Surface Science
Room: 309 - Session SS+AS+NS-ThA

Semiconductor Surfaces and Interfaces 1
Moderator: Ludwig Bartels, University of California - Riverside, Kurt Kolasinski, West Chester University

2:20pm **SS+AS+NS-ThA1 A Study of the InAs(001) Surface Electronic Structure**, ***Jacek Kolodziej***, *N. Tomaszewska, P. Ciochon*, Jagiellonian University, Poland

Angle-resolved photoelectron spectroscopy (ARPES) is used to study electronic bands at the n-type InAs(001) surfaces, having several different reconstructions. Indium-rich (8x2)/(4x2)and arsenic-rich c(2x8)/(2x4) surfaces as well as sulphur passivated (2x1) surface are prepared and investigated. Measured electronic bands are identified by analysis of their symmetries in the k-space.

In InAs crystal bulk the conduction band minimum (CBM) is located very close to the Fermi level (FL). Downward band bending, typical for the studied surfaces, causes formation of two dimensional electron gas, confined in a subsurface well, also known as the electron accumulation layer. This is indicated by characteristic quantized subband states visible in the ARPES spectra.

It is shown that the band bending magnitude and the quantization (of the accumulated electron energies associated with the coordinate normal to the surface) depend on the surface reconstruction as well as on the crystal doping. In most cases the electron accumulation bands are found at the Fermi level and close to the Γ_{1x1} symmetry point in the center of the surface Brillouin zone. The most clear picture is observed for the sulphur passivated (2x1) surface, where three distinct subbands with minima at E_1=-0,276eV, E_2=-0,096eV and E_3=-0,039eV with reference to Fermi level are found. Unexpectedly, for the indium rich surface, occupied conduction states are found also at Γ_{4x2} symmetry points indicating that, for this case, surface resonances mix with the electron accumulation states.

It is also shown that the observed surface bands are sensitive to surface treatment. Two surface preparation techniques have been used: cycles of ion beam annealing (IBA) and *ex situ* wet chemical treatment (WCT). Although low electron energy diffraction (LEED) indicates no increased disorder on the IBA surfaces they yield considerably worse electronic band images. This is most likely due to scattering of photoelectrons on the electrically active antisite defects.

We acknowledge financial support by Polish NCN (contract 2011/03/B/ST3/02070). The research was carried out with the equipment purchased thanks to European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

2:40pm **SS+AS+NS-ThA2 Control of Point Defect Behavior in Metal Oxides via Surface Band Bending**, *M. Li, P. Gorai*, ***Edmund Seebauer***, University of Illinois at Urbana-Champaign

Point defects within metal oxide semiconductors such as ZnO affect the material's performance in applications for nanoelectronics, gas sensing, photonics and photocatalysis. Past work in this laboratory has shown that the presence of a nearby surface can influence the concentrations and spatial distributions of defects deep within the semiconductor – often in a controllable way. One mechanism for this influence involves band bending near the surface. The present work employs the optical modulation technique of photoreflectance to measure the magnitude V_S of band bending at polar c-axis ZnO surfaces, and demonstrates that V_S can be manipulated over a significant range (roughly 0.23-0.44 eV) through variations of both temperature and the ambient partial pressure of O_2. Separate modeling of charged oxygen interstitial motion within the ZnO indicates that the near-surface concentration of these defects scales quadratically with V_S, thereby pointing to a novel general approach by which bulk point defect concentrations can be controlled.

3:00pm **SS+AS+NS-ThA3 Evolution of Surface-Assisted Oxidation of GaAs by Gas-Phase N_2O, NO and O_2**, ***Xueqiang Zhang***, *S. Ptasinska*, University of Notre Dame

Interests in metal-insulator-semiconductor field effect transistors (MISFETs) have been re-ignited recently due to the approaching of the scaling limit of Si complementary metal-oxide-semiconductors (CMOS). The fate of the III-V semiconductors relies strongly on the availability of a suitable surface passivation technology for fabrication of high quality insulator/III-V semiconductor interface. Gallium oxides on GaAs represent one of contenders for suitable surface passivated oxide-based dielectrics that could produce device-quality electrical interfaces between the oxide and semiconductor. However, there has been a debate on possible GaAs oxidation mechanisms over years. A comparisonal study between O_2 and other reactive but heteronuclear molecules (such as NO and N_2O) near realistic conditions would provide new insights for a better understanding of the GaAs oxidation process.

A near-ambient pressure X-ray photoelectron spectroscopy (NAP XPS) study of interfacial chemistry between GaAs (100) and three oxidizing gases, N_2O, NO and O_2, are carried out in a wide range of pressures and temperatures. At room temperature, surface oxidation, involving the formation of both Ga_2O and Ga_2O_3 is observed with the extent of oxidation in the order of NO>O_2>N_2O at elevated pressures. At elevated temperatures, the extent of oxidation is in the order of O_2> NO >N_2O. Our experimental results show that the oxidation of GaAs (100) by N_2O and NO is primarily determined by the probability and nature of interactions at the gas/semiconductor interface, whereas the limiting factor in the case of O_2 is the energy requirement for O-O bond dissociation.

3:20pm **SS+AS+NS-ThA4 Morphology Dependence of Gas-Phase Molecule Interactions with GaAs Surfaces**, ***Sylwia Ptasinska***, *X.Q. Zhang*, University of Notre Dame

A great deal of progress has been made in understanding molecular interactions at the interface of two-dimensional GaAs systems under ultra-high vacuum (UHV) conditions. While research on understanding of such interactions with lower-dimensional GaAs-based structures, such as one-dimensional nanowires (NWs), has not been performed despite the potential importance of these structures for developing nano-electronic circuits. Moreover, surface characterization of GaAs under more realistic than the UHV studies, are critical in any attempt to correlate surface chemistry with device properties.

Nowadays, due to recent developments in the surface characterization techniques, and especially the development of Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP XPS) [1], we are able to track surface chemistry in-situ under elevated pressures and temperatures for different morphologies.

In our present study we used NAP XPS to investigate the interaction of a radically non-planar GaAs surface comprised of an ensemble of GaAs NWs with O_2 and H_2O molecules. In this study the evolution of O_2 and H_2O molecule dissociation on GaAs NWs is tracked under in-situ conditions as a function of temperature and gas pressure to establish whether these processes depend on surface morphology. In contrast to ideally flat GaAs single crystal surfaces that are previously studied [2], gas molecules experienced the enhanced dissociation on GaAs NW ensembles due to an increase in the surface area ratio and the presence of stepped edges, atom vacancies, and other defects on non-flat semiconductor surfaces [3].

[1] D. E. Starr, Z. Liu, M. Havecker, A. Knop-Gericke, and H. Bluhm, Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy, Chem. Soc. Rev. 42, 5833-5857 (2013)

[2] X. Zhang, S. Ptasinska, Dissociative Adsorption of Water on an H_2o/GaAs(100) Interface-in-Situ near Ambient Pressure XPS Studies, J. Phys. Chem. C 118, 4259-4266 (2014)

[3] X. Zhang, E. Lamere, X. Liu, J. K. Furdyna, S. Ptasinska, Morphology Dependence of Interfacial Oxidation States of Gallium Arsenide under near Ambient Conditions, Appl. Phys. Lett. DOI:10.1063/1.4874983 (2014)

4:00pm **SS+AS+NS-ThA6 STM Imaging of the Buried Interface Structures at Ultra-thin Ag Films/Si(111) Substrates**, *Y. Yoshiike, I. Kokubo, Y. Aoki, K. Nakatsuji*, ***Hiroyuki Hirayama***, Tokyo Institute of Technology, Japan

The Schottky barrier height (SBH) has been reported to change sensitively to the variety of reconstructions at the Si substrates before depositing metal films in such systems as Pb/Si(111) and Ag/Si(111). Meanwhile, metal and Si do not mix, and the interfaces between the metals films and Si substrates are atomically abrupt in these systems. Thus, reconstructions at the Si(111) substrate are regarded to be preserved at buried interfaces under metal films, and have an influence on the SBH. In this respect, direct characterization of the buried interface structures in real space is required.

Scanning tunneling microscopy (STM) is a potentially promising method to achieve this, although it is conventionally considered to be useful only for exposed surfaces. Substantially, two different patterns, which were regarded to reflect the periodicity of the lattice at the buried interfaces, were observed on ultra-thin Pb films on the Si(111) substrates. However, the relation to the buried interface structures and the reason for the visualization were still not elucidated. With regard to these points, it is of significant interest to

examine whether a different reconstruction on the Si(111) substrate could cause various periodic patterns in abrupt interface systems other than the Pb/Si(111). It is also of interest to investigate the origin of the new periodic pattern. From this perspective, we investigated the STM images of ultra-thin Ag films on Si(111)√3×√3-B and Si(111)7x7 substrates in this study.

As results, ripples were observed at the surface of ultra-thin Ag films on a Si(111)√3×√3-B substrate system in STM and dI/dV images. The ripples were faint, independent of the bias voltage, and had the 3×3 periodicity. These indicate that the ripples were geometric corrugations formed at the Ag film surface, which were induced by the commensuration of the Ag(111)1×1 and Si(111)√3×√3-B lattices at the buried interface. In the meantime, a different ripples were observed at the surface of ultra-thin Ag films on a Si(111)7x7 substrate. The ripples were less periodic, but the Fast Fourier Transform of the images revealed that they had the 7x7 periodicity. In contrast to the Pb/Si(111)7x7 system, the ripples were independent of the bias voltage. Thus, the 7x7 ripple was also regarded to reflect the interface commensuration-induced geometric corrugations at the Ag film surfaces. More detailed results and Synchrotron radiated X-ray diffraction data of these buried interfaces will be shown and discussed in the presentation.

4:20pm **SS+AS+NS-ThA7 Ge on Si Epitaxy: Formation of 3D Ge Islands on Si(100)-2x1 by Annealing of Ge Wetting Layers**, ***Gopalakrishnan Ramalingam***, *P. Reinke*, University of Virginia

The epitaxial growth of Ge on Si(100)-(2x1) proceeds by Stranski-Krastanow (SK) mode where the formation of a wetting layer (WL) is followed by the emergence of quantum dots (QD). New growth modes have been reported recently which can lead to highly anisotropic Ge-wires and are achieved by annealing of the WL prior to the onset of QDs. The goal of the current work is to understand the atomistic processes involved in the transformation of the WL during annealing. We have investigated the WL structure during post-growth annealing at 400 to 600 C and report the transformation of epitaxial two dimensional Ge wetting layers into three dimensional islands, referred to here as pre-quantum dots (p-QDs). The p-QDs include hillocks with a stacked, wedding-cake type structure which show a progression to partial {105} faceting in case of thicker Ge WLs and longer anneal times. At low WL thickness (1-1.5 ML), the p-QDs have a stacked structure while thicker WLs (2-3.5 ML) lead to partial {105} faceted structures. All p-QDs, irrespective of the faceting or size, are characterized by an amorphous mound at the apex; this is strictly limited to p-QDs and not observed for regular QDs. The transition from the WL to p-QDs depends sensitively on the WL thickness (for a given annealing temperature): a six-fold increase in the island number density and a similar decrease in average island volume are observed when the initial WL thickness was increased from 1.2 to 3.5 ML. A small but notable increase in the island number density is observed when samples are annealed for longer durations (after the initial anneal to form the p-QDs) confirming that Ostwald ripening is not a dominant process in this system. Our observations will be integrated with a simulation of the growth process which will inform on the relevant mass transport and the role of strain on the WL transformation to p-QDs.

4:40pm **SS+AS+NS-ThA8 In Search of Nanopatterns: STM Provides Mechanistic Insights into Silicon Functionalization**, ***Erik Skibinski***, Cornell University, *W.J.I. DeBenedetti, Y.J. Chabal,* University of Texas at Dallas, *M.A. Hines*, Cornell University

Functionalization reactions leave characteristic patterns on surfaces that can be read by STM, providing insight into reaction mechanisms. The functionalization of silicon surfaces with organic monolayers has attracted interest for applications ranging from chemical and biological sensing to renewable energy. A wide variety of surface functionalization reactions have been developed based on dehydration reactions that target surface -OH groups on oxidized silicon. Uniform functionalization therefore requires a uniform, high density of surface –OH groups. Hydroxylating silicon surfaces without concomitant oxidation of the substrate was long thought impossible; however, a novel three-step strategy was recently reported.[1] A hydrogen-terminated silicon surface is first methoxylated in methanol, and then the Si–OCH_3 sites are converted first to Si–F then to Si-OH by successive immersion in hydrofluoric acid and water. Original spectroscopic evidence suggested the creation of nanopatterned surface, in which every other site on the surface is functionalized. New STM and spectroscopic data show selective reaction at step edges and an unexpected functionalization pattern. The mechanistic implications of this pattern will be discussed.

[1] D. J. Michalak, S. R. Amy, D. Aureau, M. Dai, A. Estève, and Y. J. Chabal, *Nat. Materials* **9,** 266 (2010).

5:00pm **SS+AS+NS-ThA9 Benzene and Chlorobenzene Dissociation Pathways Involving Singlet-Triplet Crossing on the Si(100) Surface Modeled Using Small Clusters**, ***Nicholas Materer***, *E. Butson,* Oklahoma State University, *Q. Zhu*, University of Pittsburgh

The dimer rows in the Si(100) surface have di-radical character, which can be configured as a singlet or triplet. At the minimum energy crossing point of the singlet to triplet crossing for a single Si-dimer cluster, the spin-orbit coupling (SOC) coefficient was determined to be approximately 25 cm^{-1}. Using this SOC, the Landau-Zener spin-crossing probability at room temperature was computed to be approximately 0.5%. Similar computational methods were used to investigate possible adsorption and dissociation processes for benzene and chlorobenzene. The 1,2 product (a tilted configuration) for benzene adsorption was proposed to undergo C-H bond cleavage to form lower-energy products. However, this process requires a spin-crossing of the initial 1,2 bond product, followed by a transition state with large activation barriers. Chlorobenzene can absorb on the SI(100) by breaking one double bond on the phenyl ring and forming two new carbon-silicon bonds with the dimer cluster. Again, for dissociation to occur, the system must undergo a spin crossing process from the singlet to the triplet state. After this spin crossing event, the carbon-chlorine bond is cleaved and a new silicon-chloride bond is formed. The final product is a dissociation product with chlorine and a phenyl ring attached directly to the (100) surface of silicon. Both cases illustrate that spin crossing could be more common than realized in the adsorption and dissociation of organic molecules on Si(100).

5:20pm **SS+AS+NS-ThA10 Adsorption of Organic Triols on Ge(100)-2x1 Surface**, ***Tania Sandoval***, *S.F. Bent*, Stanford University

Organic functionalization of semiconductor surfaces can provide tunable control of interfacial properties in organic-inorganic hybrid devices. The key step toward applications in this area is to understand the selectivity in the reactions of organic molecules on these surfaces.

In this work, adsorption of 1,3,5-benzenetriol and 2-hydroxymethyl-1,3-propanediol on Ge(100)-2x1 surface was studied. Both molecules have three hydroxyl groups available for reaction with the Ge surface. While the reactions of these molecules with the surface may be similar, differences in reactivity can be expected due to their different backbone structures. The aim of this study is to investigate whether a difference in reactivity exists and how the reaction with the surface is affected by the structure of the molecules.

Energy diagrams for both molecules were calculated by density functional theory. In both cases, proton transfer reactions from two or three hydroxyl groups to the Ge dimer atoms are suggested as thermodynamically favored pathways. However, the reaction through 3 OH groups in 2-hydroxymethyl-1,3-propanediol is more than 15 kcal/mol more stable than the same reaction in 1,3,5-benzenetriol. This difference can be associated with strain of the aromatic ring.

Infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) were performed to investigate the adsorption products. IR results show the presence of a ν(Ge-H) mode for both molecules, suggesting the proton transfer reaction as the main pathway. XPS spectra of each molecule both chemisorbed and physisorbed on the surface were obtained. The differences between these two spectra can be used to indicate the reaction products. For both molecules, no change in the C(1s) spectra is observed, suggesting that carbon does not form a bond directly with Ge. On the other hand, clear differences between the chemisorbed and physisorbed O(1s) spectra are observed for both molecules. A second peak with a lower binding energy only in the chemisorbed spectra, assigned to a Ge-O bond confirms that both molecules react with the Ge surface through O-H dissociation. The ratio between O(1s) peaks indicates that about 80% of the total hydroxyl groups are involved in reaction with Ge, suggesting that a significant fraction of the adsorbates react with the surface through all 3 of their hydroxyl groups.

In conclusion, both 1,3,5-benzenetriol and 2-hydroxymethyl-1,3-propanediol react with the Ge(100)-2x1 surface through O-H dissociative adsorption. Little difference in reactivity was observed between these triols, suggesting that other factors besides backbone structure are governing the reactivity in these systems.

5:40pm **SS+AS+NS-ThA11 The Chemistry of Adsorbed Water on Semiconductor Surfaces for Aqueous Photoelectrochemistry**, ***Coleman Kronawitter***, *B. Koel*, Princeton University

The surface chemistry of water molecules adsorbed on single crystals, model structures relevant to photoelectrode-water interfaces in solar photoelectrochemical systems, is discussed. In heterogeneous processes relevant to photoelectrochemistry, the interaction of water with semiconductor and metal oxide surfaces is often a critical event whose character influences subsequent chemical pathways that ultimately dictate the reactions' efficiencies and selectivities. A surface science approach is

used to characterize adsorbed water molecules on copper oxide and III-V semiconductor surfaces known to actively facilitate solar energy conversion in photoelectrochemical fuel synthesis devices. In this approach, ultrahigh vacuum conditions are used to facilitate the fabrication of highly characterizable adsorbate systems, and the use of single crystal substrates permits analysis of surface chemistry independent of sample grain boundaries and morphology. An understanding of the surface chemistry of adsorbed water is developed through core-level spectroscopies and scanning probe microscopy.

Authors Index

Bold page numbers indicate the presenter

— A —

Aoki, Y.: SS+AS+NS-ThA6, 1

— B —

Bent, S.F.: SS+AS+NS-ThA10, 2
Butson, E.: SS+AS+NS-ThA9, 2

— C —

Chabal, Y.J.: SS+AS+NS-ThA8, 2
Ciochon, P.: SS+AS+NS-ThA1, 1

— D —

DeBenedetti, W.J.I.: SS+AS+NS-ThA8, 2

— G —

Gorai, P.: SS+AS+NS-ThA2, 1

— H —

Hines, M.A.: SS+AS+NS-ThA8, 2
Hirayama, H.: SS+AS+NS-ThA6, **1**

— K —

Koel, B.: SS+AS+NS-ThA11, 2
Kokubo, I.: SS+AS+NS-ThA6, 1
Kolodziej, J.: SS+AS+NS-ThA1, **1**
Kronawitter, C.: SS+AS+NS-ThA11, **2**

— L —

Li, M.: SS+AS+NS-ThA2, 1

— M —

Materer, N.: SS+AS+NS-ThA9, **2**

— N —

Nakatsuji, K.: SS+AS+NS-ThA6, 1

— P —

Ptasinska, S.: SS+AS+NS-ThA3, 1; SS+AS+NS-ThA4, **1**

— R —

Ramalingam, G.: SS+AS+NS-ThA7, **2**
Reinke, P.: SS+AS+NS-ThA7, 2

— S —

Sandoval, T.: SS+AS+NS-ThA10, **2**
Seebauer, E.G.: SS+AS+NS-ThA2, **1**
Skibinski, E.S.: SS+AS+NS-ThA8, **2**

— T —

Tomaszewska, N.: SS+AS+NS-ThA1, 1

— Y —

Yoshiike, Y.: SS+AS+NS-ThA6, 1

— Z —

Zhang, X.Q.: SS+AS+NS-ThA3, **1**; SS+AS+NS-ThA4, 1
Zhu, Q.: SS+AS+NS-ThA9, 2