Thursday Afternoon, October 22, 2015

Surface Science
Room: 113 - Session SS+AS+EM+EN-ThA

Atomistic Modeling of Surface Phenomena & Semiconductor Surfaces and Interfaces - II
Moderator: Talat Rahman, University of Central Florida

2:20pm SS+AS+EM+EN-ThA1 Ideas Old and New Applied to Non-Ideal Surface Adsorption and Reaction, *William Schneider*, University of Notre Dame **INVITED**
Free energies of adsorption are arguably the most elementary quantities in heterogeneous catalysis. These free energies depend on the surface and adsorbate (reactant, intermediate, or product) of interest, system temperature and adsorbate coverage. The free energy represents a balance between the energetic driving force for creating bonds between an adsorbate and a surface and the entropic cost of moving an adsorbate from a fluid phase to a surface. Standard density functional theory (DFT) approaches generally begin by optimizing the location of an adsorbate on a surface, computing a binding energy, and approximating the internal, translational, and configurational contributions to the free energy. In this work we examine the reliability of standard approximations and describe easily applied improvements that give reliable free energy estimates. We describe applications to adsorption at metal surfaces and in the pores of zeolites.

3:00pm SS+AS+EM+EN-ThA3 Insights into the Oxidation of Stepped Cu Surfaces using Multiscale Investigations, *Q. Zhu, W.A. Saidi, **Judith Yang***, University of Pittsburgh
Surface defects can induce non-canonical oxidation channels on metal surfaces that may lead to the formation of novel nanostructures. Recently, in situ environmental transmission electron microscopy (ETEM) experiments showed that the oxidation of stepped Cu surfaces promotes the formation of a flat metal-oxide interface through Cu adatoms detachment from steps and diffusion across the terraces. To bridge the gap between experiments and theory, we are investigating Cu oxidation using a multiscale computational approach. Our previous MD simulations based on a reactive force field (ReaxFF) demonstrated that the oxidation of stepped Cu(100) takes place on the upper terrace at a faster rate than the lower terrace due to a preferable oxygen diffusion from the lower to upper terraces. We have extended this study using first-principles density functional theory (DFT) and kinetic Monte Carlo (KMC), and performed a systematic study of all stepped Cu surfaces with a low Miller index. The DFT results show that the oxygen diffusion trend varies with the surface type, where in most cases the oxygen ascending diffusion is more favored. This result is confirmed also with ReaxFF MD and KMC simulations. The MD simulations, with a fine-tuned ReaxFF force field parametrization, have also indicated that oxygen adatoms on the upper terrace can enhance the interlayer Cu atom mass transport. These theoretical simulations provide essential fundamental understanding of the experimentally observed smoothing of the Cu surface during in situ oxidation.

3:20pm SS+AS+EM+EN-ThA4 Reconciling Complimentary Analyses of Epitaxial Growth: Role of Transient Mobility for para-Hexaphenyl on Mica, *Josue Morales-Cifuentes, T.L. Einstein*, University of Maryland, College Park, *A. Pimpinelli*, Rice University
In studies of epitaxial growth, a major goal is to assess the size of the smallest stable cluster (with $i + 1$ monomers, where i is the critical nucleus size). This is accomplished by analyzing either the capture zone distribution (CZD), the scaling of incident flux F to the density of stable islands N or the island-size distribution (ISD). For CZD, generalized Wigner distributions (GWD) have proven useful, [1,2] with successful applications to, non-comprehensively: polar-conjugated molecule Alq_3 on passivated Si(100), self-assembled Ge/Si(001) nanoislands and para-Hexaphenyl (6P) films on amorphous mica. [3] We concentrate on the last, for which the Winkler group found that $i \approx 3$.

Scaling of N usually follows $N \propto F^\alpha$, where α is the growth exponent. For 6P films, a difference in scaling behaviors at small and large F is attributed to DLA and ALA dynamics (i.e. $i = 5 \pm 2$, and $i = 7 \pm 2$, respectively). [4] This discrepancy motivates our current work, where transient mobility effects modify scaling non-trivially. [5]

Consider that monomers begin in a (ballistic) hot precursor state before thermalizing (random walk). The competing times of ballistic monomers becoming thermalized vs. being captured by an island naturally define a "thermalization" scale for the system. We obtain an analytic solution and elaborate on the physical meaning behind the energies and dimensionless

parameters used. Novel scaling regimes are retrieved for which power-law scaling applies, with non-monotonic crossovers between them and the growth exponent exclusively dependent on i. Applying the model to the 6P films results in good agreement for the scaling and the activation energies: experimental values of the activation energies of 0.26eV (high-T) and 0.04eV (low-T) match model predictions of 0.3eV (high-T) and 0.04eV (low-T). Furthermore, the high-flux regime is interpreted not as ALA (attachment-limited aggregation) or HMA (hot monomer aggregation) but rather as an intermediate scaling regime related to DLA (diffusion-limited aggregation). Lastly, we discuss a simplifying approximation for the model and connections to some capture zone distribution considerations of α. [6]

[1] T.L. Einstein, A. Pimpinelli, D. González, J. Cryst. Growth 401, 67 (2014)

[2] T.L. Einstein, A. Pimpinelli, D. González, and J. R. Morales-Cifuentes, Proc. CCP2014, J. Phys.: Conf. Series (2015), in press.

[3] T. Potocar, G. Lorbek, D. Nabok et al. 2011 Phys. Rev. B 83 075423

[4] L. Tumbek & A. Winkler, Surf. Sci. 606, L55 (2012)

[5] J. R. Morales-Cifuentes, T. L. Einstein, and A. Pimpinelli. Phys. Rev. Lett. 113, 246101(2014)

[6] J. R. Morales-Cifuentes, T. L. Einstein, and A. Pimpinelli (in preparation)

4:00pm SS+AS+EM+EN-ThA6 Probing 2-DEG at InN Surface by Electrolyte-Gated Raman Spectroscopy, *E. Alarcon Llado*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, ***Tommaso Brazzini***, Lawrence Berkeley Lab, University of California, Berkeley, *J.W. Ager*, Lawrence Berkeley National Laboratory (LBNL)
Indium nitride has attracted much attention as its narrow bandgap (~0.67eV) expands the range of the direct gaps of the group III-N alloys into the visible and near-IR and thus offers an outstanding potential for solar energy conversion and optoelectronic applications. However, experimental demonstration of high efficiency In-rich III-V pn rectification junctions has been hampered by the existence of an intrinsic interface electron accumulation layer, which seems to persist regardless of surface treatment. The large capacitance of the Helmholtz double layer that forms on a surface of an object in contact with an electrolyte allows the 2-DEG at the surface of InN to be tuned and even depleted. Using this effect, we demonstrated the first pn rectification behavior in InN.[1]

In addition, the 2-DEG accumulation layer affects not only the electrical properties, but also has brought many controversies in the interpretation of optical experiments. Raman spectroscopy probes not only the lattice dynamics in a crystal, but also the electronic structure and free carriers. In particular, the interaction between the free electrons at the surface and the longitudinal optical (LO) phonon in InN has been addressed by several studies. However some questions still remain.

In this work, we present an in-situ micro-Raman study that confirms the presence of a surface related Raman mode in InN and shows its interaction with accumulated electrons at the surface. Electrolyte gated Raman spectroscopy (EGRS) on InN layers was performed in order to modulate and in-situ probe the surface electron accumulation region in InN. A reversible shift of the LO phonon with the applied gate potential is found (see figure 1). The peak position and shift depends on the probing light energy, however it is independent of bulk doping. We explain these findings by Martin's double scattering mechanism and bandgap narrowing at the surface tuned by the gate voltage. InN nanocolumns were also investigated by EGRS. The LO mode lies at higher frequencies in all nanocolumn samples. This fact corroborates the nature of the scattering mechanism, which is strongly dependent on the surface orientation. In summary, our results clearly demonstrate the surface origin of this feature and allow the fundamental study and understanding of the electronic structure of InN.

1.Alarcón-Lladó, E. et al. PN junction rectification in electrolyte gated Mg-doped InN. Appl. Phys. Lett. 99, 102106 (2011).

4:20pm SS+AS+EM+EN-ThA7 Surface Termination of Single Crystal Bi_2Se_3 Investigated by Low Energy Ion Scattering, *Weimin Zhou, J.A. Yarmoff*, UC Riverside
Bismuth Selenide (Bi_2Se_3) is a prototypical topological insulator (TI) with a two-dimensional layered structure that enables clean and well-ordered surfaces to be prepared by cleaving. Although some surface structure studies have concluded that the cleaved surface is terminated with Se, as is expected from the bulk crystal structure, there are other reports that show either a Bi- or mixed-termination [1]. Low Energy Ion Scattering (LEIS) and low energy electron diffraction (LEED) are used here to compare surfaces prepared by *ex-situ* cleaving, *in-situ* cleaving and Ar^+ ion

bombardment and annealing (IBA) in ultra-high vacuum. Surfaces prepared by *in-situ* cleaving always have a sharp 1x1 LEED patterns and are Se-terminated. Surfaces prepared by IBA show a transition from Bi- to Se-termination with increasing annealing temperature. Samples inserted into the vacuum chamber following *ex-situ* cleaving have much dimmer LEED patterns, show surface contamination with Auger electron spectroscopy, and could be terminated either with Se or Bi. The angular dependence of LEIS spectra, which is sensitive to the surface atomic structure, doesn't indicate any substantial differences between surfaces prepared by IBA or *in-situ* cleaving. Ion scattering simulations using Kalypso are compared to experimental angular data to obtain more details about the structure. Exposure of clean surfaces to gaseous species will also be discussed in an effort to determine the surface chemical reactions responsible for the termination change.

[1] X. He, W. Zhou, Z. Y. Wang, Y.N. Zhang, J. Shi, R.Q. Wu and J.A. Yarmoff, Phys. Rev. Lett. **110**, 156101 (2013).

4:40pm SS+AS+EM+EN-ThA8 Real-Time Imaging with Atomic-level Spatial Resolution of Silicon Oxidation, *Bryan Wiggins*, *L.G. Avila-Bront, R. Edel, S.J. Sibener*, University of Chicago
The investigation of the initial stages of molecular oxygen adsorption on Si(111)-7x7 with real-time and real-space visualization will be discussed in this presentation. We will present the first results from a newly built supersonic molecular beam paired with a scanning probe microscope instrument. The system is designed with an oil free differentially pumped supersonic beam and has a custom scanning probe microscope with the surface plane normal to the beam. This geometric arrangement allows us to perform real-time and real-space *in-situ* experiments. This study consists of exploring the potential energy surface for molecular oxygen adsorption on Si(111)-7x7. The questions that are being addressed are fundamental for issues relating to semiconductor oxidation as well as being of direct relevance to semiconductor processing. The site-specific locations of molecular oxygen reactivity on Si(111)-7x7 surfaces are not clear and remains a topic of current discussion. Recent spectroscopic studies show that by controlling the molecular beam energy (E_k) one can activate different adsorption pathways for molecules on surfaces. However, the effect of collimated and energy-selected beams impacting the surface at different incident angles has not been observed *in-situ* at the local molecular level until now. We will show high-resolution spatial images of the initial stages of oxygen adsorption on Si(111)-7x7 at different beam energies. The comparison of Si(111)-7x7 oxidation *via* thermal oxygen versus the specific adsorption sites that arise at different beam energies will also be discussed. The results indicate that using supersonic beams in this matter may provide enhanced control of semiconductor oxidation chemistry.

5:00pm SS+AS+EM+EN-ThA9 Surface Band-Bending Upon Oxidation of Wurtzite and Zincblende InAs Depending on Surface Orientation and atomic Structure, *Rainer Timm*, *M. Hjort, J. Knutsson, O. Persson, A. Troian, S. Lehmann, K.A. Dick, A. Mikkelsen*, Lund University, Sweden
InAs is known to typically show n-type behavior with an electron accumulation layer at the surface. Many studies have been performed for evaluating to which extend this behavior is due to adsorbates such as a native oxide layer, or to specific surface orientations and reconstructions of clean InAs. InAs nanowires (NWs) add an extra degree of complexity, since they can exist both in zincblende and wurtzite crystal structure, typically exhibiting unintended switching between both stacking orders during epitaxial growth. During recent years, a strong debate has been going on about how far such crystal phase mixing influences the conductivity of InAs NWs and therewith their suitability for high-mobility device application [1]. A staggered band alignment with band offsets in the range of up to 0.1 eV between zincblende and wurtzite conduction band edges has been reported, based on transport measurements in ambient atmosphere [2]. In contrast, our recent study of clean and unreconstructed InAs NW surfaces based on scanning tunneling microscopy and spectroscopy (STM/S) in ultrahigh vacuum showed aligned conduction band edges for zincblende [110[and wurtzite [11-20[surfaces [3].

Here, we present a systematic study of surface band-bending upon cleaning and oxidation of various InAs surfaces, including purely zincblende or purely wurtzite NWs, obtained by synchrotron-based X-ray photoemission spectroscopy (XPS). We were able to clean all investigated InAs surfaces from their native oxide by annealing them in the presence of atomic hydrogen [3]. Different rates of cleaning and re-oxidation were observed for the different surfaces. Even more importantly, from the energy shifts of the investigated core-levels upon oxidation, varying between 0.1 and 0.3 eV for various surfaces, we obtained significant differences in oxide-induced surface band-bending for different surface orientations. We will compare our XPS results with the atomic and local electronic structure of the specific surfaces as obtained by STM/S [4]. Our results indicate that the band alignment along InAs heterostructures, and therewith the transport properties of InAs NWs, depend on the surface orientation, composition, and atomic structure rather than the crystal phase of the specific InAs segments.

[1] Thelander *et al.*, Nano Lett. **11**, 2424 (2011)

[2] Dayeh *et al.*, Adv. Funct. Mater. **19**, 2102 (2009)

[3] Hjort *et al.*, ACS Nano **12**, 12346 (2014)

[4] Knutsson *et al.*, ACS Appl. Mater. Interfaces **7**, 5748 (2015)

5:20pm SS+AS+EM+EN-ThA10 Control of Oxygen Defect Surface Injection in ZnO via Sub-Monolayer Sulfur Adsorption, *Ming Li*, *E. Seebauer*, University of Illinois at Urbana-Champaign
Native oxygen defects within metal oxide semiconductors such as ZnO affect the material's performance in applications for photovoltaics, nanoelectronics, gas sensing, and photocatalysis. Previous work in this laboratory has shown that the semiconducting metal oxides surfaces can be used to manipulate the concentrations and spatial distributions of bulk oxygen defects, particularly oxygen vacancies. The interaction chemistry between bulk point defects and reactive sites on semiconductor surfaces is comparable in richness to the reactions of surfaces with gases. The present work discusses a novel mechanism of controlling oxygen defect injection in c-plane ZnO(0001) through surface active sites blocking with sub-monolayer sulfur adsorption. Oxygen diffusion rates were measured by exposing single-crystal ZnO to isotopically labeled oxygen ($^{18}O_2$) gas. Sulfur was deposited controllably via an electrochemical cell and characterized *in situ* by Auger Electron Spectroscopy (AES). The resulting diffusion profiles were measured by secondary ion mass spectrometry (SIMS). Kinetic parameters were extracted by fitting the diffusion profiles with a previously derived mass transport model. The preliminary data shows that sulfur adsorption decreases the oxygen defect injection rate by roughly three times through affecting the injection flux, which points to a site blocking model. Subsequent temperature and pressure dependence study will help us gain insights into detailed injection kinetic pathways.

5:40pm SS+AS+EM+EN-ThA11 Investigation of the Role of Electronic Defects and Grain Boundaries in Sputter Deposited CdS/CdTe Junctions and Solar Cells, *Mohit Tuteja*, University of Illinois at Urbana Champaign, *P. Koirala*, University of Toledo, *J. Soares*, University of Illinois at Urbana Champaign, *R. Collins*, University of Toledo, *A. Rockett*, University of Illinois at Urbana Champaign
Device quality CdS/CdTe heterostructures and completed solar cells (~12% efficient) have been studied using low-temperature photoluminescence (PL) as a function of temperature (82-295 K) and laser excitation power (0.02-2 mW). The CdS/CdTe junctions were grown on transparent conducting oxide covered soda lime glass using rf-sputter deposition. It was found that the luminescence shifts from being dominated by sub-gap defect-mediated emission at lower excitation powers to near band edge excitonic emission at higher excitation powers. The effect of copper (Cu) used in making back contacts was studied in connection with the CdS/CdTe junction PL. It was found that the presence of Cu suppresses the sub-band gap PL emissions. This effect was concluded to be due either to Cu occupying cadmium vacancies (V_{Cd}) or forming acceptor complexes with them. This points to a potential role of Cu in plugging sub-band gap recombination routes and hence increasing charge separation ability of the device. An energy band diagram is presented indicating various observed transitions and their possible origins.

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