terraces are observed for film thicknesses in excess of 3 nm. At larger film thicknesses, large oriented crystallites form as a result of the coalescence of smaller islands. Within a given crystallite, either (4x1) or (1x4) reconstructed terraces account for majority of the surface. The anatase grows in units of bilayers, resulting in a step height of 2 ML. This result explains the fact that the measured period of the RHEED specular-beam intensity oscillations corresponds to the time required for deposition of 2 ML. Ar ion sputtering and UHV annealing results in a transformation to coexisting (4x1) and (1x4) reconstructed terraces on individual crystallites, as commonly observed by *ex-situ* STM studies. In addition, we show that the nucleation and growth of anatase films are influenced by Nb doping in the SrTiO₃ substrates by comparing with similar growth occurring on pure SrTiO₃ substrates.

8:40am **IS+AS+OX+ET-WeM3 In Situ Synchrotron X-Ray Studies of Epitaxial Oxide Thin Film Synthesis Behavior**, *J.A. Eastman, M.J. Highland, P.H. Fuoss*, Argonne National Laboratory, *T.M. McCleskey*, Los Alamos National Laboratory, *D.D. Fong, C.M. Folkman, S.K. Keun, E. Perret, P.M. Baldo*, Argonne National Laboratory, *E. Bauer, Q. Jia*, Los Alamos National Laboratory

INVITED

Intense interest is focused on the growth science of epitaxial oxide thin films because of continuing discoveries of new interesting and important properties. The key to achieving desired maximum functionality of oxide heterostructures is the ability to synthesize high-quality films with full control of factors such as composition, crystallographic orientation, surface termination, and strain state. Many of the most promising thin film synthesis techniques involve non-vacuum, high-temperature environmental conditions that are difficult or impossible to probe using standard spectroscopic or structural probes. However, the use of high-energy x-rays available at synchrotron sources such as the Advanced Photon Source (APS) provides an opportunity to obtain real-time atomic-level structural and chemical information during synthesis. This talk will describe results from recent studies at APS Sector 12ID-D using an *in-situ* x-ray approach

to understand and control the synthesis behavior of complex oxide epitaxial thin films prepared by two very different techniques: sputter deposition or polymer assisted deposition (PAD).

We recently built a new RF magnetron sputter deposition system at the APS, which brings to bear state-of-the-art real-time *in-situ* x-ray scattering and spectroscopy techniques to provide insight into the growth behavior of epitaxial oxide thin film heterostructures. Initial studies of the growth behavior of epitaxial films such as (001) LaGaO₃, SrZrO₄, and LaGaO₃/SrZrO₃ multilayer heterostructures during off-axis sputtering will be described, focusing on the effects of epitaxial strain and electrical compensation (e.g., surface polarity) on growth behavior.

PAD is a solution technique capable of synthesizing dense epitaxial thin films. Past work at Los Alamos has demonstrated that PAD can be used to prepare aligned epitaxial films of many different materials. We recently performed initial *in-situ* synchrotron x-ray experiments aimed at obtaining a fundamental understanding of the nucleation and growth processes associated with epitaxial film formation. Studies of the synthesis behavior of (001) BaTiO₃ epitaxial films will be described in this talk, focusing on the effects of thermal history and choice of substrate material on crystallization behavior and the development of epitaxy.

Argonne researchers were supported by the U. S. Department of Energy (DOE), Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Los Alamos researchers were supported by the DOE through the LANL/LDRD Program. Use of the APS was supported by BES, under Contract DE-AC02-06CH11357 between UChicago Argonne LLC and the Department of Energy.

9:40am **IS+AS+OX+ET-WeM6 Understanding the Dynamic Electronic Properties of Electrode Materials by In Situ X-ray Absorption Spectroscopy**, *M. Bagge-Hansen, J.R.I. Lee, A. Wittstock, M.D. Merrill, M.A. Worsley, T. Ogitsu, B.C. Wood, T. Baumann, M. Stadermann, M. Biener, J. Biener, T. van Buuren*, Lawrence Livermore National Laboratory

In situ characterization of the evolution in electronic structure of electrode materials during repeated charge-discharge cycling is fundamentally important for more fully understanding the processes of charge storage and degradation, which, in turn, is essential for the development of new electrical energy storage (EES) materials with tailored properties and improved performance. X-ray spectroscopies provide ideal tools with which to obtain enhanced insight into the origins of electrode behavior in EES systems due to their capabilities for direct, element specific, characterization of the electronic densities of states. To date, *in situ* studies of EES materials have primarily focused on hard x-ray experiments due to the challenges associated with UHV compatibility and high photon attenuation of cells for soft x-ray measurements. Nonetheless, the use of soft x-ray spectroscopies to EES systems is vital since they provide complementary information that cannot be obtained via hard x-ray studies. We report the development of a cell for *in situ* soft x-ray emission spectroscopy and x-ray absorption spectroscopy studies of EES materials and will discuss experiments focused upon the x-ray spectroscopy characterization of a series of novel electrode materials. Prepared by LLNL under Contract DE-AC52-07NA27344.

10:40am **IS+AS+OX+ET-WeM9 In Situ Studies of Al₂O₃ ALD Growth and Self-cleaning on III-V Surfaces by STM and XPS**, *L.N.J. Rodriguez, A. De Clercq*, IMEC, Belgium, *M. Tallarida*, BTU Cottbus, Germany, *D. Cuyppers*, IMEC, Belgium, *J.P. Locquet*, KU Leuven, Belgium, *S. Van Elshocht, C. Adelman, M. Caymax*, IMEC, Belgium

A custom built ALD UHV-compatible reactor has been used to study the growth of TMA on InP and InAlAs by STM in conjunction with additional studies performed in a reactor attached to a synchrotron XPS. The effects of selected *ex-situ* cleans has been measured along with the subsequent cycles of ALD growth from TMA and water. The STM data shows morphological differences between the *ex-situ* cleans on InP, with sulphuric acid cleans yielding plateaus but ammonium sulphide cleans yielding rough surfaces. *In-situ* measurements of these surfaces after TMA dosing shows the growth of islands which converge to film closure after ten cycles of ALD growth. *In-situ* measurements of the I-V curves by STS allowed the creation of bandgap maps of the III-V interfaces after TMA dosing. These bandgap maps showed a non-uniform distribution with regions of either higher or lower bandgap. The mean bandgap was seen to decrease with increasing numbers of ALD cycles. *In-situ* XPS data on similar systems showed a reduction in surface oxides for InAlAs but not for InP. The reduction of arsenic oxides with a creation of metallic arsenic, along partial reduction of indium oxides and a conversion of aluminium sub-oxides to aluminium oxide was seen in the former case. In the latter case, a formal oxidation of

the phosphorus was seen with increased TMA dosing instead of a self-cleaning effect.

11:00am **IS+AS+OX+ET-WeM10 *In Situ* Transport Measurement of Kinetically Controlled Bi Atomic Layers**, *Y. Fujikawa, E. Saitoh*, Tohoku University, Japan

Thin film growth of Bi and related compounds has been attracted much attention because of their exotic properties originating in the large spin-orbit interaction of Bi. Growth of its simple substance is known to result in the formation of a thin-film phase in the initial stage, which is taken over by the bulk growth when the coverage exceeds several monolayers (ML). [1] With typical growth conditions, this transition takes place before the completion of the thin-film layer, which tends to agglomerate to form 4-ML thick islands, making it difficult to measure the intrinsic property of the thin-film phase. In this work, Bi growth on Si(111)-7x7 has been performed in a multi-probe VT-STM system, which provides wide-ranging opportunity of kinetic control and *in-situ* transport measurement during the thin film growth. By tuning the kinetic condition of the growth, it becomes possible to grow the thin-film phase uniformly covering the substrate. Its conductivity, monotonically increasing with the increase of the temperature, would suggest the variable-range hopping conduction rather than the carrier excitation of semiconductors. *In-situ* transport measurement has been performed during the layer-by-layer growth of the Bi thin-film phase, distinguishing the conductivity of each growth unit. It fluctuates with periods of 2 and 4 ML, which may reflect the atomic structure of the thin-film phase.

[1] Nagao *et al.*, Phys. Rev. Lett. **93**, 105501 (2004).

11:20am **IS+AS+OX+ET-WeM11 CAMECA IMS Series Advanced Ion Microscopy: High Throughput, Repeatability & Automation**, *P. Peres, F. Desse, F. Hllion, M. Schuhmacher*, Cameca, S.a., France, *A.N. Davis*, CAMECA Instruments, Inc.

The advantage of CAMECA IMS Series high performance secondary ion mass spectrometers are well established: extreme sensitivity, high mass resolution, and high dynamic range, providing low detection limits while keeping high analysis throughput. This instrument delivers high analytical performance for a wide range of applications: Si based devices, III-V and II-VI devices, both bulk materials and thin-film technology, as well as for different material science applications.

In order to meet the growing demand in terms of reproducibility and throughput performance as well as ease of use, CAMECA has developed a new IMS series, 7F-Auto.

The primary column has been redesigned in order to provide an easier and faster primary beam tuning. For high efficiency operation, automated routines for tuning the instrument are added for both primary and secondary columns, nominally: aperture adjustment, secondary ion beam centering, detector adjustment, among others. These routines not only increase the ease of use, but also enhance the reproducibility of the instruments by minimizing operator-related biases.

A motorized storage chamber has also been developed allowing to keep, under UHV environment, up to six sample holders. The holder exchange between the storage chamber and analysis chamber is fully motorized and computer controlled, allowing a set of analyses to be performed in automated, unattended mode on multiple sample holders. This significantly improves the throughput of the tool, since up to 24 samples (assuming 4 samples per holder) can be analysed in chained mode, possibly overnight. These developments will be presented and discussed in detail.

Scanning Probe Microscopy Focus Topic

Room: 16 - Session

SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM

Probe-Sample Interactions, Nano-Manipulation and Fabrication

Moderator: S. Allen, The University of Nottingham, UK,
A.-P. Li, Oak Ridge National Laboratory

8:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM2 Controlled Coupling of Silicon Atomic Quantum Dots at Room Temperature: A Basis for Atomic Electronics?**, *R.A. Wolkow*, University of Alberta and The National Institute for Nanotechnology, Canada, *J. Pitters*, The National Institute for Nanotechnology, Canada, *G. DiLabio, M. Taucer, P. Piva, L. Livadaru*, University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

Quantum dots are small entities, typically consisting of just a few thousands atoms, that in some ways act like a single atom. The constituent atoms in a dot coalesce their electronic properties to exhibit fairly simple and potentially very useful properties. It turns out that collectives of dots exhibit joint electronic properties of yet more interest. Unfortunately, though extremely small, the finite size of typical quantum dots puts a limit on how close multiple dots can be placed, and that in turn limits how strong the coupling between dots can be. Because inter-dot coupling is weak, properties of interest are only manifest at very low temperatures (milliKelvin). In this work the ultimate small quantum dot is described – we replace an “artificial atom” with a true atom - with great benefit.

It is demonstrated that the zero-dimensional character of the silicon atom dangling bond (DB) state allows controlled formation and occupation of a new form of quantum dot assemblies - at room temperature. Coulomb repulsion causes DBs separated by less than ~2 nm to experience reduced localized charge. The unoccupied states so created allow a previously unobserved electron tunnel-coupling of DBs, evidenced by a pronounced change in the time-averaged view recorded by scanning tunneling microscopy. It is shown that fabrication geometry determines net electron occupation and tunnel-coupling strength within multi-DB ensembles and moreover that electrostatic separation of degenerate states allows controlled electron occupation within an ensemble.

Some speculation on the viability of a new “atomic electronics” based upon these results will be offered.

9:00am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM4 Atomic Forces and Energy Dissipation of a Bi-Stable Molecular Junction**, *C. Lotze*, Freie Universität Berlin, Germany, *M. Corso, K.J. Franke, F.V. Oppen, J.I. Pascual*, Freie Universität Berlin, Germany

Tuning Fork based dynamic STM/AFM is a well established method combining the advantages of scanning tunneling and dynamic force microscopy. Using tuning forks with high stiffness, stable measurements with small amplitudes, below 1 Å can be performed. In this way, conductance and frequency shift measurements of molecular junction can be obtained simultaneously [1] with intramolecular resolution [2].

One of the most intriguing aspects of molecular junctions relates to the effect of structural bi-stabilities to the properties of the junction. These lead, for example, to conductance fluctuations, telegraph noise and the possibility to switch the electrical transport through the junction.

In this presentation, we characterize a model bi-stable molecular system using dynamic force spectroscopy. The effect of current-induced stochastic fluctuations of conductance are correlated with fluctuations in force. In our experiment we identified the last from both, frequency shifts and energy dissipation measurements, picturing a regime in which electrical transport and mechanical motion are coupled.

[1] N. Fournier *et al.*, PhysRevB **84**, 035435 (2011),

[2] L. Gross *et al.*, Science **324**, 1428 (2009)

9:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5 Acetylene on Cu(111): Imaging a Molecular Pattern with a Constantly Rearranging Tip**, *Y. Zhu, J. Wyrick, K.D. Cohen, K. Magnone, C. Holzke, D. Salib, Q. Ma, D.Z. Sun, L. Bartels*, University of California Riverside

Abstract: Using variable temperature STM and DFT simulation, we identify the phases of acetylene adsorbed on the Cu(111) surface. Depending on the coverage, a diffraction-derived surface pattern of acetylene on Cu(111) is validated by STM. The modification of the STM image transfer function

through the adsorption of an acetylene molecule onto the tip apex is taken into account. In this case, the images of acetylene patterns on Cu(111) also include direct evidence of the **rotational orientation and dynamics of the acetylene species attached to the tip apex**. DFT modeling of acetylene/Cu(111) reveals that the molecular orientation and separation is governed by a balance of repulsive interactions associated with stress induced in the top surface layer and attractive interactions mediated by the electronic structure of the substrate. Computationally modeling of the substrate with 3 layers obtains the periodicity of the intermolecular interaction that provides a theoretical underpinning for the experimentally observed molecular arrangement.

9:40am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM6 Atomic Scale Imaging and Electronic Structure of Trimethylaluminum Deposition on III-V Semiconductor (110) Surfaces, T.J. Kent*, M. Edmonds, E. Chagarov, A.C. Kummel**, University of California San Diego

Silicon based metal oxide semiconductor field effect transistors (Si-MOSFETs) are quickly approaching their theoretical performance limits, as a result many semiconductors are being explored as an alternative channel material for use in MOSFETs. III-V semiconductors are an appealing alternative to Si because of their higher electron mobilities. The limiting factor in III-V based MOSFET performance is defect states which prevent effective modulation of the Fermi level. The InGaAs (001) As-rich (2x4) surface contains two types of unit cells: ideal unit cells with double As-dimers and defect unit cells with single As-Dimers. The missing As-dimer unit cells, which comprise ~50% of the surface, are believed to cause electronic defect states at the semiconductor-oxide interface, specifically at the conduction band edge of the semiconductor. *In-situ* scanning tunneling microscopy and spectroscopy (STM/STS) and density function theory (DFT) modeling show that TMA readily passivates the As-As dimers in the ideal unit cell but the missing InGaAs(001)-2x4 may not be fully passivated by TMA. To improve the electronic structure of the interface, the sidewalls of the finFETs on InGaAs(001) can be fabricated along the (110) direction. The (110) surface contains only buckled III-V heterodimers in which the lower group III atom is sp² hybridized with an empty dangling bond and the upper group V atom is sp³ hybridized with a full dangling bond. This results in an electrically unpinned surface.

To investigate the benefits of using a (110) surface as a channel material, the atomic and electronic structure of the ALD precursor trimethylaluminum (TMA) monolayer deposited on III-V (110) surfaces has been studied using *in-situ* STM and STS. Both GaAs and InGaAs samples were studied. GaAs wafers were obtained from Wafertech with a Si doping concentration of 4x10¹⁸/cm³. The (001) samples were cleaved *in-situ* to expose the (110) surface. Samples were transferred to the STM chamber (base pressure 1x10⁻¹¹ torr) where the atomic bonding structure of the precursor monolayer unit cell was determined. STS, which probes the local density of states (LDOS), was used to determine Fermi level pinning. A model of TMA chemisorption was developed in which TMA chemisorbs between adjacent As atoms on the surface, giving a highly ordered monolayer with a high nucleation density which could allow for aggressive effective oxide thickness (EOT) scaling.

10:40am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM9 A New Experimental Method to Determine the Torsional Spring Constants of Microcantilevers, G. Haehner, J.D. Parkin**, University of St Andrews, UK
Cantilever based technologies have seen an ever increasing level of interest since the atomic force microscope (AFM) was introduced more than two decades ago. Recent developments employ microcantilevers as stand-alone sensors by exploiting the dependence of their oscillating properties on external parameters such as adsorbed mass [1], or the density and the viscosity of a liquid environment [2,3]. They are also a key part in many microelectromechanical systems (MEMS) [4]. In order to quantify measurements performed with microcantilevers their stiffness or spring constants have to be known. Following calibration of the spring constants a change in oscillation behavior can be quantitatively related to physical parameters that are probed. The torsional modes of oscillation have attracted significant attention due to their high sensitivity towards lateral and friction forces, and recent developments in torsional-tapping AFM technology [5]. However, the methods available to determine the torsional spring constants experimentally are in general not simple, not very reliable, or risk damage to the cantilever [6].

We demonstrate a new method to determine the spring constants of the torsional modes of microcantilevers experimentally with high accuracy and precision. The method is fast, non-destructive and non-invasive. It is based on measuring the change in the resonance frequencies of the torsional

modes as a function of the fluid flow escaping from a microchannel. Results for rectangular cantilevers will be presented and compared to results obtained with other methods [7].

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11:00am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM10 A Torsional Device for Easy, Accurate and Traceable Force Calibration of AFM Cantilevers, J.F. Portoles, P.J. Cumpson**, Newcastle University, UK

Accurate measurement of biologically-relevant forces in the range of pN to µN is an important problem in nanoscience.

A number of force probe techniques have been applied in recent years. The most popular is the Atomic Force Microscope (AFM). Accuracy of force measurement relies on calibration of the probe stiffness which has led to the development of many calibration methods[1], particularly for AFM microcantilevers. However these methods typically exhibit uncertainties of at best 15% to 20% and are often very time consuming. Dependency on material properties and cantilever geometry further complicate their application and take extra operator time. In contrast, one rapid and straightforward method involves the use of reference cantilevers (the "cantilever-on-cantilever" method) or MEMS reference devices. This approach requires that a calibrated reference device is available, but it has been shown to be effective in providing measurement traceability[2].

The main remaining difficulty of this approach for typical users is the positional uncertainty of the tip on the reference device, which can introduce calibration uncertainties of up to around 6%. Here we present a new reference device based on a torsional spring of relatively large dimensions compared to the typical AFM cantilever and demonstrate how it is calibrated. This method has the potential to calibrate the reference device traceably[3] to the SI with a 1% accuracy by applying techniques typically used for the characterisation of micromechanical devices. The large dimensions of the device reduce the positional uncertainty below 1% and simultaneously allow the use of the device as an effective reference array with different reference stiffnesses at different positions ranging from 0.090 N/m to 4.5 N/m

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11:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM11 Nanoscale Surface Assembly by Single-Molecule Cut-and-Paste, H.E. Gaub**, Ludwig-Maximilians Universität, Germany

INVITED
Bottom up assembly of functional molecular ensembles with novel properties emerging from composition and arrangement of its constituents is a prime goal of nanotechnology. With the development of Single-Molecule Cut-and-Paste (SMC&P) we provided a platform technology for the assembly of biomolecules at surfaces. It combines the Å-positioning precision of the AFM with the selectivity of DNA hybridization to pick individual molecules from a depot chip and allows to arrange them on a construction site one by one. An overview on different applications of this technology will be given in this talk. One recent example demonstrates the functional of receptors for small molecules. By SMC&P we assembled binding sites for malachite green in a molecule-by-molecule assembly process from the two halves of a split aptamer. We show that only a perfectly joined binding site immobilizes the fluorophore and enhances the fluorescence quantum yield by several orders of magnitude. To corroborate the robustness of this approach we produced a micron-sized structure consisting of more than 500 reconstituted binding sites. To the best of our knowledge this is the first demonstration of a one by one bottom up functional bio-molecular assembly. Figure included in supplemental document. S. Kufer, Puchner E. M., Gump H., Liedel T. & H. E. Gaub *Science* (2008), Vol 319, p 594-S. Kufer, Strackham, M., Stahl S.W., Gump H., Puchner E. M. & H. E. Gaub *Nature Nanotechnology* (2009), Vol 4, p 45-M. Erdmann, R. David. A.N. Fornof, and H. E. Gaub, *Nature*

* ASSD Student Award Finalist

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, $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$, BiFeO_3 , and $\text{Y}_x\text{Zr}_{1-x}\text{O}_2$. 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. Bonnelli*, 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 – H₂-based environments (anode side) and O₂-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. Bonnelli*, 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.

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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 $\tan\delta$ 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**, F.J. 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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Thursday Morning, November 1, 2012

Electron Transport at the Nanoscale Focus Topic

Room: 16 - Session ET+NS+EM-ThM

Electron Transport at the Nanoscale: Nanowires and Junctions

Moderator: K. Clark, Oak Ridge National Laboratory, A.-P. Li, Oak Ridge National Laboratory

8:00am ET+NS+EM-ThM1 Functional Imaging of Semiconductor Nanowires and Devices, L.J. Lauhon, Northwestern University INVITED

Microscopy has played a central role in the advancement of nanoscience and nanotechnology by enabling the direct visualization of nanoscale structure, and by extension predictive models of novel physical behaviors. Correlated imaging of nanoscale structure and properties is an important frontier that can provide a rational basis for engineering new materials and devices. I will describe our approach to correlated functional imaging with a focus on semiconductor nanowires. Nanocrystal growth modes such as the vapor-liquid-solid process provide the ability to tailor nanoscale structure and composition in three dimensions, creating new opportunities in a range of applications including light harvesting and solid state lighting. In this context, we have explored a number of important processing-structure-property relationships using atom probe tomography, scanning transmission electron microscopy, Raman microspectroscopy, and scanning photocurrent microscopy. From these studies, we develop a more comprehensive understanding of the influence of geometry, size, defects, dopants, and interfaces on carrier generation, recombination, and transport in nanostructured materials. This quantitative approach to characterization of model systems aims to identify applications that can derive significant benefits from the adoption of unconventional nanostructured materials.

8:40am ET+NS+EM-ThM3 Electronic Transport and Structure Relations in Self-Assembled GdSi₂ Quantum Wires, S.Y. Qin, T. Kim, Oak Ridge National Laboratory, Y. Zhang, W. Ouyang, University of California Irvine, H. Weitering, The University of Tennessee, C. Shih, The University of Texas at Austin, A.P. Baddorf, Oak Ridge National Laboratory, R. Wu, University of California Irvine, A.-P. Li, Oak Ridge National Laboratory

Quantum wires are extremely narrow one-dimensional (1D) materials where electron motion is allowed only along the wire direction, and is confined in the other two directions. Quantum wires, as a smallest electronic conductor, are expected to be a fundamental component in all quantum electronic architectures. The electronic conductance in quantum wires, however, is often dictated by structural instabilities and electron localization at the atomic scale. Adding interwire coupling can often lead to the formation of change density waves. In both cases, the metallic state is not stable and a metal to insulator transition (MIT) occurs at low temperature. [1] Here we show that robust metallic conductance can be stabilized by interwire coupling, while the isolated single nanowires exhibit a MIT due to quantum localization.

We grow the quantum wires of GdSi₂ on Si(100) and study the evolution of electronic transport as a function of temperature and interwire coupling as the quantum wires are self-assembled *wire-by-wire*. As shown in Fig. 1, individual nanowires have a width of 16.7 Å, a height of 4 Å, and lengths of micrometers. These nanowires can be grown either in the form of isolated nanowires or bundles with a number of constituent wires separated by an atomic interwire spacing. We perform the correlated study of electronic properties by utilizing both scanning tunneling microscopy and nanotransport measurements on the same nanowire. [2] The approach takes advantage of our developments in fabricating nanocontacts using a field-induced atom emission process to bridge the atomic wires and the mesoscopic transport electrodes. [3] A MIT is revealed in isolated nanowires, while a robust metallic state is obtained in wire bundles at low temperature. The results provide a rare glimpse of the intrinsic structure-transport relations and the influence of local environments at the atomic scale. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

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9:00am ET+NS+EM-ThM4 Multi-Segment Nanowire Heterojunctions of AuGe and Ge: Fabrication and Electrical Transport, X.D. Li, G.W. Meng, Chinese Academy of Sciences, China, S.Y. Qin, A.-P. Li, Oak Ridge National Laboratory

One-dimensional (1D) multiple segment nanostructures that contain heterojunctions between various metals and semiconductors are of great interest due to their fascinating chemistry and size-, shape-, and material-dependent properties. Here we report on the synthesis and electronic characterization of multi - segment nanowire (NW) junctions of Au1-xGex and Ge. The 1D heterostructures are grown with a low - temperature chemical vapor deposition process, assisted by electrodeposited Au NWs inside nanochannels of anodic aluminum oxide template.[1,2] The Au-catalyzed vapor-liquid-solid growth process occurs simultaneously in multiple locations along the nanochannel, which leads to multi-segment Au1-xGex/Ge heterojunctions. The structures of the as-grown hybrid NWs, analyzed by using transmission electron microscopy and energy dispersive X-ray spectroscopy elemental mapping, show clear compositional modulation with variable modulation period and controllable junction numbers. Remarkably, both GeNW and Au1-xGexNW segments are single crystalline with abrupt interfaces and good crystallographic coherences. The electronic and transport properties of individual NW junctions are measured by using a multi-probe scanning tunneling microscope (STM). The semiconducting nature of Ge segments and the metallic behavior of Au1-xGex segments are examined by scanning tunneling spectroscopy (STS). The transport current-voltage curves across the heterojunctions show a characteristic rectifying behavior, which is discussed in association with the potential barriers at the junction. The high yield of multiple segment NW junctions and the ability to control predictably the properties of a metal-semiconductor can facilitate the applications in nanoelectronics and optoelectronics that harness multiple functionalities of hetero-interfaces.

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9:20am ET+NS+EM-ThM5 Single Charge Nano Memory using Nano Carbon Material, K. Matsumoto, T. Kamimura, Osaka University, Japan

Single charges nano memory which can shift the threshold voltage by the stored single charge and operated at room temperature was realized using the carbon nanotube as an ultra short channel of 10nm.

The double gate stack insulator layers of Al₂O₃(3nm) and SiN_x (27nm) are deposited using the atomic layer deposition to the suspended carbon nanotube with source and drain electrodes of 70nm separation. The carbon nanotube channel was then surrounded by this double gate stack insulator layers and the gap between the source drain electrodes with the insulator layers reduced down to as small as 10nm. The gate metal was then deposited through this gap to form the gate electrode of 10nm.

The dependence of the drain current on the top gate bias shows weak oscillation along the gate bias with the period of 220mV. The oscillation is attributed to the single charge injection from CNT channel to the Al₂O₃/SiN_x interface trap, which make the threshold voltage shift of 220mV. The injection of charge is regulated by the Coulomb blockade that stops the next charge to be injected to the trap. The around trip of the gate bias produces the hysteresis. The width of the hysteresis was also regulated by the single charge injection and shows the stepwise increase.

Thus, we have succeeded in fabricating the single charge memory operated at room temperature.

9:40am ET+NS+EM-ThM6 Combining Atomic Structure, Local Band Alignment, and Electron Transport through Individual Semiconductor Nanowires using Scanning Tunneling Microscopy, R. Timm, O. Persson, M. Hjort, M.T. Borgström, L. Samuelson, A. Mikkelsen, Lund University, Sweden

III-V semiconductor nanowires offer tremendous possibilities for device application in energy and information technology [1]. Due to their unique properties and extreme surface-to-volume ratio, it is both essential and challenging to investigate their atomic structure and to combine this information with electrical measurements on individual nanowires. Recently, we have managed to clean InAs nanowires from their native oxide and obtained first atomically resolved images of their side surfaces by

using scanning tunneling microscopy (STM) [2]. Here, we present a systematic STM study covering various nanowire surface structures emerging from different III-V material systems and different crystal structures. By combining STM imaging with scanning tunneling spectroscopy (STS) measurements we simultaneously study the surface structure and local electronic properties across the interfaces of nanowire heterostructures like polytypic nanowires, p - n -junctions, and material heterostructures.

In order to go further in combining local structural and electronic characterization as well as transport measurements of nanowire devices, we have developed a new method to perform STM/S on individual nanowires *in-situ* under device operation: For this, specific heterostructure nanowires, distributed on a SiO₂/Si substrate, are contacted with metal electrodes defined by electron beam lithography. Using a combined Atomic Force Microscopy (AFM) / STM setup, we can first locate an individual nanowire in AFM mode and then acquire STM images and STS spectra on the contacted nanowire. Thus, we obtain the LDOS spatially resolved along the nanowire, even while the nanowire is externally biased via the metal contacts, allowing simultaneous transport studies. We will show and discuss initial results for different heterostructure nanowire devices, demonstrating the large potential of this new method.

Finally, we can also use the STM to measure electron transport through individual upright standing nanowires still on their growth substrate: After imaging the nanowires from top by STM [3], a point contact between the STM tip and the Au particle on top of the nanowire can be established in ultrahigh vacuum, thereby overcoming the problems in contacting single nanowires known from conventional setups. A high accuracy and reproducibility of this method has been demonstrated for InP and InAs nanowires with different doping levels [4] as well as for Schottky barrier measurements on Au/GaAs nanowires.

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10:40am **ET+NS+EM-ThM9 Point-Contact Spectroscopy Study of Topological Insulators and Superconductors**, Z. Jiang, Georgia Institute of Technology

Recently, much attention has been given to an intriguing class of materials, the so-called topological insulators. This type of material exhibits a band gap in the bulk, but gapless states on the edge or surface, which are protected by topological order and cannot be analogized to previous conventional semiconductors or insulators. When topological insulators are in contact with a superconductor (e.g., Nb, a conventional s -wave superconductor), novel proximity effect occurs. Theory predicts that the proximity induced superconducting state is spinless and p -wave like, and Majorana bound states may appear at the edges. On the other hand, in a related research avenue topological superconductors are predicted to possess unconventional pairing symmetries and gapless surface Andreev bound states. Theoretically massless Majorana fermions could be realized in such materials and used as a building block for topological quantum computation.

Here we present our point-contact spectroscopy studies of topological insulators and superconductors. Specifically, we use a superconducting Nb tip to approach the surface of topological insulators and measure the interface conductance as a function of bias voltage, temperature and magnetic field. Indeed, we find that a superconducting state can be induced at the interface when the Nb tip is in good contact with the topological insulator, as evidenced by observation of a zero-bias conductance peak in the point-contact spectra at a temperature below the superconducting transition temperature of Nb. Such an induced superconducting state is robust even in a magnetic field up to 1T. In the study of topological superconductors, we use a normal-metal Au tip to approach the surface, and a zero-bias conductance peak is also observed. Owing to accurate control of the point-contact barrier strength (tip/sample) in our experiments, the obtained spectra are free of artificial background, and therefore can be quantitatively compared with existing theories; good agreement is achieved.

11:00am **ET+NS+EM-ThM10 Identifying and Measuring the State Variables in TaOx Memristors**, P.R. Mickel, M. Marinella, C.D. James, Sandia National Laboratories

We present evidence of the identification and characterization of a new state variable in TaOx memristors. Thus far, the state variable controlling the resistive switching has been believed to be the oxygen concentration in the conducting Ta filament. However, using voltage pulse measurements sensitive to small changes in resistance, we shown that the changing area of the conducting filament is in fact the dominant switching mechanism. The oxygen concentration in the Ta filament is shown to control the memristor

resistance for low resistances, after which we observe a clear crossover to the area state variable dominated resistance range. Voltage and temperature dependence are investigated for the switching time-scales, τ , and magnitudes of filament area change, providing insight into their driving mechanisms and the resolution limits of their modulation.

11:20am **ET+NS+EM-ThM11 Terahertz Spectroscopy and Carrier Dynamics of Al Doped ZnO Nanowires**, S. Balci, W. Baughman, D.S. Wilbert, G. Shen, N. Dawahre, P. Kung, S.M. Kim, The University of Alabama

Terahertz time domain spectroscopy (THz-TDS) has been widely investigated for many applications in sensing and imaging technologies over the past two decades. Terahertz wave, with a frequency between 300GHz to 10THz, is especially attractive for various applications including security monitoring, biomedical imaging, high speed electronics and communications, and chemical and biological sensing. There is also an increasing interest for nondestructive testing using the THz waves because they have unique properties of propagation through certain media and cover a number of important frequencies. For such applications, THz-TDS has become a powerful tool and measurement technique that can probe carrier dynamics at high frequencies, and thus may yield a better understanding of the characteristics of high frequency optoelectronics and many other fundamental properties of materials. Using THz-TDS, one can determine the frequency dependence of basic properties of materials, including their complex dielectric constant, refractive index and electrical conductivity. Unlike conventional Fourier-Transform spectroscopy, THz-TDS is sensitive to both the amplitude and the phase of the wave, thereby allowing for a direct approach to determining complex values of material parameters with the advantage of high signal to noise ratio and coherent detection. In addition, it is possible to carry out THz-TDS experiments without any electrical contact to the sample being probed, which significantly facilitates electrical measurements on nanostructures and nanomaterials.

In this work, we investigated the physical properties of ZnO:Al nanowires (NWs) in using THz-TDS both at room temperature and elevated temperatures for the first time. ZnO NWs were grown by thermal chemical vapor deposition and in-situ doped with Al, which increased their electrical conductivity by one order of magnitude compared to undoped nanowires. THz-TDS measurements yielded the relative change in the transmitted THz electric field magnitude and phase caused by the samples being probed, which was used to extract the nanowire material refractive indices through mathematical iterative calculations. These subsequently allowed a determination of the complex conductivity, refractive index, and absorption coefficient. To obtain the carrier dynamics parameters, we showed that the Drude-Smith model had to be applied to the frequency dependent complex conductivity in order to determine the plasma frequency and relaxation time. To gain a better understanding of the dependence on doping, the measurements were performed for both undoped ZnO NWs and Al-doped ZnO NWs, as well as a function of temperature in each case.

11:40am **ET+NS+EM-ThM12 Probing Surface-Independent Minority Carrier Transport in Semiconductor Nanowires using Kelvin Probe Microscopy**, A. Soudi, C. Hsu, Y. Gu, Washington State University

In advancing semiconductor nanowire-based device technologies, a quantitative knowledge of carrier transport properties is required for a rational design of devices with controlled performance. The one-dimensional confinement of charge carriers and phonons can lead to novel transport properties, and thus represents an advantage of semiconductor nanowires in electronic and opto-electronic applications. However, due to the high surface-to-volume ratio, surface effects are prevalent in nanowires, and the measured carrier transport properties are usually dominated by surface-related processes, such as carrier trapping and recombination processes facilitated by surface states. To evaluate the intrinsic transport properties, especially those related to the confinement effects, the capability to probe surface-independent carrier transport properties is desired. Here we present studies of bulk limited minority carrier transport properties in semiconductor nanowires using the scanning Kelvin probe microscopy technique. Specifically, by measuring and modeling the spatial variations of the nanowire surface potential close to a nanowire-metal Schottky junction, both under an above-bandgap illumination and in the dark, the surface-independent minority carrier diffusion length was obtained.

Thursday Afternoon, November 1, 2012

Electron Transport at the Nanoscale Focus Topic

Room: 16 - Session ET+SS+GR+SP-ThA

Electron Transport at the Nanoscale: Molecules and Defects

Moderator: S. Allen, The University of Nottingham, UK, J. Wendelken, Oak Ridge National Laboratory

2:00pm **ET+SS+GR+SP-ThA1 Molecule Substrate Interactions Probed by Scanning Tunneling Microscopy, H.-J. Gao, Chinese Academy of Sciences** **INVITED**

Molecule substrate interactions play an important role in constructing nanostructures of functionalities and controlling of the physical properties and thus have stimulated a great interest in the past decades. One of the challenges in this top is to make a single molecule or small quantum systems stably connected to a single metal atom on metal surfaces, and further to make the nanostructure create electric energy and optical/electro radiation. In the talk, I will present that by using Au adatoms of the Au(111) surface we have successfully formed a single molecule rotor array, isolated tetra-*tert*-butyl Zinc Phthalocyanine ((*t*-Bu)₄-ZnPc) molecules sticking to the Au adatoms of the Au(111) and rotating on the surface at 78 K. This kind of single molecular rotor was also found to be controlled by the different sites of the Au(111) surface using low temperature scanning tunneling microscopy (STM). Furthermore, by changing the molecular structure the same molecular family of the Pc, ZnPc and FePc can also modulate the rotation behavior of the molecular rotors. Given that the lateral structure of a molecule/substrate interface can be modified by the attachment of ligands, our results will be helpful for opening up the possibility to tailor physical properties of a single molecule or complex aggregates to the desired specifications.

2:40pm **ET+SS+GR+SP-ThA3 Electron Localization in Single Mixed-Valence Molecules, R.C. Quardokus, N.A. Wasio, Y. Lu, S.A. Kandel, University of Notre Dame**

Scanning tunneling microscopy (STM) is used to study two dinuclear organometallic molecules, meta-Fe₂ and para-Fe₂. These molecules share identical molecular formulas but differ in their positions of connectivity to the central phenyl ring. STM images of neutral meta-Fe₂ and para-Fe₂ show symmetrical distribution of electron density across the two metal centers. Chemical oxidation of these molecules leads to mixed-valence species. STM images of mixed-valence meta-Fe₂ show an asymmetric distribution of the electron density between the two metal centers. Despite the greater distance between the two metal centers, the electron density remains symmetric in mixed-valence para-Fe₂. Comparison with constrained density functional (CDFT) calculations leads to the conclusion that through-bond coupling of the two metal centers is more prevalent than through-space coupling. Further investigation of mixed-valence dinuclear organometallic molecules with asymmetric electron state density may open up the possibility for their use in molecularly based electronic devices.

3:00pm **ET+SS+GR+SP-ThA4 Rectification by a Single Molecular Diode, L. Adamska, University of South Florida, M. Kozhushner, Institute of Chemical Physics, Russian Academy of Sciences, I.I. Oleynik, University of South Florida**

Single-molecule rectification has been recently observed using the STM modulated break-junction technique in non-symmetric diblock dipyrimidinyl-diphenyl molecule covalently bound to metallic electrodes. To provide an insight to the nature of the rectification, first-principles calculations of atomic, electronic and transport properties of gold/molecule/gold junctions have been performed for both symmetrical tetraphenyl and asymmetrical dipyrimidinyl-diphenyl diblock molecules. The charge transport was found to occur by hole resonant tunneling mechanism via positively-charged hole states of the molecule, which are very susceptible to the external electric field and dispersive interactions with the metallic electrodes. It was found that the rectification effect in chemically-asymmetric dipyrimidinyl-diphenyl molecule is due to strong localization of the hole wave function at one end of the diblock under applied electric field. Such behavior is contrasted by symmetric I-V curves exhibited by symmetric tetraphenyl molecule.

3:40pm **ET+SS+GR+SP-ThA6 Electron Transport Study of Graphene Grain Boundaries Using Scanning Tunneling Potentiometry, K. Clark, X.-G. Zhang, I. Vlasiouk, A.-P. Li, Oak Ridge National Laboratory**

Graphene, due to its unique electronic structures, has quickly become one of the most notable "super-materials" poised to transform the electronics and nanotechnology landscape. The symmetry of the graphene honeycomb lattice is a key element for determining many of graphene's unique electronic properties, such as the linear energy-momentum dispersion and the reduced backscattering (i.e., high carrier mobility). However, topological lattice defects, such as grain boundaries and step edges, break the sublattice symmetry and can affect the electronic properties, especially in transport of graphene in unexpected ways. To utilize the full potential of graphene a complete understanding of the physical and electronic properties of defects in this system is needed. By using a scanning tunneling potentiometry method with a low temperature four-probe scanning tunneling microscope, two-dimensional maps of electrochemical potentials have been measured across individual grain boundaries on the graphene films grown on copper foil and transferred to SiO₂. An Atomic Force Microscope (AFM) is implemented to image the grain boundary that forms between individual graphene flakes that grow on the surface. The AFM imaging along with scanning tunneling potentiometry characterize the grain boundaries formed between coalesced grains on the SiO₂ surface. Results of the influence of the grain boundary on the electronic transport across this potentially revolutionary new electronic system will be presented. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

4:00pm **ET+SS+GR+SP-ThA7 Static and Dynamic Conductance in Topological Defects in Ferroelectrics, S.V. Kalinin, Oak Ridge National Laboratory** **INVITED**

Topological defects in ferroic materials are attracting much attention both as a playground of unique transport, magnetic, and ferroic phenomena and due potential applications in reconfigurable electronic devices. In this presentation, I will summarize recent studies of transport phenomena in 2D (domain walls) and 1D (vortexes and antivortexes) in ferroelectric materials by combination of piezoresponse force microscopy, phase-field modelling, and density functional theory. In particular, the observations such as memory effects and hysteresis in domain wall conductance, metallic conductivity of ferroelectric walls, and conductivity in vortex cores will be discussed. For domain walls, these observations are consistent with carrier accumulation due to presence of charged wall segments. We further demonstrate that a continuum of non-volatile metallic states across decades of conductance can be encoded in the size of ferroelectric nanodomains using electric field. For vortexes, modelling predicts that the core structure can undergo a reversible transformation into a metastable twist structure, extending charged domain walls segments through the film thickness. The vortex core is therefore a dynamic conductor controlled by the coupled response of polarization and electron/mobile vacancy subsystems with external bias. This controlled creation of conductive 1D channels opens a pathway for design and implementation of integrated oxide electronic devices based on domain patterning. Finally, recent insight on domain walls structure from combination of aberration corrected scanning transmission electron microscopy and phase-field theory will be discussed. Research supported (SVK) by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division and partially performed at the Center for Nanophase Materials Sciences, a DOE-BES user facility.

4:40pm **ET+SS+GR+SP-ThA9 Transport and Mechanical Properties of Molecular Junctions formed by Acetophenon Deposited on Si (100) Surface, M. Setvin, Z. Majzik, O. Krejci, P. Hapala, P. Jelinek, Institute of Physics of ASCR, Czech Republic**

One of the main challenges of Molecular electronics is to understand and control charge transfer through a reproducible single molecule contact between electrodes. Most investigations of electron transport through molecules have been performed in "blind" junction experiments, where the molecular conformation and contact geometry cannot be probed. Therefore large gaps in our knowledge remains since in molecular electronics the atomic-scale structure of the entire junction including the leads is important for its conductance properties.

Our goal is to study electrical transport through well-defined molecular junction on semiconductor surfaces. Formation of molecular junctions using organic molecules on semiconductor surfaces might lead to interesting phenomena. For example, the presence of the band gap in electrodes can

lead to the negative differential resistance observed in transport through molecules bonded to dangling-bond sites[1].

In this contribution, we investigate formation of molecular junction consisting of a single acetophenone molecule deposited on Si(100) surface in upright position by means of simultaneous AFM/STM measurements and DFT calculations. We used a modified UHV VT STM/AFM Omicron machine allowing simultaneous acquisition of the current and forces with atomic resolution using a tuning fork sensor[2]. The simultaneous acquisition of the tunneling current and force during tip approach allows precise control of contact formation and its consequence on the charge transport through molecular junction[3]. On other hand, DFT simulations provide more insight into interaction mechanism between probe and molecule. It also helps to understand induced structural and electronic relaxations during tip approach.

References

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5:00pm ET+SS+GR+SP-ThA10 Experimental Determination of the Charge Neutrality Level (CNL) of Conjugated Polymers, *W. Wang, R. Schlaf*, University of South Florida

The charge neutrality levels (CNL) of poly-(3-hexylthiophene) (P3HT) and poly-[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) were determined. This was achieved by investigating a number of interfaces between these conjugated polymers and metals with varying work function. The interfaces were fabricated using the electrospray deposition technique, which allows the direct deposition of polymers from solution into vacuum environment without interference of significant surface contamination. This enabled the measurement of the charge injection barriers at clean polymer interfaces without contamination interlayer with photoemission spectroscopy. The results of these measurements enabled the establishment of the correlation between barrier heights and substrate. The results indicate that conjugated polymer interfaces form in a similar fashion as small molecular materials interfaces to metals as described by the 'induced density of states' (IDIS) model. In contrast, the presented results also suggest that the 'integer charge transfer' (ICT) model, which was developed for polymer/metal interfaces, only describes interfaces prepared under atmosphere or inert environment, where the presence of contamination weakens the interaction between the materials in contact.

5:20pm ET+SS+GR+SP-ThA11 Investigation on the Electronic Structure of Arylthio (ArS)-functionalized CdSe Nanoparticle Hybrid Materials, *Z. Li*, University of South Florida, *K. Mazzi*, University of Washington, *S. Gutmann*, University of South Florida, *C.K. Luscombe*, University of Washington, *R. Schlaf*, University of South Florida

CdSe nanoparticles are a promising material for 3D heterojunction solar cells due to their tunable electronic and optical properties through size control. By covalently bonding these nanoparticles to organic ligands, a novel light absorption, charge separation and transportation system can be formed. This presentation will discuss efforts to measure the hybrid-internal orbital line-up at the nanoparticle/ligand junction. Photoemission spectroscopy was used to characterize a prototypical arylthio (ArS)-functionalized CdSe molecule nanoparticle/ligand hybrid. Generally, in such hybrid molecules, the highest occupied molecular orbital (HOMO) emission is a superposition of the emissions of the nanoparticles and that of the organic ligands. This superposition makes the direct study of the orbital line-up through PES measurements impossible. Hence, a new technique needed to be developed to delineate the orbital line-up at such inner-molecular contacts. This was achieved through the additional investigation of the isolated components, which yielded detailed information of their electronic structure. Combination of this data with measurements on the assembled hybrid molecules enabled the determination of the orbital line-up at the interface. The influence of the covalent bond on the orbital line-up was investigated by comparing the hybrid line-up with the electronic structure of a physisorbed interface formed between the hybrid components. This interface was prepared through in-vacuum electrospray deposition of a thin film sandwich of CdSe and ArSH films, while measuring the transition from the CdSe to the ArSH electronic structure.

Thursday Afternoon Poster Sessions

Electron Transport at the Nanoscale Focus Topic

Room: Central Hall - Session ET-ThP

Electron Transport at the Nanoscale Poster Session

ET-ThP1 The Performance of Organic Light-Emitting Diodes with Rb₂CO₃-doped Alq₃ Layer for Improving Carrier-Injecting Probability.
J.W. Park, J.T. Lim, J.S. Oh, G.Y. Yeom, Sungkyunkwan University, Republic of Korea

Organic light-emitting diodes (OLEDs) is strongly influenced by both the injection barrier height and the number of carriers in the metal/organic contact formed between the Fermi levels (EF) of the electrodes and the relevant levels for conduction in the OLED.

In this study, this study elucidates the enhancement of the optoelectronic properties of OLEDs by n-doping effect of rubidium carbonate (Rb₂CO₃)-doped tris(8-quinolinolato)aluminum (III) (Alq₃). The device performance strongly depends on both doping concentrations of the Rb₂CO₃-doped Alq₃ layer and the thickness. As the doping concentration is increased from 2.5% to 50%, the electron ohmic properties of the electron-only device with the glass/ITO/ Rb₂CO₃-doped Alq₃ (10 nm)/Al structure were improved at doping concentration of 10%, due to the increase in the *n*-type doping effect. However, the Alq₃ molecules were decomposed above the doping concentration of 10%. Also, the photoemission spectra revealed that the *n*-type doping effect cause the lowering of the electron-injecting barrier height, as well as the improvement of the electron conductivity. The OLED with the glass/ITO/MOOX-doped NPB (25%, 5 nm)/NPB (63 nm)/Alq₃ (32 nm)/ Rb₂CO₃-doped Alq₃ (10%, 10 nm)/Al (100 nm) structure showed both a high maximum luminance of 114,400 cd/m² at 9.8 V and a high power efficiency of 2.7 lm/W at about a luminance of 1000 cd/m².

Friday Morning, November 2, 2012

Electron Transport at the Nanoscale Focus Topic

Room: 16 - Session ET+SS+GR+SP-FrM

Electron Transport at the Nanoscale: Development of Theories and Techniques

Moderator: C. Su, Bruker Nano

8:20am **ET+SS+GR+SP-FrM1 What is Missing in the Space Charge Limited Current Theory?**, X.-G. Zhang, Oak Ridge National Laboratory, S.T. Pantelides, Vanderbilt University **INVITED**

Space-charge-limited currents are important in energy devices such as solar cells and light-emitting diodes, but the available theory from the 1950's finds it necessary to postulate defect states that are distributed in energy in order to match data. This has prevented the theory to be used in extracting reliable defect information such as energy level and trap density from measurements. Here we revisit the theory and show that this postulate is not warranted. Instead, we demonstrate that dopants and the concomitant Frenkel effect, which have been neglected, control the shape of measured current-voltage characteristics. For highly disordered material, there is a significant inter-trap tunnelling current in the Ohmic regime, which accounts for the observed peak in the noise power. The new theory can anchor efforts to develop experimental techniques to measure deep-trap levels.

This research was conducted at the Center for Nanophase Materials Sciences, sponsored at ORNL by the Division of Scientific User Facilities (XGZ), and by Division of Material Science and Engineering, Basic Energy Sciences, U.S. Department of Energy (STP), and the McMinn Endowment at Vanderbilt University (STP).

9:00am **ET+SS+GR+SP-FrM3 Mapping Solar Cell Internal Fields and Band Offsets**, H. Cohen, Y. Izhaik, G. Hodes, Weizmann Institute of Science, Israel

The internal fields and band offsets across device interfaces are key features in various applications and, yet, this information is generally inaccessible by standard electrical tools. A systematic approach addressing this problem is demonstrated here, based on chemically resolved electrical measurements (CREM). Studying nanoporous photovoltaic cells, we resolve the internal details layer-by-layer and, thus, extract a realistic band diagram for the multi-interfacial structure. We show the spontaneous evolution of two p-n-like junctions and quantify the associated band bending at corresponding domains. An account for the 'real' working conditions of the device is attempted by exposing the cell to optical and electrical stimuli, revealing the charge trapping at each specific layer and showing how certain sample treatments affect the trapping mechanisms. Our methodology overcomes a critical missing link in device characterization and in fundamental studies of nanoscale solid-state devices.

9:20am **ET+SS+GR+SP-FrM4 Quantum Degeneracy Revealed by the Relation between the Tunneling Current and the Chemical Force**, P. Jelinek, M. Ondracek, Institute of Physics of ASCR, Czech Republic, F. Flores, Universidad Autonoma de Madrid, Spain

Recent progress has allowed merging AFM and STM into a new experimental setup where tunneling current and atomic forces are recorded simultaneously. The possibility to collect both quantities simultaneously opens new horizons not only in advanced characterization at the atomic scale but also in understanding fundamental relations between the electron transfer and formation of the chemical bond between two bodies.

Actually, there is a long-standing debate in the scientific community about the relation between the chemical force and the tunneling current (see e.g. [1]) on the atomic scale. Both the tunneling current and the short-range component of the force, induced by the formation of the chemical bond, exhibit in atomic contacts an exponential decay with increasing distance in the range of several angstroms. As the quantities depend directly on the wave-function overlap between outermost atoms of tip and surface, the corresponding exponential functions should have similar characteristic decay length. In particular, the relation between the chemical force F and the tunneling current I follows the law $F^n \sim I$, where n is an integer number. Over the last 10 years, several different scaling factors n , varying from 1 to 4, have been proposed by different groups based on both theoretical analysis and experimental measurements (see reference in [2]); still there is no consensus on the relation between the chemical force and the tunneling current.

In this contribution, we explain the relation between the tunneling current and the interaction force at the atomic scale using a simple analytical model

[2]. The model unveils the existence of two characteristic scaling regimes, where the tunneling current is either proportional to the chemical force $I \sim F$ or to the square of the chemical force, i.e. $I \sim F^2$. We show that the existence of a given regime is basically controlled by two parameters: (i) the electronic level degeneracy and (ii) the hopping between electronic levels involved in the interaction process. Finally, we will collate our theoretical prediction with experimental AFM/STM measurements of single-atom point contacts and complex DFT simulations [3] to confirm the existence of these two characteristic regimes.

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9:40am **ET+SS+GR+SP-FrM5 Understanding the Influence of the Tunneling Current and the Chemical Force on the Contrast Formation in KPFM**, Z. Majzik, M. Ondráček, M. Švec, J. Berger, P. Jelinek, Institute of Physics of ASCR, Czech Republic

Kelvin Probe Force Microscopy (KPFM) [1] senses the variation in the electrostatic force. The electrostatic force is $F_{el} = -dCTS/dz(V_{bias} - V_{lcpd})^2$, where V_{lcpd} denotes to the local contact potential difference (LCPD). Atomic scale resolution was achieved by KPFM on the prototypical Si(111)- 7×7 surface [2]. It was shown that the formation of a chemical bond between the closest tip-surface atoms induces significant variation in the LCPD [2]. Lately it was observed that the tunneling current leads to the raise of an additional electrostatic (phantom) force [3]. Consequently, the total electrostatic force must be the combination of several components where the contribution of each component is defined by the tip-sample separation.

Recent progress in Scanning Probe Microscopy opens the possibility of simultaneous acquisition of the tunneling current, atomic forces and local potential difference with atomic resolution [4]. The aim of this contribution is to discuss the origin of electrostatic force contribution at different tip-sample separations. In particular, we performed simultaneous site-specific AFM/STM measurements on Si(111)- 7×7 using a modified Omicron qPlus (tuning fork based) system [5]. We found that along the tip approach three characteristic regions can be well distinguished. At large tip-sample separations, the capacitance is a function of tip geometry and the tip-sample distance. Approaching the tip closer towards the surface, quantum effects become to play important role. The overlap between the tip and sample wave functions produces electron tunneling, which induces additional electrostatic force. Formation of the chemical interaction between the tip apex atom and the adatoms of the 7×7 surface induces changes in the electron charge distribution reflected in variation of the LCPD [2] and the permittivity in the tunneling gap. Hence the capacitance is modified accordingly. In order to have better understanding of the impact of the chemical interaction, atomic hydrogen was deposited to saturate the dangling bonds of adatoms. Over the hydrogenated adatoms, nor strong shift in the LCPD or sudden change in the capacitance was observed. Further to gain more insight into ongoing processes we carried out DFT calculations for tip-sample interaction to understand affect of the formation of covalent bond between tip apex and surface adatoms on the Si 7×7 surface.

References

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10:00am **ET+SS+GR+SP-FrM6 An In Situ Technique for Using Ballistic Electron Emission Microscopy to Measure Hot Electron Transport at Metal Semiconductor Interfaces**, R. Ralsano, V.P. LaBella, University at Albany-SUNY

Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM) technique that can measure transport of hot electrons through materials and interfaces with high spatial and energetic resolution. BEEM requires an additional contact to ground the metal base layer of a metal semiconductor junction. Performing BEEM *in situ* with the sample fabrication requires a custom built STM or modifying a commercial one to facilitate the extra contact, which leaves the technique to highly trained experts. This presentation will describe our work to develop a special silicon substrate that has the extra contact and oxide hard mask built in to enable *in situ* BEEM without modifications to the STM. Electrically

isolated contact traces are lithographically patterned *ex situ* onto the silicon substrate. Then a hard mask is grown and lithographically patterned and connected to the BEEM sample plate which is then inserted into the ultra-high vacuum chamber. The metal is then deposited on top of the hard mask and then mounted *in situ* onto the STM for BEEM measurements. BEEM measurements comparing both *in situ* and *ex situ* deposited films will be presented.

10:20am **ET+SS+GR+SP-FrM7 Electronic Transport on the Nanoscale, R. Moeller**, University of Duisburg-Essen, Germany **INVITED**

To study the transport through objects at the nanoscale a scanning tunneling microscope with several tips is used. Two different configurations will be discussed. The lateral transport of electrons may be studied by using two tips to drive a current parallel to the surface. A third tip enables to map the corresponding electrochemical potential. Measurements for a 2D conducting layer will be discussed. To analyze the transport perpendicular to the surface, a thin metallic layer is placed on a semiconducting surface. At the interface a Schottky barrier is formed, which can only be overcome by electrons of sufficient energy. This may be used to split the current of electrons coming from the tip of the microscope into two parts, the ballistic electrons and the electrons which have been scattered. This technique has been applied to study the ballistic transport of electrons through individual molecules. On the other hand inelastic processes may be revealed by analyzing the fluctuations in the tunneling current observed at different positions of the tunneling tip above an adsorbed molecule.

Graphene and Related Materials Focus Topic

Room: 13 - Session GR+EM+ET+MS+NS-FrM

Graphene Device Physics and Applications

Moderator: A. Turchanin, University of Bielefeld, Germany

8:20am **GR+EM+ET+MS+NS-FrM1 Heterointegration of Graphene with Nano and Molecular Scale Structures for High Performance Devices, X. Duan**, University of California, Los Angeles **INVITED**

Nanoscale integration of dissimilar materials with distinct compositions, structures and properties has the potential to create a new generation of integrated systems with unique functions and/or unprecedented performance to break the boundaries of traditional technologies. In this talk, I will focus my discussion on the heterointegration of graphene with a variety of nano and molecular scale structures of designed architectures to open up exciting opportunities for nanoscale device engineering. In particular, I will discuss our recent effort in integrating graphene with a self-aligned nanowire gate to create the highest speed graphene transistors, integrating graphene with plasmonic nanostructures to create multi-color high speed photodetectors, integrating graphene with nanoscale templates for the creation of graphene nanostructures, and integrating graphene with various π -conjugating molecular systems for band gap engineering and molecular sensing.

9:00am **GR+EM+ET+MS+NS-FrM3 Graphene RF: From Fundamentals to Opportunities, J.S. Moon, H.-C. Seo, M. Antcliffe, S. Lin, A. Schmitz, D. Le, C. McGuire, D. Zehnder**, HRL Laboratories LLC, L.O. Nyakiti, V.D. Wheeler, R.L. Myers-Ward, C.R. Eddy, Jr., D.K. Gaskill, P.M. Campbell, Naval Research Laboratory, K.-M. Lee, P. Asbeck, UC San Diego **INVITED**

Graphene is a topic of very active research from basic science to potential applications. Various RF circuit applications are under evaluation, which include low-noise amplifiers, frequency multipliers, mixers and high-speed radiometers. Potential integration of graphene on Silicon substrates with CMOS compatibility would also benefit future RF systems. The future success of the RF circuit applications depends on vertical and lateral scaling of graphene MOSFETs to minimize parasitics and improve gate modulation efficiency in the channel. In this presentation, we highlight recent progress in graphene materials and devices. For example, with hydrogen intercalation, a graphene wafer showed an electron mobility of 2500 cm²/Vs at 6.8 x 10¹²/cm² carrier density, and sheet resistance of 230 ohm/square. The Ti-based ohmic contact resistance is below 100 ohm* μ m and hysteresis in HfO₂/Graphene MOSFET transfer curves are no longer concerns in RF applications. We will show graphene MOSFETs in mixer and detector applications with performances comparable to and better than the current state-of-the-art technologies. Also, we will present recent progress in graphene heterostructure based diodes with on/off ratio greater than 10⁶. In summary, while graphene is relatively new material, it shows a strong potential to become disruptive in RF applications.

This work was partially supported by DARPA, monitored by Dr. J. Albrecht, under SPAWAR contract number N66001-08-C-2048.

The views, opinions, and/or findings contained in this article/presentation are those of the author/presenter and should not be interpreted as representing the official views or policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the Department of Defense.

[1] J. S. Moon and D. K. Gaskill, IEEE Trans. Microwave Theory and Techniques, p. 2702, 2011

9:40am **GR+EM+ET+MS+NS-FrM5 Graphene and Dielectric Integration: A Sticky Situation?, V.D. Wheeler, N.Y. Garces, L.O. Nyakiti, R.L. Myers-Ward, D.J. Meyer**, U.S. Naval Research Laboratory, A. Nath, George Mason University, C.R. Eddy, Jr., D.K. Gaskill, U.S. Naval Research Laboratory **INVITED**

Scalable high- κ dielectric integration is needed to realize graphene-based THz transistors. Yet, the inert nature of graphene inhibits direct application of high-quality uniform atomic layer deposition (ALD) dielectrics. While several methods have rendered the surface more susceptible to ALD[1], they often degrade mobility and/or shift the Dirac voltage due to charges within the gate stack. Recently, we developed a dry chemical functionalization approach using XeF₂ that results in conformal, thin high- κ ALD oxide films with a 10-25% improvement in graphene mobility[2], high dielectric constants (HfO₂=18.5, Al₂O₃=8.9), and small Dirac voltage shifts (HfO₂=2V, Al₂O₃=0.1V), indicating the effectiveness of F functionalization. We will present in-depth details of our fluorination process, discuss its advantages and limitations with respect to other methods used to enhance ALD reactivity with graphene, and provide future directions for this field of study.

Fluorination of EG surfaces was performed in a Xactix X3 XeF₂ etcher operating in pulse mode. Results show that 15 nm pinhole-free Al₂O₃ and HfO₂ films are obtained with an optimized XeF₂ surface treatment prior to ALD consisting of six, 20s pulses (XeF₂=1 torr, N₂=35 torr). This optimal treatment resulted in ~6% fluorine surface coverage, as semi-ionic C-F bonds (F1s ~687eV) only, which provided additional ALD reaction sites needed to obtain uniform oxide films. This unique semi-ionic nature of the C-F bond allows the graphene lattice to maintain planarity and minimize degradation to transport properties.

Theoretical studies suggest that the semi-ionic nature of the C-F bond is related to the graphene electron sheet carrier density (n_e), requiring at least 10¹³ cm⁻² to form[3]. To test this, EG samples with similar thickness but varying n_e (2x10¹²-1.3x10¹³ cm⁻²) were fluorinated simultaneously using the optimal conditions above. Samples with $n_e > 1 \times 10^{13}$ cm⁻² had only semi-ionic C-F bonding, but those with $n_e < 1 \times 10^{13}$ cm⁻² had both covalent and semi-ionic bonding – verifying the theoretical calculations. The amount of covalent bonding increased as n_e decreased, and an increased pinhole density was seen in subsequent Al₂O₃ films. This implies that the underlying EG properties can impact the effectiveness of this fluorination method. Yet, by adjusting the pulse conditions one can tailor this method to still obtain uniform ALD oxides on low carrier density and even p-type EG. To this end, results of our XeF₂ approach on p-type H₂ intercalated EG samples will be shown.

1. Garces, et.al. *JVST B* **30(3)** 03D104 (2012)
2. Wheeler, et.al. *Carbon* **50** 2307 (2012)
3. Sofo, et.al. *Phys Rev B* **83(8)** 081411(R) (2011)

10:20am **GR+EM+ET+MS+NS-FrM7 Achieving Scaled Dielectrics on Graphene Using Atomic Layer Deposition, S. Jandhyala, G. Mordi, R.M. Wallace, J. Kim**, University of Texas at Dallas

In order to realize high-performance graphene-based field-effect-devices, local gating of graphene channel is one of the foremost requirements [1]. Therefore, deposition of high-quality, scalable dielectrics on graphene is required. The ability to precisely control thickness and conformally deposit materials makes atomic layer deposition (ALD) an ideal technique for achieving such dielectrics [2]. However, ALD is a surface-reaction limited process [2] and graphene, being sp² bonded, has no *out-of-plane* covalent functional groups [3] and this can cause difficulties in initiating the ALD reaction [4]. In previous studies we have shown that using a reversibly physisorbed ozone (O₃) functionalization approach, we can deposit high quality ALD oxides (such as Al₂O₃) on graphene with thicknesses below 5 nm [5]. Further understanding regarding the interaction of O₃ and metal precursors with graphene is required for successfully applying the ozone process to deposit different oxides.

In this study, we will use *in-situ* electrical measurements of graphene devices inside an ALD chamber as a characterization technique in order to understand the adhesion mechanisms of oxidants (such as O₃ and H₂O) and

metal precursors (such as trimethylaluminum-TMA, titanium tetrachloride-TiCl₄) on graphene surfaces. The characterization scheme used is packaged back-gated graphene-FETs which can detect the molecules adsorbed on the graphene surface. We will compare exfoliated graphene and chemical vapor deposited (CVD) graphene (which tends to have a higher number of defect sites). Using such *real-time* electrical measurements, the observed charge scattering mechanisms and the effect on mobility and doping due to the interaction of these molecules with graphene will be presented.

Acknowledgement

This work was funded through the South West Academy of Nanoelectronics (SWAN) program of NRI under SRC.

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- [4] L. Liao, X. Duan, *Mat. Sci. Eng. R* 70 (3-6), pp. 354-370, (2010)
- [5] S. Jandhyala, et al., *ACS Nano*, 6 (3), pp. 2722-2730 (2012)

10:40am **GR+EM+ET+MS+NS-FrM8 Atomically-Smooth MgO Films Grown on Epitaxial Graphene by Pulsed Laser Deposition.** *S.C. Stuart, A.A. Sandin*, North Carolina State University, *O. Nayfeh, M.D. Dubey*, Army Research Laboratory, *J.E. Rowe, D.B. Dougherty*, North Carolina State University, *M.D. Ulrich*, Army Research Office

The growth of high quality insulating films on graphene is a crucial materials science task for the development of graphene-based spintronics because graphene is a potentially revolutionary material for electronic and spintronic applications. For efficient spin-injection, graphene is expected to suffer from the well known “conductivity mismatch” problem at metal-semiconductor spin electrode interfaces. The standard approach to mitigating this problem has been to grow thin, insulating tunnel barriers between the graphene and the magnetic metallic electrode to provide a spin-dependent resistance via the tunneling magnetoresistance effect. It has been demonstrated by several experiments that direct spin injection from a magnetic electrode to graphene is possible but using aluminum oxide or MgO tunnel barriers to assist injection in graphene spin-valve devices is more efficient if suitable oxide-graphene interfaces can be formed. To address this problem we have used pulsed laser deposition (PLD) to grow thin (1-1000 nm) magnesium oxide films directly on epitaxial graphene on SiC(0001). We observe very smooth film morphologies (typical rms roughness of ~0.4 nm) that are nearly independent of film thickness and conform to the substrate surface which had ~0.2 nm rms roughness. Surface roughness is less than 0.5 nm for thicknesses up to 1000 nm and is independent of deposition laser pulse energy within the range 300-700 mJ/pulse at rates of 1-50 Hz. X-ray diffraction shows predominant (111) and (100) orientations, indicating the possibility of doping the graphene by the polar (111) interface. Raman spectroscopy indicates that the graphene is not measurably damaged by magnesium oxide growth. This work shows that PLD is a good technique to produce graphene-oxide interfaces without pre-deposition of an adhesion layer. The films are free of defects or pinholes (that can be observed by atomic force microscopy) and can be grown at arbitrary thicknesses without increasing the roughness or damaging the graphene. The details and kinetics of the deposition process will be described with comparisons being made to other dielectric-on-graphene deposition approaches.

11:00am **GR+EM+ET+MS+NS-FrM9 Facile, Controllable Graphene-based P-N Junctions Using Self-Assembled Monolayers.** *J. Baltazar, H. Sojoudi, J. Kowalik, L. Tolbert, S. Graham, C.L. Henderson*, Georgia Institute of Technology

In this study we investigate the use of a self-assembled monolayer (SAM) to create a p-n junction in graphene films. Previous techniques rely on charge transfer from adsorbants or electrostatic gate/potentials. Here we demonstrate that, by successfully modifying the SiO₂ surface with an aminopropyltriethoxysilane (APTES) layer, and using intrinsically p-doped transferred CVD graphene films, a well-defined junction can be achieved. Field-effect transistors and p-n junction regions are fabricated prior to graphene film transfer, in order to preserve the pristine properties of the graphene. The I-V characteristic curve indicates the presence of two thermally-controllable neutrality points. This method allows a facile, controllable and low temperature fabrication of graphene p-n junctions.

11:20am **GR+EM+ET+MS+NS-FrM10 Impact of Cleaning Procedures on the Performance of Graphene-Based Field Effect Transistors.** *M. Lodge, M. Ishigami*, University of Central Florida

It is now widely accepted that surface contaminants have large effects on the performance of graphene-based field effect transistors. Various techniques are now available to clean processing residues from graphene, yet some of these techniques are chemically aggressive leaving concerns that they may damage graphene and affect the device performance. In addition, there are no consensus on the best method to produce the cleanest and, therefore, the best graphene devices.

Here, we have performed a study on the impact of various chemical treatments on the performance of field effect transistors fabricated from graphene grown using chemical vapor deposition. By measuring the impact of hydrogen-annealing, oxygen-annealing, and various solvent-based cleaning on 50 graphene field effect transistors, we generate a statistically-significant conclusion on the best cleaning technique for producing the highest performance. We will present our results along with our scanning tunneling microscopy images and Raman spectra to shed a light on the mechanism involved in each cleaning technique.

11:40am **GR+EM+ET+MS+NS-FrM11 High Efficiency Graphene Solar Cells by Chemical Doping.** *X. Miao, S. Tongay, M.K. Petterson, K. Berke, A.G. Rinzler, B.R. Appleton, A.F. Hebard*, University of Florida

We demonstrate single layer graphene/n-Si Schottky junction solar cells that under AM1.5 illumination exhibit a power conversion efficiency (PCE) of 8.6%. This performance, achieved by doping the graphene with bis(trifluoromethanesulfonyl)amide, exceeds the native (undoped) device performance by a factor of 4.5 and is the **highest PCE** reported for graphene-based solar cells to date. Current-voltage, capacitance-voltage, and external quantum efficiency measurements show the enhancement to be due to the doping-induced shift in the graphene chemical potential that increases the graphene carrier density (decreasing the cell series resistance) and increases the cell's built-in potential (increasing the open circuit voltage) both of which improve the solar cell fill factor.

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 — M —
 Ma, Q.: SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5, 8
 Magnone, K.:
 SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5, 8
 Majzik, Z.: ET+SS+GR+SP-FrM5, 18;
 ET+SS+GR+SP-ThA9, 15;
 SP+AS+BI+ET+MI+NS-TuA4, 5
 Marcott, C.: SP+AS+BI+ET+MI+TF-WeA9, 12
 Marinella, M.: ET+NS+EM-ThM10, 14
 Matsumoto, K.: ET+NS+EM-ThM5, 13
 Mazzio, K.: ET+SS+GR+SP-ThA11, 16
 McCleskey, T.M.: IS+AS+OX+ET-WeM3, 7
 McGuire, C.: GR+EM+ET+MS+NS-FrM3, 19
 Mehr, T.: SP+AS+BI+ET+MI+TF-WeA11, 12
 Meng, G.W.: ET+NS+EM-ThM4, 13
 Merrill, M.D.: IS+AS+OX+ET-WeM6, 7
 Meyer, D.J.: GR+EM+ET+MS+NS-FrM5, 19
 Meyer, G.: SP+AS+BI+ET+MI+NS-TuA1, 4
 Miao, X.: GR+EM+ET+MS+NS-FrM11, 20
 Mickel, P.R.: ET+NS+EM-ThM10, 14
 Mikkelsen, A.: ET+NS+EM-ThM6, 13
 Minne, S.C.: SP+AS+BI+ET+MI+TF-WeA8, 11
 Moeller, R.: ET+SS+GR+SP-FrM7, 19
 Mohn, F.: SP+AS+BI+ET+MI+NS-TuA1, 4
 Moll, N.: SP+AS+BI+ET+MI+NS-TuA1, 4
 Mönig, H.: SP+AS+BI+ET+MI+NS-TuA10, 6
 Moon, J.S.: GR+EM+ET+MS+NS-FrM3, 19
 Mordi, G.: GR+EM+ET+MS+NS-FrM7, 19
 Morita, S.: SP+AS+BI+ET+MI+NS-TuA11, 6
 Moshar, A.: SP+AS+BI+ET+MI+TF-WeA11, 12
 Muirhead, L.: IS+AS+BI+ET+GR+NS-TuA3, 3
 Mutombo, P.: SP+AS+BI+ET+MI+NS-TuA4, 5
 Myers-Ward, R.L.: GR+EM+ET+MS+NS-FrM3, 19;
 GR+EM+ET+MS+NS-FrM5, 19;
 GR+EM+ET+NS+TF-MoA1, 1
 — N —
 Nanayakkara, S.: SP+AS+BI+ET+MI+TF-WeA4, 11
 Nath, A.: GR+EM+ET+MS+NS-FrM5, 19;
 GR+EM+ET+NS+TF-MoA1, 1
 Nayfeh, O.: GR+EM+ET+MS+NS-FrM8, 20
 Nepal, N.: GR+EM+ET+NS+TF-MoA1, 1
 Nigge, P.: IS+AS+BI+ET+GR+NS-TuA9, 4
 Nonnenmann, S.S.: SP+AS+BI+ET+MI+TF-WeA3, 11
 Nyakiti, L.O.: GR+EM+ET+MS+NS-FrM3, 19;
 GR+EM+ET+MS+NS-FrM5, 19;
 GR+EM+ET+NS+TF-MoA1, 1
 — O —
 Ogitsu, T.: IS+AS+OX+ET-WeM6, 7
 Oh, J.S.: ET-ThP1, 17
 Oleynik, I.I.: ET+SS+GR+SP-ThA4, 15
 Ondracek, M.: ET+SS+GR+SP-FrM4, 18;
 SP+AS+BI+ET+MI+NS-TuA4, 5
 Ondráček, M.: ET+SS+GR+SP-FrM5, 18
 Oppen, F.V.:
 SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM4, 8
 Ouyang, W.: ET+NS+EM-ThM3, 13

— P —
 Pan, M.H.: SP+AS+BI+ET+MI+NS-TuA12, 6
 Pantelides, S.T.: ET+SS+GR+SP-FrM1, 18
 Park, J.W.: ET-ThP1, 17
 Parkin, J.D.:
 SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM9, 9;
 SP+AS+BI+ET+MI+TF-WeA7, 11
 Pascual, J.I.:
 SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM4, 8
 Perdue, S.M.: SP+AS+BI+ET+MI+NS-TuA3, 5
 Peres, P.: IS+AS+OX+ET-WeM11, 8
 Perez Medina, G.J.: GR+EM+ET+NS+TF-MoA7, 1
 Perez, R.: SP+AS+BI+ET+MI+NS-TuA10, 6;
 SP+AS+BI+ET+MI+NS-TuA11, 6
 Perret, E.: IS+AS+OX+ET-WeM3, 7
 Persson, O.: ET+NS+EM-ThM6, 13
 Petford-Long, A.: IS+AS+BI+ET+GR+NS-TuA7, 3
 Petterson, M.K.: GR+EM+ET+MS+NS-FrM11, 20
 Pittenger, B.: SP+AS+BI+ET+MI+TF-WeA8, 11
 Pitters, J.: SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM2, 8
 Piva, P.: SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM2, 8
 Portoles, J.F.:
 SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM10, 9
 Pou, P.: SP+AS+BI+ET+MI+NS-TuA11, 6
 Prater, C.B.: SP+AS+BI+ET+MI+TF-WeA9, 12
 Proksch, R.: SP+AS+BI+ET+MI+TF-WeA11, 12
 — Q —
 Qin, S.Y.: ET+NS+EM-ThM3, 13; ET+NS+EM-ThM4, 13
 Quardokus, R.C.: ET+SS+GR+SP-ThA3, 15
 — R —
 Rahman, T.S.: GR+EM+ET+NS+TF-MoA2, 1
 Ralsano, R.: ET+SS+GR+SP-FrM6, 18
 Ratner, B.D.: IS+AS+BI+ET+GR+NS-TuA1, 3
 Revenko, I.: SP+AS+BI+ET+MI+TF-WeA11, 12
 Rinzler, A.G.: GR+EM+ET+MS+NS-FrM11, 20
 Roberts, C.J.: SP+AS+BI+ET+MI+NS-TuA9, 5
 Rodriguez Perez, A.: SP+AS+BI+ET+MI+NS-TuA3, 5
 Rodriguez, L.N.J.: IS+AS+OX+ET-WeM9, 7
 Rosa, L.: GR+EM+ET+NS+TF-MoA7, 1
 Rotenberg, E.: GR+EM+ET+NS+TF-MoA8, 2
 Routaboul, L.: GR+EM+ET+NS+TF-MoA7, 1
 Rowe, J.E.: GR+EM+ET+MS+NS-FrM8, 20
 — S —
 Sadowski, J.T.: IS+AS+BI+ET+GR+NS-TuA8, 4
 Saitoh, E.: IS+AS+OX+ET-WeM10, 8
 Sales, B.C.: SP+AS+BI+ET+MI+NS-TuA12, 6
 Salib, D.: SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5, 8
 Samuelson, L.: ET+NS+EM-ThM6, 13
 Sandin, A.A.: GR+EM+ET+MS+NS-FrM8, 20
 Sasi-Szabo, L.A.: IS+AS+BI+ET+GR+NS-TuA3, 3
 Schafer, K.C.: IS+AS+BI+ET+GR+NS-TuA3, 3
 Schlaf, R.: ET+SS+GR+SP-ThA10, 16;
 ET+SS+GR+SP-ThA11, 16
 Schmitz, A.: GR+EM+ET+MS+NS-FrM3, 19
 Schuhmacher, M.: IS+AS+OX+ET-WeM11, 8
 Schwarz, U.D.: SP+AS+BI+ET+MI+NS-TuA10, 6
 Schwendemann, T.C.: SP+AS+BI+ET+MI+NS-TuA10, 6
 Sefat, A.S.: SP+AS+BI+ET+MI+NS-TuA12, 6
 Seo, H.-C.: GR+EM+ET+MS+NS-FrM3, 19
 Setvin, M.: ET+SS+GR+SP-ThA9, 15;
 SP+AS+BI+ET+MI+NS-TuA4, 5
 Seyller, Th.: GR+EM+ET+NS+TF-MoA8, 2
 Shen, G.: ET+NS+EM-ThM11, 14
 Shepard, K.L.: GR+EM+ET+NS+TF-MoA10, 2
 Shetty, R.: SP+AS+BI+ET+MI+TF-WeA9, 12
 Shih, C.: ET+NS+EM-ThM3, 13

Sojoudi, H.: GR+EM+ET+MS+NS-FrM9, 20
 Souidi, A.: ET+NS+EM-ThM12, 14
 Stadermann, M.: IS+AS+OX+ET-WeM6, 7
 Stein, M.J.: IS+AS+BI+ET+GR+NS-TuA1, 3
 Stroschio, J.A.: GR+EM+ET+NS+TF-MoA10, 2
 Stuart, S.C.: GR+EM+ET+MS+NS-FrM8, 20
 Su, C.: SP+AS+BI+ET+MI+TF-WeA8, 11
 Sugimoto, Y.: SP+AS+BI+ET+MI+NS-TuA11, 6
 Sun, D.Z.: SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5, 8
 Švec, M.: ET+SS+GR+SP-FrM5, 18
 — T —
 Takats, Z.: IS+AS+BI+ET+GR+NS-TuA3, 3
 Tallarida, M.: IS+AS+OX+ET-WeM9, 7
 Taucer, M.:
 SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM2, 8
 Tendler, S.J.B.: SP+AS+BI+ET+MI+NS-TuA9, 5
 Thevuthasan, S.: IS+AS+BI+ET+GR+NS-TuA12, 4
 Timm, R.: ET+NS+EM-ThM6, 13
 Tivanski, A.: IS+AS+BI+ET+GR+NS-TuA9, 4
 Todorovic, M.: SP+AS+BI+ET+MI+NS-TuA10, 6
 Tolbert, L.: GR+EM+ET+MS+NS-FrM9, 20
 Tongay, S.: GR+EM+ET+MS+NS-FrM11, 20
 Tyliczszak, T.: IS+AS+BI+ET+GR+NS-TuA9, 4
 — U —
 Ulrich, M.D.: GR+EM+ET+MS+NS-FrM8, 20
 Ünverdi, Ö.: SP+AS+BI+ET+MI+NS-TuA10, 6
 — V —
 van Buuren, T.: IS+AS+OX+ET-WeM6, 7
 Van Elshocht, S.: IS+AS+OX+ET-WeM9, 7
 Vlassioux, I.: ET+SS+GR+SP-ThA6, 15
 Vohs, J.M.: SP+AS+BI+ET+MI+TF-WeA3, 11
 — W —
 Wallace, R.M.: GR+EM+ET+MS+NS-FrM7, 19
 Walter, A.: GR+EM+ET+NS+TF-MoA8, 2
 Walters, D.: SP+AS+BI+ET+MI+TF-WeA11, 12
 Wang, B.: IS+AS+BI+ET+GR+NS-TuA9, 4
 Wang, L.: GR+EM+ET+NS+TF-MoA10, 2
 Wang, W.: ET+SS+GR+SP-ThA10, 16
 Wasio, N.A.: ET+SS+GR+SP-ThA3, 15
 Waterton, C.: IS+AS+BI+ET+GR+NS-TuA1, 3
 Weitering, H.: ET+NS+EM-ThM3, 13
 Wheeler, V.D.: GR+EM+ET+MS+NS-FrM3, 19;
 GR+EM+ET+MS+NS-FrM5, 19;
 GR+EM+ET+NS+TF-MoA1, 1
 Wilbert, D.S.: ET+NS+EM-ThM11, 14
 Wittstock, A.: IS+AS+OX+ET-WeM6, 7
 Wolkow, R.A.:
 SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM2, 8
 Woll, A.R.: IS+AS+BI+ET+GR+NS-TuA2, 3
 Wood, B.C.: IS+AS+OX+ET-WeM6, 7
 Worsley, M.A.: IS+AS+OX+ET-WeM6, 7
 Wu, R.: ET+NS+EM-ThM3, 13
 Wyrick, J.: SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5, 8
 — Y —
 Yang, L.: IS+AS+BI+ET+GR+NS-TuA12, 4
 Yeom, G.Y.: ET-ThP1, 17
 Young, A.: GR+EM+ET+NS+TF-MoA10, 2
 Yu, X.-Y.: IS+AS+BI+ET+GR+NS-TuA12, 4
 Yurtsever, A.: SP+AS+BI+ET+MI+NS-TuA11, 6
 — Z —
 Zehnder, D.: GR+EM+ET+MS+NS-FrM3, 19
 Zhang, L.: GR+EM+ET+NS+TF-MoA11, 2
 Zhang, X.-G.: ET+SS+GR+SP-FrM1, 18;
 ET+SS+GR+SP-ThA6, 15
 Zhang, Y.: ET+NS+EM-ThM3, 13
 Zhao, Y.: GR+EM+ET+NS+TF-MoA10, 2
 Zhitenev, N.B.: GR+EM+ET+NS+TF-MoA10, 2
 Zhu, J.F.: GR+EM+ET+NS+TF-MoA11, 2
 Zhu, Y.: SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5, 8
 Zhu, Z.: IS+AS+BI+ET+GR+NS-TuA12, 4

