

Wednesday Afternoon, October 30, 2013

Surface Science

Room: 201 A - Session SS+EM-WeA

Semiconductor Surfaces and Interfaces

Moderator: M.A. Hines, Cornell University

2:00pm **SS+EM-WeA1 Monte Carlo Simulation Studies of Ge(100)-2 × 1 Surface Chemistry**, *B. Shong**, *S.F. Bent*, Stanford University

Organic functionalization of semiconductor surfaces is of interest due to its possibilities for forming tailorable organic-inorganic interfaces. The (100) surface of Si or Ge reconstructs to a highly ordered 2×1 pattern under proper vacuum preparation. On these surfaces, only a few possible two-dimer configurations exist [1], and such a simple geometry allows facile introduction of stochastic simulations. However, to date, such methods have not been well utilized in organic functionalization studies. In this talk, we will introduce recent results in the integration of Monte Carlo (MC) simulations with other widely used techniques, and will show that the addition of MC simulations leads to deeper understanding of many coverage-dependent behaviors.

In the first example, self-assembly of two small organic building block molecules, ethylene and methanol, on the Ge(100) surface is explained through MC simulations based on density functional theory (DFT) calculations [2]. Characteristic one-dimensional adsorbate patterns along the rows of Ge(100) were observed in previous scanning tunneling microscope (STM) studies, where the dimers linearly aligned within the same rows are the nearest neighbor sites on Ge(100). Our DFT calculations show that the adsorption of ethylene is hindered next to another ethylene, whereas adsorption of methanol is facilitated by the presence of an adjacent methanol. Kinetic MC simulations based on the DFT-calculated adsorption probabilities predict adsorbate patterns that agree well with the experimental observations.

In another example, the adsorption of a bifunctional molecule, 1,3-benzenediol, is explored by a similar MC approach. Whether dual or single reaction occurs during attachment of bifunctional molecules is critical, since dual binding adsorbates terminate the reaction site. Fourier transform infrared (FTIR) spectroscopy experiments as well as DFT calculations show that 1,3-benzenediol adsorbed on Ge(100) assumes only one type of dual binding configuration. This limitation simplifies the geometrical dimension of the adsorption phenomena. The fraction of singly bound adsorbates increases nonlinearly with increasing coverage according to X-ray photoelectron spectroscopy (XPS) measurements. This behavior is explained through MC simulations showing that unreacted functionalities appear on the reactive surface due to limitations in available adjacent sites. In conclusion, we demonstrate the potential of combining MC simulations with other techniques in studies of semiconductor surface chemistry.

1. B. Shong, K.T. Wong, S.F. Bent, *J. Phys. Chem. C* 116, 4705 (2012).
2. B. Shong, S.F. Bent, *J. Phys. Chem. C* 117, 949 (2013).

2:20pm **SS+EM-WeA2 Structural Instability in the Adatom Vacancy on Si(111)-√3×√3 Surface: An STM/S Study**, *D. Eom*, *C.-Y. Moon*, *J.-Y. Koo*, Korea Research Institute of Standards and Science, Republic of Korea
We report a direct probe of the structural instability in the adatom vacancy on heavily boron doped Si(111)-√3×√3 surfaces by using a low-temperature scanning tunneling microscopy/spectroscopy (STM/S). Three dangling bonds (DBs) are generated inside an adatom vacancy on Si(111)-√3×√3 surface, each of which is located at one of three second layer Si atoms with Si(111)-1×1 spacing. The conductance maps of this triple DBs exhibit dissimilar spatial distributions with varying eigenenergies, indicating that the electronic coupling between three DBs is significant due to the proximity. Also, the reduced C_s symmetries of ground and excited states' wavefunctions of triple DBs, which are probed at -0.25 eV below and +0.3 eV above the Fermi level respectively, contrast to C_{3v} symmetry of underlying 1×1 lattice and are ascribed to Jahn-Teller type instability accompanying degenerate orbital configurations. More detailed analysis of multi-electron configurations and structural instabilities in triple DBs will be reported.

2:40pm **SS+EM-WeA3 Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting**, *N. Lewis*, California Institute of Technology **INVITED**

We are developing an artificial photosynthetic system that will only utilize sunlight and water as the inputs and will produce hydrogen and oxygen as the outputs. We are taking a modular, parallel development approach in which the three distinct primary components—the photoanode, the photocathode, and the product-separating but ion-conducting membrane—are fabricated and optimized separately before assembly into a complete water-splitting system. The design principles incorporate two separate, photosensitive semiconductor/liquid junctions that will collectively generate the 1.7-1.9 V at open circuit necessary to support both the oxidation of H₂O (or OH⁻) and the reduction of H⁺ (or H₂O). The photoanode and photocathode will consist of rod-like semiconductor components, with attached heterogeneous multi-electron transfer catalysts, which are needed to drive the oxidation or reduction reactions at low overpotentials. The high aspect-ratio semiconductor rod electrode architecture allows for the use of low cost, earth abundant materials without sacrificing energy conversion efficiency due to the orthogonalization of light absorption and charge-carrier collection. Additionally, the high surface-area design of the rod-based semiconductor array electrode inherently lowers the flux of charge carriers over the rod array surface relative to the projected geometric surface of the photoelectrode, thus lowering the photocurrent density at the solid/liquid junction and thereby relaxing the demands on the activity (and cost) of any electrocatalysts. A flexible composite polymer film will allow for electron and ion conduction between the photoanode and photocathode while simultaneously preventing mixing of the gaseous products. Separate polymeric materials will be used to make electrical contact between the anode and cathode, and also to provide structural support. Interspersed patches of an ion conducting polymer will maintain charge balance between the two half-cells. The modularity of the system design approach allows each piece to be independently modified, tested, and improved, as future advances in semiconductor, polymeric, and catalytic materials are made. Hence, this work will demonstrate a feasible and functional prototype and blueprint for an artificial photosynthetic system, composed of only inexpensive, earth-abundant materials, that is simultaneously efficient, durable, manufacturably scalable, and readily upgradeable.

4:20pm **SS+EM-WeA8 Dual Passivation of the In_{0.53}Ga_{0.47}As (001)-(2x4) Surface with TMA and an Oxidant**, *T. Kent*, *M. Edmonds*, *E. Chagarov*, University of California San Diego, *R. Droopad*, Texas State University, *A.C. Kummel*, University of California San Diego

III-V semiconductors are expected to be used as the channel material in future metal oxide semiconductor field effect transistors (MOSFETs) due to their intrinsically higher electron mobilities. Previous work has shown that the InGaAs (2x4) surface reconstruction has promising CV characteristics and is a viable choice for use as the channel[1], but there is a fundamental problem with this surface. Edmonds et al. showed that all In/GaAs (2x4) surfaces contain at least 8% α2-(2x4) unit cells and when alloying In/Ga to form InGaAs that number jumps to a minimum of 48%. [2] The α2-(2x4) unit cell is missing one As-As dimer on the row which results in metallic In-Ga bonds. These metallic bonds cause bond angle strain in the edge As atoms which prefer to be in tetrahedral sp³ bonding configuration. This strain causes a conduction band edge state in the (2x4) density of states (DOS), and prevents the Fermi level from being efficiently modulated without proper passivation techniques. In order to improve III-V based MOSFET performance it is crucial to passivate the intrinsic α2-(2x4) defect unit cells. Trimethylaluminum (TMA) does not react with the defect unit cells; therefore, in order to achieve an ideal interface a dual passivation scheme is necessary. In this study density functional theory (DFT) was used to show that there is a conduction band (CB) edge state associated with the defect unit cells. By inserting -OH, -SH, or -NH₂ into the metallic In-Ga bonds and to the edge In/Ga dangling bonds after TMA passivation, it is possible to fully passivate the CB edge state. Scanning tunneling microscopy and spectroscopy (STM/STS) was utilized to show that it is possible selectively passivate the α2-(2x4) by dosing H₂O (g) and maintain an unpinned Fermi level. Subsequently TMA was dosed to passivate the β2-(2x4) unit cells, STM shows an atomically ordered surface exists and ALD of Al₂O₃ was nucleated in each unit cell. STS showed that by using this dual passivation technique the Fermi level remained unpinned. Using the optimized oxidant dosing temperatures, the McIntyre group at Stanford has shown this dual passivation technique results in superior CV characteristics in MOSCAPs consistent with the dual passivation technique improving InGaAs based MOSFETs.

* Morton S. Traum Award Finalist

1)Hwang, Y,et al., *Influence of trimethylaluminum on the growth and properties of HfO₂/In_{0.53}Ga_{0.47}As interfaces*. Applied Physics Letters, 2011. 98(5): p. 052911.

2)M. Edmonds, W.M., T. Kent, E. Chagarov, A. C. Kummel, ECS Transactions, 2012. 50(4): p. 129-140.

4:40pm **SS+EM-WeA9 Specific Attachment of Ethylenediamine on Modified Si(111) Surfaces**, *T. Peixoto, Y.J. Chabal*, University of Texas at Dallas

Silicon nitridation is of fundamental interest to the microelectronics, biotechnology and nanotechnology communities, with its ability to act as an oxygen diffusion barrier for devices while concurrently optimizing the effective dielectric constant. The Si-N bond plays a key role in the stability of silicon nitride layers, used in devices due to its durability and thermal stability; amine groups aid in additional functionalization of surfaces enabling the attachment of quantum dots, nanoparticles, and biological molecules allowing for development of new surfaces/devices. The incorporation of nitrogen groups on the silicon surface thus allows for the creation of modified surfaces with expanded properties and extensive tailorability. Despite these advantages, a clear understanding of the underlying mechanisms towards well controlled nitride and amino group attachment on Si surfaces, is not completely developed.

To uncover the reaction mechanisms, we have performed experiments with several different Si(111) surfaces terminations (SiH, SiF, and SiCl) and reacted with the bifunctional molecule ethylenediamine (NH₂-CH₂-CH₂-NH₂). With its amine termination on ends of the molecule, ethylenediamine makes it possible to obtain amine functionality following Si-N attachment on the surface. Our results indicate that ethylenediamine only physisorbs on hydrogen-terminated Si(111) surfaces, as evidenced by the intensity and high wavenumber of the (N-H) deformation and stretch modes and the binding energy of the main N1s peak in XPS. When exposed to a 1/3 nanopatterned Si(111)-F surface, the intensities of the stretch and deformation modes are consistent with a 1/3 coverage, and their frequencies associated with interacting amine groups expected of an ordered monolayer. Importantly, XPS shows a component of the N1s core level that is associated with direct bonding to silicon. In contrast, ethylenediamine molecules appear to adsorb by bridge configuration on fully chlorine-terminated Si surfaces, indicating that both NH₂ ends dissociate and react, as evidenced by a dominance of Si-N bonds in XPS and undetectable (N-H) deformation and stretch in IR spectra.

These results provide a means to controlling amine functionalization of silicon surfaces, and further understanding of the reaction mechanism for nitrogen group attachment on F, Cl, H terminated Si(111) surfaces.

5:00pm **SS+EM-WeA10 Lowering the Density of Electronic Defects on Organic-Functionalized Si(100) Surfaces**, *W. Peng, W.J. De Benedetti, S. Kim*, University of Texas at Dallas, *M.A. Hines*, Cornell University, *Y.J. Chabal*, University of Texas at Dallas

The integration of self-assembled monolayers (SAM) with semiconductor surfaces helps to provide the functionality necessary for various application possibilities, ranging from molecular electronics, hybrid optoelectronics to chemical sensing. So far, Si(111) surfaces have been the most explored systems mainly due to the fact that atomically flat hydrogen terminated Si(111) surfaces can be easily prepared for further chemical functionalization. Recently a method to produce quasi atomically flat H-Si(001) surfaces has been developed¹ and the surface structure carefully studied with FTIR analysis, STM imaging and kinetic Monte Carlo simulations.

In this work, we compare the density of interface electronic states after organic functionalization (hydrosilylation) on both atomically rough and atomically flat Si(100) surfaces. Although differences in surface morphology are not detectable with FTIR or XPS, conductance voltage measurements² are able to detect a clear difference in interface state densities D_{it} (i.e., defect densities). Specifically, atomically flat Si(100) surfaces functionalized with C₁₁H₂₃ monolayers have D_{it} values three times lower than those of rough functionalized surfaces, leading to D_{it} values very close to our previous results on atomically-flat Si(111) surfaces functionalized with the same molecule.² These findings open the way for integrating common functionalization methods using the technologically important Si(100) surfaces to meet the needs of critical applications.

¹M. A. Hines, M. F. Faggin, A. Gupta, B. S. Aldinger, and K. Bao, J. Phys. Chem. C **116** (35), 18920 (2012).

²W. Peng, O. Seitz, R. A. Chapman, E. M. Vogel, and Y. J. Chabal, Appl. Phys. Lett. **101** (5) (2012).

5:20pm **SS+EM-WeA11 Monolayer Doping via Arsenic Acid Grafting on Silicon Surfaces**, *A. Vega, W. Cabrera, R. Longo, Y. Lu*, The University of Texas at Dallas, *P. Thissen*, Karlsruhe Institute of Technology, Germany, *Y.J. Chabal*, The University of Texas at Dallas

Density scaling and subsequent device dimension reduction continue to drive significant advances in the materials, processing, and architecture of advanced transistors. As gate lengths approach the sub-10 nm regime, junction doping has become an increasing concern due to its importance in controlling short channel effects. Source/drain junction depths must be extremely shallow and abrupt, typically around 1/3 of gate length (L_g). Unfortunately, the conventional technique for junction doping, ion implantation and anneal, is incapable of producing uniform and abrupt junctions shallower than 10 nm in depth due to random dopant fluctuations and ion-induced damage leading to broadened dopant profiles. Monolayer doping (MLD) is a promising technique for creating ultra-shallow junctions (USJs). The self-limiting nature of self-assembled monolayers (SAMs) of MLD provides uniform coverage of a specific quantity of dopant containing molecules. Subsequent high temperature anneals drive the dopant atoms into the semiconductor via diffusion mechanism.

In this work we explore how methyl arsonic acid molecules can be grafted on H-terminated Si(111) surfaces. This approach has recently been demonstrated for alkylphosphonic acids by Longo et al.¹, showing that the weak link of a molecule such as octadecylphosphonic acid (ODPA), is the P-C bond, with typical release of the carbon ligand around 500°C. First-principles calculations predict that the dissociation of the As-C bond occurs at lower temperature (barrier is 1 eV lower) and shallower junctions can be achieved due to the lower diffusion rate of arsenic compared to phosphorus. We have further used infrared absorption spectroscopy to determine the extent of chemisorption of the methyl arsonic acid molecules by quantifying the amount of H remaining and directly detecting the monolayer-Si bond (Si-O-As) at $\sim 1080\text{cm}^{-1}$. The final stage of the process (dopant diffusion) is characterized in-situ with Low Energy Ion Scattering (LEIS) with angstrom resolution, and supported by first-principles calculations.

(1) Longo, R. C.; Cho, K.; Schmidt, W. G.; Chabal, Y. J.; Thissen, P. *Advanced Functional Materials* 2013.

5:40pm **SS+EM-WeA12 Defect Engineering in Metal Oxides via Control of Surface-Bulk Defect Interactions**, *P. Gorai, E. Ertekin, E.G. Seebauer*, University of Illinois at Urbana Champaign

Control of native oxygen defects in transition metal oxides like ZnO plays an important role in photovoltaic, catalytic, photonic and gas sensing applications. The interaction chemistry between bulk point defects and reactive sites on clean semiconductor surfaces is comparable in richness to the reactions of gases with surfaces. Surfaces of semiconducting metal oxides can be used to manipulate the concentrations and spatial distributions of oxygen defects, particularly oxygen vacancies. Such surface-based defect engineering methods should play an especially important role in nanostructured devices where the surface to volume ratio is high. The present work discusses a novel mechanism of bulk defect interaction with c-axis polar ZnO surfaces that enables control of oxygen defect injection. Oxygen diffusion rates were measured by exposing natural-abundance single-crystal c-axis wurtzite ZnO to isotopically-labeled oxygen (¹⁸O₂) gas. The resulting diffusion profiles were measured by secondary ion mass spectrometry (SIMS) and modeled with mass transport equations for the reaction and diffusion of mobile and stagnant oxygen point defect species. The effective oxygen diffusivity is determined by fitting this model to experimental diffusion profiles. In addition, first principles calculations based on density functional theory (DFT) were performed to identify the elementary-step oxygen defect injection mechanism for active site exchange. Influence of the surface polarity on defect injection rates was also investigated. Gas-solid exchange experiments coupled with continuum and *ab initio* modeling will help us understand mechanistically the effect of each of the elementary steps on the defect injection rates at polar ZnO surfaces.

Authors Index

Bold page numbers indicate the presenter

— B —

Bent, S.F.: SS+EM-WeA1, 1

— C —

Cabrera, W.: SS+EM-WeA11, 2

Chabal, Y.J.: SS+EM-WeA10, 2; SS+EM-WeA11, 2; SS+EM-WeA9, 2

Chagarov, E.: SS+EM-WeA8, 1

— D —

De Benedetti, W.J.: SS+EM-WeA10, 2

Droopad, R.: SS+EM-WeA8, 1

— E —

Edmonds, M.: SS+EM-WeA8, 1

Eom, D.: SS+EM-WeA2, 1

Ertekin, E.: SS+EM-WeA12, 2

— G —

Gorai, P.: SS+EM-WeA12, 2

— H —

Hines, M.A.: SS+EM-WeA10, 2

— K —

Kent, T.: SS+EM-WeA8, 1

Kim, S.: SS+EM-WeA10, 2

Koo, J.-Y.: SS+EM-WeA2, 1

Kummel, A.C.: SS+EM-WeA8, 1

— L —

Lewis, N.: SS+EM-WeA3, 1

Longo, R.: SS+EM-WeA11, 2

Lu, Y.: SS+EM-WeA11, 2

— M —

Moon, C.-Y.: SS+EM-WeA2, 1

— P —

Peixoto, T.: SS+EM-WeA9, 2

Peng, W.: SS+EM-WeA10, 2

— S —

Seebauer, E.G.: SS+EM-WeA12, 2

Shong, B.: SS+EM-WeA1, 1

— T —

Thissen, P.: SS+EM-WeA11, 2

— V —

Vega, A.: SS+EM-WeA11, 2