

Surface Science

Room: 113 - Session SS+AS+EM+EN-ThM

Semiconductor Surfaces and Interfaces - I

Moderator: Yves J. Chabal, University of Texas at Dallas

8:00am SS+AS+EM+EN-ThM1 Reaction of 1,2,3-Benzenetriol with the Ge(100)-2x1 Surface, *Tania Sandoval, S.F. Bent*, Stanford University

Functionalization of semiconductor surfaces can provide tunable control of interfacial properties in organic-inorganic hybrid devices. In particular, multifunctional molecules have the potential to change the surface chemistry by leaving unreacted functional groups available after adsorption. Understanding the adsorption of these complex molecules could lead to various applications as sensors, selective film deposition, and molecular electronics.

In this work, the reaction of 1,2,3-benzenetriol on Ge(100)-2x1 surface was investigated. While the reaction of hydroxyl groups has been previously studied, differences in selectivity can be expected due to the position of the functional groups along the ring. The purpose of this study is to determine the extent of these differences and the effect on product distribution.

An analysis of the adsorption energetics was carried out by density functional theory. As expected, a proton transfer reaction was shown to be the most stable adsorbate configuration. However, after the adsorbate reacts with the surface through its first OH group, the energetics of the second OH dissociation showed differences based on two factors: (i) surface configuration (cross or diagonal trench and end or cross bridge) and more interestingly (ii) which two of the OH groups (1 and 2 or 1 and 3) are reacting with Ge. The latter constraint affects the adsorption energy of the second dissociation, where adsorption regardless of the surface configuration is less stable when the OH groups are next to each other. Finally, transition states for dissociation of the third OH were found to be limited by the configuration of the second dissociation, and in some cases were not possible to find without unrealistic distortions of the molecule.

Chemisorbed and physisorbed O(1s) and C(1s) spectra were obtained by X-ray photoelectron spectra. Differences between these spectra can be used to identify the reaction products. No change in the C(1s) spectra was observed, suggesting that no carbon forms a bond directly with the Ge surface. On the other hand, clear differences between the chemisorbed and physisorbed O(1s) spectra are observed. The presence of a second peak with a lower binding energy only in the chemisorbed spectra, assigned to oxygen bonded to Ge, confirms that 1,2,3-benzenetriol reacts with the Ge surface through OH dissociation. Quantitative analysis of the chemisorbed O(1s) spectra provides information on the fraction of OH groups reacting with the surface. Interestingly, about 66% of the total hydroxyl groups in 1,2,3-benzenetriol are involved in reaction with Ge, indicating that there is a significant fraction of unreacted OH groups.

8:20am SS+AS+EM+EN-ThM2 Ethylenediamine Grafting on Oxide-free H-, F-, and Cl-terminated Si(111) Surfaces, *Tatiana P. Chopra**, R.C. Longo, K.J. Cho, University of Texas at Dallas, M.D. Halls, Schrodinger, Inc., P. Thissen, Karlsruhe Institute of Technology, Germany, Y.J. Chabal, University of Texas at Dallas

Amine termination of surfaces constitutes a core platform for fields as diverse as microelectronics and bioengineering, and for nanotechnology in general. Diamines are particularly attractive for surface amination because, unlike ammonia or simple amine molecules, they have a metal chelating capability useful in fabricating heterostructures. They can act as a linker molecule between inorganic electronic materials and biomolecules or photoactive quantum dots for applications in microelectronic, photonics and biosensing. Most work in the field utilizes self-assembled monolayers (SAMs) on oxidized substrates to present an amine termination of the surface. However, grafting on oxides through silanes or phosphonates is not robust. Moreover, several applications require as short a distance between the substrate and the amine group, which is hindered by the thickness of the oxide. Therefore, diamine grafting directly on oxide-free substrates is important, yet remains unexplored.

In this work, the attachment of liquid and vapor-phase ethylenediamine on three types of oxide-free (H-, F- and Cl-terminated) Si(111) surfaces is examined by infrared absorption spectroscopy and X-ray photoelectron spectroscopy in conjunction with first-principles calculations. We find that chemisorption is only possible on F- and Cl-terminated Si surfaces, with H-

terminated Si surfaces yielding only physisorbed diamine molecules. On Cl-terminated Si surfaces, diamines adsorb in a mixture of monodentate and bridging configurations (chemical reaction of both amine endgroups), while on partially F-terminated Si surfaces the adsorption occurs primarily at one end of the molecule. The reaction of ethylenediamine with Cl-terminated Si surfaces is also characterized by complete removal of Cl and partial Si-H (~25% ML) formation on the surface. This unexpected result suggests that a proton-chlorine exchange may take place, with the endothermic barrier possibly reduced via a silicon lattice assisted process after an initial attachment of ethylenediamine to the surface.

8:40am SS+AS+EM+EN-ThM3 Reaction of Phenylhydrazine with Cl-Si(111) Surface by Wet Chemistry and with Clean Silicon Surface in UHV, A.V. Tepyakov, Fei Gao, University of Delaware

The monolayer coatings with aromatic functional groups can be used to tune mechanical, electronic, and chemical properties of semiconductor surfaces. This work focuses on obtaining well-defined surface of silicon functionalized with phenylhydrazine to produce an oxygen-free platform for further functionalization. Single crystalline Si(111) surface has been prepared using modified RCA procedure to produce well-ordered H-Si(111) surface. Next, Cl-terminated Si(111) surface is prepared from H-terminated Si(111) surface using PCl₅ in chlorobenzene solvent with trace amount of benzoyl peroxide as a reaction initiator under nitrogen atmosphere following previously established procedures. Phenylhydrazine-functionalized Si(111) sample is obtained from Cl-Si(111) surface with phenylhydrazine at 38°C under N₂ atmosphere. To confirm the presence of Si-N bonds following this procedure, establish the structures of surface species produced and to investigate the oxidation mechanism, we followed the reaction by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry. To study the formation of Si-NH₂ groups, this result was compared with the results of phenylhydrazine reactions on clean silicon surface under ultra-high vacuum (UHV) conditions. Density functional theory (DFT) calculations were performed to infer the mechanisms of surface reactions and further oxidation steps, and to compare the predicted vibrational spectra and core-level energies with the results of experimental studies.

9:00am SS+AS+EM+EN-ThM4 Anomalously Low Surface Recombination Velocity for Fluorine Terminated Nanopatterned Si Surfaces, W.N. Peng, Jonghan Park, L.-H. Liu, R.C. Longo, University of Texas at Dallas, D.J. Michalak, Intel Corporation, D.M. Pak, Y.J. Lee, J.X. Hsu, K.J. Cho, Y.J. Chabal, University of Texas at Dallas

Recently, oxide-free and partially methoxy-terminated Si surfaces¹ have been developed as a novel platform for surface reactions because of their superior reactivity compared to hydrogen termination². As a result, strong polar bonds such as Si-F could be stabilized on these surfaces. Since the electrical quality is critical for many applications (i.e. surface defects can degrade the device performance), we performed contactless surface recombination velocity measurements to examine the electronic quality of partially covered surfaces. Interestingly, we found that the carrier lifetime is significantly increased after fluorine termination, with the carrier lifetime 10 times higher than that of hydrogen terminated Si surfaces, approaching 1.5 ms. This anomalously long carrier lifetime can be explained either by a better surface passivation or by surface band bending effects. We therefore performed UPS and kelvin probe measurements to investigate the band structure of these surfaces after fluorine termination and found evidence for band bending. A potential model of a surface dipole layer induced band bending is supported by DFT calculations. Regardless of the mechanism controlling the recombination time, this method is well suited to explore the fluorination mechanism of H-terminated surfaces.

[1] D. Michalak, S. Amy, D. Aureau, M. Dai, A. Esteve, and Y. J. Chabal, *Nature Materials*, **9**, (2010)

[2] P. Thissen, T. Peixoto, R. Longo, W. Peng, W. Schmidt, K. Cho, and Y.J. Chabal, *JACS*, **134** (2012)

9:20am SS+AS+EM+EN-ThM5 Molecular Functionalization of Semiconductor Surfaces: From Single Crystals to Quantum Dots, *Stacey Bent*, Stanford University

INVITED

Because the surfaces of small structures can dominate their properties, implementing functional nanoscale materials depends to a large extent upon understanding and controlling the surface reactivity. This talk will focus on studies of the adsorption of organic molecules at semiconductor surfaces, toward the ultimate goal of controlling the chemical and electrical properties of the substrate. We will describe model studies of molecular functionalization on both flat and nanostructured surfaces. The presentation

* Morton S. Traum Award Finalist

will begin by examining adsorption on the Ge(100)-2×1 surface. Using a combination of experimental (infrared spectroscopy, X-ray photoelectron spectroscopy) and theoretical (density functional theory calculation, Monte Carlo simulation) methods, we will show how the molecular structure as well as the identity of the reactive moieties of organic molecules can affect the product distribution upon adsorption. We will then present results of a study in which the organic ligands bonded to semiconductor quantum dots (QDs) are used to tune the electronic properties of the QDs. We will describe experimental and theoretical studies of the effects of such interface engineering on the band gap and relative band positions in lead sulfide (PbS) QDs. These ligand-exchanged quantum dots are tested in multilayer colloidal QD solar cells, and the results show that molecular functionalization can be used to achieve enhanced photogenerated carrier collection in the devices.

11:00am **SS+AS+EM+EN-ThM10 Periodic Trends in the Hydrogen Elimination Thermal Decomposition Reaction on Si(100)-2×1: Linear and Branched Alkyl Halides, Alcohols, and Amines**, *Andrew Pohlman, K.L. Romolino, N.J. Burgener, S.M. Casey*, University of Nevada

The hydrogen elimination thermal decomposition reaction was studied on the Si(100)-2×1 surface using temperature programmed desorption mass spectrometry (TPDMS) and electronic structure methods for a selection of linear and branched alkyl halides, alcohols, and primary amines. Desorption activation energies and pre-exponential factors were determined using several analysis techniques from TPDMS spectra and compared to calculations based on ab initio canonical transition state theory using density functional theory (DFT). Values for activation energies and pre-exponential factors for dissociative desorption are compared within an adsorbate class based on a varying ratio of available alpha:beta:gamma hydrogens for elimination. Kinetic parameters are also compared between classes of adsorbates for general structure-activity periodic trends. TPDMS experiments reveal desorbing masses consistent with hydrogen elimination in all cases; however, the different elimination channels remain convoluted. Rate constants for each desorption channel were calculated using DFT and used to determine branching ratios for each dissociative desorption reaction. Reaction barrier trends are consistent with previous reports; however, numerical values were found to be much lower when considering inter-dimer reaction mechanisms.

11:20am **SS+AS+EM+EN-ThM11 Diffusion of Arsenic Oxides During the Atomic Layer Deposition of Metal Oxide Films on GaAs(100) Surfaces**, *Alex Henegar, T. Gougousi*, University of Maryland, Baltimore County

It is known that native oxides of III-V semiconductors are consumed during atomic layer deposition using certain subsets of precursors. It was believed these surface oxides were completely removed during the first few deposition cycles because once the surface was covered by a coalesced film the native oxides would be protected. It has been observed, however, that native oxide consumption in systems such as ALD TiO₂ on GaAs(100) and InAs(100) proceeds continuously well after the surface is completely covered. Therefore there must be a transport mechanism that continuously moves these oxides through the developing film in order to interact with the precursor at the surface and be removed.

The aim of this work was to find unequivocal evidence of the transport mechanism needed for continuous oxide removal during ALD at typical processing conditions. ALD processes using metal organics and H₂O were used to deposit TiO₂, Al₂O₃ and HfO₂ films on GaAs(100). The experiments were designed so as to decouple the native oxide consumption from the native oxide transport and provide convincing evidence for the existence of this unacknowledged thus far mechanism. We will provide results that solidify the hypothesis that native oxide diffusion is a critical component in the complete and continuous removal of the interfacial layer.

11:40am **SS+AS+EM+EN-ThM12 Ultrafast Non-Equilibrium Effects in Ti Overlayers on P-Type GaAs(100) Investigated by Femtosecond XUV Photoemission Spectroscopy**, *Mihai E. Vaida*, University of California, Berkeley, *S.R. Leone*, University of California, Berkeley and Lawrence Berkeley National Laboratory

Time resolution, surface sensitivity and element specificity are technical ingredients required to investigate ultrafast photoinduced processes and charge localization at semiconductor surfaces. All these requirements are fulfilled by a new experimental apparatus that consists of a tunable femtosecond high harmonics XUV source, a pump-probe setup, and an ultra-high vacuum surface science chamber for surface preparation and investigation.

The present contribution focuses on the charge carrier dynamics at the surface of a bare p-type GaAs(100) as well as Ti overlayers on p-type GaAs(100). The charge transfer between the bulk and the surface of the bare GaAs(100) is produced by the pump laser pulse at the central

wavelength of 800 nm and is investigated by monitoring the surface photovoltage through the shift of the Ga 3d photoemission peak with the XUV probe laser pulse as a function of the pump-probe time delay. A transient shift of the Ga 3d photoemission peak to lower binding energy at early pump-probe time delay, with a magnitude of 0.3 eV, is observed and is attributed to transport of the electrons from the bulk to the surface. Upon increasing the pump-probe time delay, a restoration of the Ga 3d peak is observed, which corresponds to the recombination of the positive and negative carriers.

When a Ti overlayer is deposited on the p-type GaAs(100) surface, a Schottky diode is formed. If the 800 nm pump laser pulse has sufficient intensity to produce a photoemission process via multi-photon excitation, non-equilibrium effects occur at the Ti-GaAs interface independently from the presence of the surface photovoltage. In this case, positive charges accumulate at the surface and are not effectively screened by the electrons coming from the bulk, and the Schottky diode is transiently driven into a reversed bias mode. The formation of the reverse bias Schottky diode, which is studied in real time with the XUV probe laser pulse by monitoring the Ti Fermi level photoemission shift as a function of the pump-probe time delay will be presented and discussed.

12:00pm **SS+AS+EM+EN-ThM13 Improving the Quality of p-type AlGaN Layers by Reactive-ion Etching**, *Joy McNamara, K.L. Phumisthikul, A.A. Baski, M.A. Reshchikov*, Virginia Commonwealth University, *J. Marini, F. Shahedipour-Sandvik*, SUNY Polytechnic Institute
AlGaN layers prepared by metal-organic chemical vapor deposition, with varying composition of Al (6 – 17%), were studied using the surface photovoltage (SPV) technique. Previous SPV studies on both *n* and *p*-type GaN allowed us to calculate the value of the surface band bending, by applying a thermionic model to explain the transfer of charges over the near surface barrier in various conditions (air, vacuum, and for a wide range of temperatures, T = 80 – 600 K). [1,2] The band bending was estimated to be 1.0 eV and – 2.0 eV, for *n*-type GaN and *p*-type GaN, respectively. SPV measurements on *p*-type AlGaN layers were expected to have similar behaviors to their *p*-type GaN counterparts. However, numerous measurements showed that this was not the case. The SPV transients (upon turning on or off the excitation source) showed significantly slower transients and smaller values than expected from the thermionic model. Moreover, the restoration of the band bending, as indicated by the restoration of the SPV signal to its dark value, did not occur within a reasonable amount of time. The data could not be fit by the thermionic model, and thus we were unable to calculate the band bending. We attribute the slow transients and lack of restoration to a defective surface region which interferes with thermionic processes. To verify this assumption, the top 40 nm of the AlGaN layer was etched using a reactive-ion etch (RIE). After etching, the SPV behavior exhibited substantially different behavior. Fast transients and close-to-thermionic behavior was recovered. Additionally, the effect of annealing the samples after etching provided even closer values to what is predicted by the thermionic model. From this study, it can be concluded that a defective, near surface region is inhibiting the transfer of holes over the near surface barrier under illumination, and hole trapping may be occurring during restoration. In both cases, this behavior cannot be modeled by theory. Etching removes the defective layer, and reveals a region of presumably higher quality as evidenced by the subsequent thermionic behavior.

[1] M. A. Reshchikov, M. Foussekis, and A. A. Baski. *J. Appl. Phys.* **107**, 113535 (2010).

[2] M. Foussekis, J. D. McNamara, A. A. Baski, and M. A. Reshchikov, *Appl. Phys. Lett.* **101**, 082104 (2012).

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