Thursday Afternoon, November 3, 2011

Surface Science Division
Room: 107 - Session SS-ThA

Semiconducting & Ferroelectric Surface

Moderator: J. Millunchik, University of Michigan

2:00pm SS-ThA1 Polarization Dependence of the Surface and Interfacial Chemistry of Ferroelectric Oxides, *E.I. Altman*, Yale University **INVITED**
In analogy to ferromagnets, ferroelectric materials develop remnant macroscopic electric fields that can be switched by applying an external field. The bulk electronic polarization is stabilized by compensating charges at the surface that can be supplied by adsorption or electronic and structural reconstructions. Because opposite compensating charges are required on oppositely poled surfaces, ferroelectric materials offer unique opportunities to create surfaces with switchable chemical properties. Further, thin ferroelectric films would be expected to switch their polarization in the presence of molecules that preferentially adsorb on one of the polar surfaces, suggesting a new avenue for chemical sensing. It will be shown that the adsorption of polar molecules such as alcohols and carboxylic acids depends on the ferroelectric polarization direction, with stronger adsorption on positively poled $LiNbO_3$. The differences in adsorption strengths are comparable to the energy required to switch 20 nm thick ferroelectric films, thus ferroelectric chemical sensing is feasible. This possibility is further explored through *in situ* measurements of changes in polarization of thin epitaxial titanate ferroelectric films in response to oxidizing and reducing environments. A limitation to switchable chemistry, however, is the low reactivity of typical ferroelectric oxides. Efforts to increase the reactivity through deposition of catalytic metals fail because the metals form three-dimensional clusters whose surfaces are too far from the ferroelectric substrate to be affected. Results of a combined experimental/theoretical approach to identifying catalytic oxides that form stable, atomically thin layers whose reactivity is influenced by the polarization direction of the ferroelectric will be presented. Specific examples include $Cr_2O_3/LiNbO_3$ and perovskite layers on ferroelectric titanates.

2:40pm SS-ThA3 Surface Reconstructions of BaTiO₃(001): STM Study, *E.H. Morales, D.A. Bonnell*, University of Pennsylvania
$BaTiO_3$ is currently used in Random Access Memories and is a versatile material with many potential applications. Ferroelectricity at a surface provides unique possibilities to examine mechanisms of molecular adsorption. Experimentally, the polarization can be manipulated in situ by negatively and positively poling the surface. In this manner, the interaction with foreign gaseous species can be controlled. It is necessary to develop fundamental understanding of $BaTiO_3$ surfaces in order to control the ferroelectric polarization and consequent interactions with adsorbates and in devices. Recent advances have indeed shown that polarization affects molecular adsorption of a variety of molecules; however, the mechanistic processes are not yet understood. Here we present STM of atomically resolved reconstructions, $(\sqrt{5}x\sqrt{5})$ R26.6°and (3×1) and relate water assoprtion to local polarization. Structural variations and adsorption sites will be discussed in terms of Density Functional Theory predictions. Preliminary results of the interaction of $BaTiO_3$ (001)'s surface and CO_2 will be presented as well.

3:00pm SS-ThA4 Polarization Dependent Interactions at Ferroelectric Surfaces, *J. Garra, M. Zhao, J.M. Vohs, E.H. Morales, D.A. Bonnell*, University of Pennsylvania
Ferroelectric polarization at surfaces has been exploited over the last several years to mediate reactions in aqueous solutions. More recently studies have shown that ferroelectric polarization at surfaces affects molecular adsorption. The study presented here uses a variety of surface techniques (scanning tunneling microscopy and spectroscopy, low energy electron diffraction, temperature programmed desorption) to examine molecular adsorption on ferroelectric surfaces. Various molecules and various substrates are chosen to determine the effect of polarization orientation and magnitude on physisorption, disassociative chemisorption, defect mediated adsorption and chemical reactions. Specifically, results of interactions of small molecules on $LiNbO_3$, and $BaTiO_3$ surfaces will be compared. We show that ferroelectric polarization can affect both physisorption and chemisorption bond energies as well as the sticking coefficients.

3:40pm SS-ThA6 An Atomic View of ALD of Dielectrics on Semiconductors Using STM, *A.C. Kummel, W. Melitz, J.B. Clemens, J.S. Lee, T. Kaufman-Osborn, T. Kent, E.A. Chagarov, J. Shen*, University of California, San Diego, *R. Droopad*, Texas State University-San Marcos **INVITED**
Scaling of gate oxides on MOSFETs requires nucleating oxide ALD in every unit cell of the semiconductor channel surface without disrupting the semiconductor surface (high mobility) while eliminating dangle bond states (low D_{it}). The reaction of TMA on the group III rich (4×2) reconstructions of the InAs(0 0 1) and InGaAs(0 0 1) surfaces were been studied using in-situ STM, scanning tunneling spectroscopy (STS), in-situ XPS, and density functional theory (DFT). When an As_2 capped III-V sample is decapped in UHV and the substrate is dosed to with TMA at 300K at annealed at 200C, the TMA reaction products (dimethyl aluminum, DMA) spontaneously forms monolayer islands insuring ALD nucleation in each unit cell. For integration of III-V MOSFETs on 300 mm silicon wafers, it is possible that a gate last process may be required for which As-decapping is not suitable. A combination of atomic hydrogen dosing, annealing, and TMA dosing is observed to produce an ordered unpinned passivation layer on air exposed InGaAs(001)-(4×2) surface with only monatomic steps. This TMA passivation layer on H cleaned air exposed III-V has the same horizontal rows of dimethyl aluminum (STM) and the same unpinned interface (STS) observed with the TMA/decapped InGaAs(100). While TMA directly reacts to create a high density of sites to nucleate gate oxide ALD on III-V surface, for Ge(100) surface functionalization is required. The direct reaction of TMA on a Ge(100) surface and the effect of monolayer H_2O pre-dosing were investigated. At 300K, a saturation TMA dose produced 0.8 monolayer (ML) of semi-ordered species on a Ge(100) surface due to the dissociative chemisorption of TMA. XPS analysis of the 200^oC annealed TMA/Ge(100) surface showed that only carbon content was reduced during annealing, while the Al coverage was maintained at 0.15 ML, consistent with the alow density of nucleation sites due to site blocks by reaction products. Conversely, saturation TMA dosing at RT on the monolayer H_2O pre-dosed Ge(100) surface followed by annealing at 200^oC formed a saturation layer of Al-O bonds with an Al coverage a factor of two greater than the TMA only dosed Ge(100). The Ge-OH sites catalyze the dissociative chemisorption of TMA even at 300K to create a a semiordered surface of Ge-O-Al bonds with an Al coverage double the coverage from a TMA surface without the H_2O predose.

4:20pm SS-ThA8 Electrostatic Coupling of Surface Charge to Bulk Defect Behavior in Metal Oxides, *P. Gorai, K. Pangan-Okimoto, A. Hollister, E.G. Seebauer*, University of Illinois at Urbana-Champaign
The technologically useful properties of semiconductor oxides such as titania and zinc oxide often depend on the concentration and diffusion of point defects. Near-surface effects are particularly important in nanoscale devices because most of the bulk is located in the vicinity of the surface. Past work in our laboratory with silicon and titania has shown that semiconductor surfaces serve as efficient pathways for generation and annihilation of point defects in the underlying bulk. Surfaces can, in addition, support electrically charged defects which create near-surface strong electric fields that can influence the local motion of charged defects resulting in the formation of space-charge layers. The electric field-driven accumulation or depletion of charged oxygen defects in such space-charge regions in metal oxides have direct implications on the performance of nanoscale devices such as gas sensors and memory resistors. Oxygen diffusion behavior was studied by exposing natural-abundance single-crystal rutile to isotopically labeled oxygen gas. The resulting profiles were measured by secondary ion mass spectrometry and subsequently modeled with continuum equations for the reaction, Fickian diffusion and electric field-driven diffusion of the key point defects. The degree of charge build-up at the surface can be quantified by an electric potential (V_i). The profiles calculated show a characteristic steep concentration gradient near the surface followed by a normal bulk diffusion profile. By identifying the charge-mediated field-driven diffusion mechanism as the controlling factor for the near-surface pile-up of oxygen, we demonstrate that this method allows the spatially resolved characterization of space charge regions near the surfaces of crystalline semiconductor metal oxides. The capability to predict oxygen pile-up in nanoscale metal oxide devices may be beneficial in device improvement via defect engineering of surfaces.

4:40pm SS-ThA9 Surface Photovoltage Behavior of n-type GaN as a Function of Orientation, *M. Foussekis, A.A. Baski, M.A. Reshchikov*, Virginia Commonwealth University
GaN is a wide-bandgap semiconductor (3.4 eV) which has approximately 1 eV of upward surface band bending for n-type material, thereby producing a

depletion region that can be detrimental to device performance. This band bending can be indirectly measured using the surface photovoltage (SPV) effect. By illuminating the surface with above-bandgap light, electron-hole pairs are created in the depletion region and holes are swept to the surface to reduce the negative charge and band bending. This change in surface charge is measured by a Kelvin probe in an optical cryostat. When the samples are illuminated with a HeCd laser, the SPV signal immediately rises to approximately 0.6, 0.3 and 0.4 eV for the Ga-polar (c-plane), N-polar, and m-plane sample orientations, respectively. The noticeably smaller SPV value for N-polar GaN indicates that this particular orientation has a smaller value of band bending. After this immediate rise, the SPV signal then begins to slowly change due to photo-induced surface processes. In an oxygen environment, the Ga-polar and m-plane orientations demonstrate a slow decrease in SPV of about 0.1 to 0.2 eV, which is attributed to the photo-induced adsorption of oxygen species [1]. There is no observable change for N-polar GaN, indicating that N-polar GaN is less reactive under UV illumination. In vacuum, all three orientations show a slow increase in the SPV signal of 0.1 to 0.2 eV over 1 h, which is due to the photo-induced desorption of charged surface species. When illumination is ceased after 1 h and the surface is restored in vacuum, subsequent illumination results in a constant, steady-state SPV signal, confirming that the photo-induced removal of any surface contamination layers is complete after approximately 1 h. The restoration behavior of the SPV can be fit for all three orientations using a thermionic model with logarithmic time decay [2]. The N-polar GaN is significantly faster, however, and fully restores in only minutes, as opposed to hours or days for the other orientations. It therefore appears that N-polar GaN has the most distinctive SPV behavior among these orientations, with the lowest SPV value, least amount of photo-induced surface reactivity, and fastest restoration behavior.

[1] M. Foussekis, A. A. Baski, and M. A. Reshchikov, Appl. Phys. Lett. **94**, 162116 (2009).

[2] M. A. Reshchikov, M. Foussekis, and A. A. Baski, J. Appl. Phys. **107**, 113434 (2010).

5:00pm **SS-ThA10 The Surface States of Lithium Tetraborate**, *L. Wang, W.-N. Mei,* University of Nebraska at Omaha*, D. Wooten, J. McClory, J. Petrosky,* Air Force Institute of Technology*, V. Adamiv, Ya. Burak,* Institute of Physical Optics, Ukraine*, I. Ketsman,* University of Nebraska - Lincoln*, Ya. Losovyj,* The J. Bennett Johnston Sr. Center for Advanced Microstructures and Devices*, **P.A. Dowben**,* University of Nebraska - Lincoln

The different low index surface terminations of lithium tetraborate, $Li_2B_4O_7$, are dominated by electronic states that fall within the projected band gap of the bulk states. As a pyroelectric material, $Li_2B_4O_7$ is a wide band gap dielectric, yet the (110) surface has a much smaller band gap because of occupied surface states that fall at binding energies between the valence band maximum and the Fermi level. The (100) surface is dominated, however, by unoccupied surface states that also fall in the gap between the conduction band minimum and valence band maximum, but at binding energies just below the conduction band minimum. These states have been identified in photoemission studies of $Li_2B_4O_7$(110) and inverse photoemission studies of $Li_2B_4O_7$(100) [1]. There is good qualitative agreement between these experiments and the electronic band structure calculations showing that the different surface terminations of lithium tetraborate yield very different surface electronic states.

[1] D. Wooten, I. Ketsman, J. Xiao, Ya.B. Losovyj, J. Petrosky, J. McClory, Ya. V. Burak, V.T. Adamiv, J.M. Brown and P.A. Dowben, *European Physical Journal: Applied Physics* **52** (2010) 31601

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