

Surface Science

Room: N - Session SS2-FrM

Semiconductor Surfaces and Interfaces II: Si

Moderator: C.L. Hinkle, University of Texas at Dallas

8:20am **SS2-FrM1 Observation of Realtime Oxidation of Si(111) Surfaces using Second Harmonic Generation**, K. Gundogdu, B. Gokce, E.J. Adles, D.E. Aspnes, North Carolina State University

Realtime material diagnostics during material growth is commonly used in industrial applications. Linear optical methods specifically spectroscopic ellipsometry (SE) probe thin film thickness with a nanometer precision by measuring the change in dielectric susceptibility during material growth. However SE is a spatially averaging technique and therefore can not probe the chemical change at the bond level. In this work we show that second harmonic generation experiments can be used to directly visualize changes in interface and surface bonds in realtime, providing a powerful bond structure characterization tool. We employed SHG experiments to probe the oxidation of hydrogen terminated Si(111) surfaces. We are able to extract the oxidation rates for different bonds on Si(111) surfaces that are nominally flat and with vicinal cut. We found that the initial hydrogen termination process effects the oxidation rate in the bond level. We compare the results of SHG measurements with that of spectroscopic ellipsometry.

8:40am **SS2-FrM2 Surface Passivation Mechanism of Atomic Layer Deposited Al₂O₃ Films on c-Si Studied by Optical Second-Harmonic Generation**, N.M. Terlinden, J.J.H. Gielis, V. Verlaan, G. Dingemans, M.C.M. van de Sanden, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

Recently, it was shown that Al₂O₃ thin films synthesized by (plasma-assisted) atomic layer deposition (ALD) provide excellent surface passivation of *n*, *p* and *p*⁺ type *c*-Si as highly relevant for *c*-Si photovoltaics. It was found that a large *negative* fixed charge density (up to 10¹³ cm⁻²) in the Al₂O₃ film plays a key role in the passivation mechanism of Al₂O₃ [1, 2]. The surface passivation quality of Al₂O₃ strongly increases with film thickness before reaching saturation around 10 nm as determined by carrier lifetime spectroscopy. In this contribution a study into the thickness effect will be presented in order to distinguish between the influence of field-effect passivation, *i.e.* electrostatic shielding of charge carriers by the fixed negative charge, and chemical passivation, *i.e.* by a reduction of the interface defect density. To this goal the nonlinear optical technique of second-harmonic generation (SHG) has been utilized. SHG is highly surface and interface specific and allows for the contactless determination of internal electric fields ($\geq 10^5$ V/cm⁻¹). Spectroscopic SHG, carried out with a femtosecond Ti:sapphire laser tunable in the 1.33-1.75 eV photon energy range, has revealed a thickness independent electric field for Al₂O₃ films with thicknesses ranging from 2 to 20 nm. This implies that the field-effect passivation is not affected by the film thickness and that the thickness dependence in passivation quality can be attributed to a changing level of chemical passivation. Moreover, this result confirms that the fixed negative charges are located at the Al₂O₃ interface as also indicated by conventional C-V measurements. In addition, SHG shows clear differences between measurements performed on Al₂O₃ films grown by thermal and plasma-assisted ALD. These are likely related to the properties of the interfacial SiO_x induced by either growth process. The presence of this oxide is suggested to be responsible for the chemical passivation quality. Furthermore, the differences indicate a smaller contribution of field-effect passivation for the Al₂O₃ grown with thermal ALD compared to the film from the plasma-assisted process. These results have led to a deeper understanding of the *c*-Si surface passivation by Al₂O₃ as will be discussed.

[1] B. Hoex *et al.* J. Appl. Phys. **104**, 044903 (2008)

[2] J.J.H. Gielis *et al.* J. Appl. Phys. **104**, 073701 (2008)

9:00am **SS2-FrM3 Influence of Alkali-Metal Adsorption on Phase Transition of In/Si(111)-4 × 1 Surface**, H. Shim, W. Lee, G. Lee, Inha University, Republic of Korea, S. Yu, J. Koo, Korea Research Institute of Standards and Science

One monolayer of In on a Si(111) surface forms 4×1 structure at room temperature (RT). This In/Si(111)-4×1 surface has a quasi-one dimensional (1D) metallic electronic structure and undergoes a symmetry-lowering phase transition into an insulating 8×2 phase at low temperature (LT) upon cooling the sample below approximately 130 K [1]. Adsorption of Na atoms on the surface was reported to convert the 4×1-RT phase into the 8×2-LT phase even at RT [2]. We investigated using low-energy electron diffraction (LEED) the influence of alkali-metals (Na, K, Li) adsorption on the

structural phase transition of this quasi-1D In/Si(111) surface. Introducing the alkali metals with low coverage on the surface at room temperature was found to affect the 4×1-to-8×2 structural phase transition by lowering the transition temperature (T_c). The T_c decreased almost linearly and the transition becomes more rounded when the amount of deposited alkali-metals atoms was increased. The decrease of T_c with the increase of the amount of adsorbed Na atoms is suggested to be due to the doping of electrons from adsorbates to the substrate [3]. In the high-coverage regime, new superstructures appear in LEED with the adsorption of alkali metals. Comparison of the adsorbate-induced superstructures in low-coverage and high-coverage regimes will be made and discussed.

[1] H. W. Yeom, *et al.*, Phys. Rev. Lett. **82**, 4898 (1999)

[2] S. S. Lee, *et al.*, Phys. Rev. Lett. **88**, 196401 (2002)

[3] H. Shim, *et al.*, Appl. Rev. Lett. *in press* (2009)

9:20am **SS2-FrM4 The First Attachment of Polybutadiene and Functionalized Polybutadiene to Hydrogen-Terminated Silicon, with Post-Derivatization of these Adsorbed Species**, E. Nelsen, T. Wickard, Brigham Young University, H. Schlaad, Max Planck Institute of Colloids and Interfaces, Germany, R.C. Davis, M.R. Linford, Brigham Young University

We report the first attachment of polymers with pendant vinyl groups to hydrogen-terminated silicon(111) (Si(111)-H) under mild conditions; 1,2-addition polybutadiene (Mw 3200-3500) in solution was attached to Si(111)-H at room temperature with only visible light activation. We also report the partial functionalization, in solution, of 1,2-addition polybutadiene with various thiols using thiol-click chemistry and the subsequent attachments of these compounds to Si(111)-H. The partially functionalized polybutadienes allow further functionalization at the surface through their unreacted carbon-carbon double bonds, as demonstrated with a perfluorinated thiol. We present this as a useful strategy for silicon surface modification. Surfaces were characterized with contact angle goniometry, spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic force microscopy (AFM).

9:40am **SS2-FrM5 Mechanistic Study of Photochemical Grafting of Alkenes to Group IV Semiconductors**, X. Wang, J. Streifer, P. Colavita, R.J. Hamers, University of Wisconsin-Madison

The grafting of organic molecules on semiconductor surfaces initiated by UV light has become an efficient means to tailor the chemical and physical properties of surfaces of materials, enabling their integration with various applications of the devices. *In situ* photoelectron yield experiments were performed in the spectral range from 3 to 6 eV on alkene liquid/nanocrystalline diamond (NCD) interfaces. *N*-Alkenes carrying different terminal functional groups: trifluoroacetamide-protected 1-aminodec-1-ene (TFAAD) and 10-*N*-Boc-aminodec-1-ene (tBoc) were used to investigate the dependence of photoelectron yield on the energy of the molecular acceptor level. Amorphous carbon was used in addition to NCD to study the influence of the substrate electronic structure on the photoelectron yield threshold. The photochemical attachment of TFAAD on H-terminated NCD surfaces at various incident photon energies was characterized by X-ray photoelectron spectroscopy (XPS) to investigate the correlation between the excitation energy and the reaction efficiency. These measurements reveal that the photochemical reaction on carbon surfaces is initiated via the photoejection of electrons from the solid valence band into the acceptor levels of the alkenes. SEM images of patterned molecular layers on two H-terminated single crystal diamonds (SCD, type Ib and IIb) with different hole mobilities reveal much sharper transition between functionalized and non-functionalized regions on the sample with much lower hole mobility (type Ib SCD). However, the surface coverage of grafted alkenes as characterized by XPS is quite similar on these two surfaces. These data imply that while the photoemission of electrons controls the reaction efficiency, the holes left in the substrates can diffuse and control the grafting sites.

Recent data exploring the mechanism on silicon will also be presented. Our comparison of silicon and diamond suggests that there are some common factors underlying the ability to graft alkenes onto various semiconductors, but also some important differences. These results suggest that photochemical grafting may be broadly applicable to a wide range of materials, and that a fundamental understanding of the mechanism facilitates the design and synthesis of well defined functional interfaces.

10:00am **SS2-FrM6 Structure and Order of Organophosphonate Self-Assembled Monolayers on Si(100)**, *M. Dubey, T. Weidner, L.J. Gamble, D. Ratner, D.G. Castner*, University of Washington

Organophosphonic acid self-assembled monolayers on oxide surfaces have seen growing use in electrical and biological sensor applications [1-2]. Molecular order in organophosphonic acid SAMs is highly desirable for reproducible electronic properties of these modified surfaces. In this regard, packing and order of the SAMs is important, as it influences the electron transport measurements. In this study, we examined the order of the phosphonate films deposited on silicon oxide surface by the Tethering By Aggregation and Growth (T-BAG) method [3] using various state-of-art surface characterization tools. Near edge x-ray absorption fine structure (NEXAFS) spectroscopy is used to study the order of a methyl- and hydroxyl- terminated phosphonate SAMs in vacuum and sum frequency generation (SFG) spectroscopy is used to study their order in aqueous condition. X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) on these samples confirm the presence of chemically intact monolayer phosphonate films. NEXAFS spectroscopy confirmed a considerable degree of molecular order in the octadecylphosphonic acid (ODPA) and 11-hydroxyundecylphosphonic acid (PUL) films with a tilt angle of 37° and 47° respectively. *In situ* SFG studies in deuterated water were conducted to determine the order of these films under biologically relevant conditions. The ODPA film showed the peaks for terminal methyl units, which are expected for ordered films. PUL films also showed a considerable degree of alignment indicated by resonances of the methylene unit next to the terminal hydroxyl group. These studies indicate that well ordered SAMs with methyl or hydroxyl termination can be prepared on oxide surfaces using phosphonate headgroups. These surfaces can be subsequently used to anchor biomolecules for biomaterial and biosensor applications.

[1] A. Cattani-Scholz, D. Pedone, M. Dubey, S. Nepl, B. Nickel, P. Feulner, J. Schwartz, G. Abstreiter, M. Tornow, *Acs Nano* **2008**, 2, 1653.

[2] H. Klauk, U. Zschieschang, J. Pflaum, M. Halik, *Nature* **2007**, 445, 745.

[3] E. L. Hanson, J. Guo, N. Koch, J. Schwartz, S. L. Bernasek, *Journal of the*

American Chemical Society **2005**, 127, 10058

10:20am **SS2-FrM7 Hydrogen-bond Mediated Chemistry of Glycine on Si(111)7×7: A Catch-And-Release Approach to Surface Functionalization**, *K.T. Leung*, University of Waterloo, Canada

The growth of glycine film by thermal evaporation on Si(111)7×7 at room temperature has been studied by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). In contrast to the common carboxylic acids, glycine is found to adsorb on the 7×7 surface through dissociation of the N-H bond (instead of the O-H bond). The presence of a transitional adlayer between the first adlayer and the zwitterionic multilayer is identified by its characteristic N 1s XPS features attributable to intermolecular N-to-HO hydrogen bond. An intramolecular proton transfer mechanism is proposed to account for the adsorption process through the amino group. We also demonstrate that the observed transitional adlayer can be used as a flexible platform to “catch-and-release” biomolecules with compatible H-bonding active sites in a controllable and reversible manner. Intricate evolution of the surface adsorption arrangement during the initial growth has also been monitored by STM. Early evidence of collective assembly of glycine into novel structures in the nanometer length scale could be found.

10:40am **SS2-FrM8 Site-selective Reactivity of Ethylene on Si(001) induced by Local Electronic Distortions**, *G. Mette, C.H. Schwalb*, Uni Marburg, Germany, *M. Dürr*, Hochschule Esslingen, Germany, *U. Höfer*, Uni Marburg, Germany

The adsorption of organic molecules on semiconductor surfaces is of special interest with respect to surface functionalisation and its use in molecular electronics. Due to the localized electronic states of a semiconductor surface, its reactivity strongly correlates with the local electronic properties of the dangling-bond states. Dissociative adsorption of H₂ on Si(001), e.g., shows pronounced site-selective reactivity at steps or preadsorbed atomic hydrogen [1].

In this study, we test the concept of site-selective reactivity at locally distorted configurations for more complex, organic molecules. On that account, the adsorption of ethylene on clean and hydrogen precovered Si(001) surfaces has been investigated by means of scanning tunneling microscopy. On the clean surface, two ethylene adsorption geometries were identified with ethylene adsorbed on one and two dimers, respectively. The latter adsorption geometry shows significantly lower reactivity and has not been observed so far. Preadsorption of atomic hydrogen and the concomitant distortion of the electronic states is found to increase the reactivity of this two-dimer adsorption pathway by almost two orders of

magnitude. Its site selective reactivity thus surpasses that of the one dimer configuration on the clean surface.

The results are rationalized in the framework of a precursor mediated adsorption process. Our experiments indicate that the conversion barrier between precursor and final chemisorbed state can be efficiently controlled by changing the local electronic structure of the surface. Thus, locally distorted dangling-bond configurations allow for the control of site-selective reactivity also in the case of barrierless, non-dissociative adsorption of an organic molecule.

[1] M. Dürr and U. Höfer, *Surf. Sci. Rep.* 61, 465 (2006)

11:00am **SS2-FrM9 Identifying Adsorbate Structures on Semiconductor Surfaces Using Simulated Scanning Tunneling Microscope Images**, *L. Yang, D. Doren*, University of Delaware

Simulated Scanning Tunneling Microscopy images, based on first-principles calculations, have been used to characterize adsorption products of organic molecules on semiconductor surfaces and assign molecular structures to specific features in experimental STM images. Three examples are presented: 1) Styrene molecular lines on the H-terminated Si(100)-2x1 surface system exhibit several novel molecular conductance phenomena. First-principles calculations show that the phenyl ring orientation at chain ends are fluxional, favoring structures with the terminal ring arranged perpendicular to the molecular line. Simulated STM images show that the tunneling current depends strongly on the phenyl ring orientation, since it controls the coupling between the charged dangling bond and the styrene π system. The perpendicular orientation shows higher conductivity than the parallel one, increasing the apparent height of the molecule at the end of the row. This is consistent with experimental observations, while the simulated images of the parallel-ring geometry are not. Because such subtle changes in molecular structure control the flow of electrical currents, STM can be used to distinguish these conformations. 2) The bonding configuration of styrene attached to the bare Si(111)-7x7 surface is not known from spectroscopic measurements, though two likely possibilities have been identified. Matching simulated empty-state and filled-state STM images to new experimental observations provides strong evidence that the attachment of styrene to Si(111)-7x7 is by a [4+2] cycloaddition, involving both the external -CH=CH₂ and a C=C inside the phenyl ring. A comparison experimental images to theoretical predictions of the bias dependence for the two binding structures is critical to this identification. 3) Three unsaturated organic molecules – styrene, phenyl acetylene, and benzaldehyde – were attached to the H-terminated Si(111) surface through analogous radical chain reactions. Both simulated and experimental STM images of the three molecules show significant differences in apparent height, despite small differences in physical height. Thus STM is sensitive to the functional group used to link the molecule to the surface. The simulations also suggest a new scanning protocol that can enhance the contrast among molecules. The so-called “local constant height” STM images, which probe the spatial variation of conductance, show distinctive features for the three molecules that can be used to tell the molecules apart very easily.

11:20am **SS2-FrM10 Defect Engineering via Modification of Semiconductor-Oxide Interfaces**, *P. Gorai, Y. Kondratenko, E.G. Seebauer*, University of Illinois at Urbana-Champaign

The behavior of defects within silicon can be changed significantly by controlling the chemical state at nearby surfaces or solid interfaces. Experiments have shown that certain chemical treatments change the ability of a free surface to act as a “sink” for point defects such as interstitials. When the surface is made chemically active, this ability rises. The surface can then remove Si interstitials selectively over impurity interstitials and such behavior can be kinetically quantified through an annihilation probability. Although annihilation probabilities for interstitials have been measured under various conditions for free surfaces, very little understanding exists for the corresponding quantity at solid-solid interfaces. Understanding of interface influence on interstitial annihilation is very important in fabrication of advanced transistors for post-implantation damage removal and dopant activation. The present work seeks to develop scientific understanding of interface activity for Si interstitial annihilation and measure the annihilation probabilities at interfaces between silicon and several kinds of oxides and nitrides. Diffusion of isotopically labeled Si (mass 30) in Si host lattice was used as a marker for elucidating how changes in the Si-SiO₂ interface affected Si self-diffusion after annealing. Marked differences are observed among the various interfaces. Continuum simulations of the measured SIMS profiles were subsequently employed to quantify annihilation rates at the Si-SiO₂ interface.

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