Thursday Morning, November 3, 2005

Surface Science
Room 202 - Session SS2-ThM
Functionalization of Semiconductor Surfaces

Moderator: J.E. Crowell, University of California, San Diego

8:20am **SS2-ThM1 Dissociative Chemisorption of SiH@sub 4@ on Si(100): Threshold Energy and Mechanism***, **H.L. Abbott**[1],* University of Virginia*; D.F. Kavulak,* University of California, Berkeley*; I. Harrison,* University of Virginia

A three-parameter local hot spot model of gas-surface reactivity is employed to analyze and predict dissociative sticking coefficients for SiH@sub 4@ incident on Si(100) under varied nonequilibrium conditions. Two Si surface oscillators and the molecular vibrations, rotations, and translational energy directed along the local surface normal are active degrees of freedom in the 15 dimensional microcanonical kinetics. The threshold energy for SiH@sub 4@ dissociative chemisorption is found to be 19 kJ/mol, in quantitative agreement with recent GGA-DFT calculations that predict an intra-dimer mechanism. A simple scheme for increasing the rate of chemical vapor deposition of silicon from SiH@sub 4@ at low surface temperatures and/or on hydrogen passivated Si(100) is discussed.

8:40am **SS2-ThM2 Organic Functionalization of Semiconductors Using Amino Acids; Quantum Resonance Coupling and Electron Transport Effects***, G.D. Guilluame, G. Zhang, **C.B. Musgrave**,* Stanford University

We have used DFT to simulate the attachment of amino acids and various unique organic molecules on Si and Ge surfaces. These structures have potential applications in molecular electronics and sensors if their structures can be controlled and if the resulting interface electronic structure provides appropriate electronic properties. We will present a summary of the various unique reactions of amino acids on Si(100)-2x1 we have investigated and focus on certain organics functionalities that are stabilized on Si and Ge by quantum mechanical resonance which stabilize the product and leads to stronger electronic coupling between the attached organic and the semiconductor substrate which might be useful in improving electrode-molecule charge transfer for organic-semiconductor molecular electronic devices. We will also discuss the accurate simulation of the electronic band structure of these molecular junctions required for correct prediction of the electron transport across these junctions. We have found that the common DFT methods are inadequate for this task, although the KMLYP method correctly predicts the HOMO and time-dependent KMLYP (TD-KMLYP) correctly predicts the LUMO energy.

9:00am **SS2-ThM3 Amide Chemistry at the Ge(100)-2x1 Interface***, **A.J. Keung**, M.A. Filler,* Stanford University*; S.F. Bent,* Stanford University, US

Organic functionalization of semiconductor surfaces has many potential applications including semiconductor processing, molecular electronics, and chemical sensors. In particular, understanding the surface reactivity of the amide linkage could be important in developing biologically-based devices. In situ vibrational spectra were obtained as a function of coverage, temperature, and time for a series of primary, secondary, and tertiary amides absorbed on the Ge(100)-2x1 surface under ultrahigh vacuum conditions. For the tertiary amides, including dimethyl formamide, 1-methyl-2-pyrrolidinone, and n,n-dimethyl acetamide, asymmetric and symmetric N-C-O stretching, aldehydic C-H bending, as well as methyl deformation modes were observed, while Ge-H stretching modes were absent. This data provides evidence that tertiary amides form a dative-bond between the carbonyl oxygen and the electrophilic germanium dimer atom. Theoretical spectra of dative-bonded structures, calculated with density functional theory, agree well with experiment. In addition, these products desorbed at 310K on the timescale of minutes suggesting dative-bonded tertiary amides are just at the cusp of stability on Ge(100)-2x1. The primary and secondary amides, formamide and n-methyl formamide, respectively, were also investigated. Two types of products were observed for each compound at room temperature. Comparison to the experimental spectra of dimethyl formamide provides evidence for dative-bonded products. Dissociation products were also formed as evidenced by the growth of Ge-H stretches. The dissociation products were favored at higher temperatures, and there is evidence for dative-bonded adducts converting to these products upon annealing. Due to a kinetic barrier to this reaction, the dative-bonded state can be isolated at low temperature. These results have implications for understanding the reactivity of larger biological molecules such as peptides.

9:20am **SS2-ThM4 Layer-by-Layer Growth on Ge(100) via Spontaneous Chemical Reaction***, **A. Kim**,* Korea Advanced Institute of Science and Technology (KAIST), Korea*; M.A. Filler,* Stanford University*; S.F. Bent,* Stanford University, US*; S. Kim,* KAIST, Korea, South Korea

We have demonstrated the layer-by-layer growth, via a urea coupling reaction between two bifunctional molecules, ethylene diamine and 1,4-phenylene diisocyanate, to form an ultrathin film on Ge(100)-2´1 at room temperature under vacuum conditions.@footnote 1@ The initial adsorption and subsequent growth of each layer was studied with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy. Ethylene diamine reacts with Ge(100)-2x1 to produce a surface-bound amine group which is available for additional reaction. Subsequent exposure of 1,4 phenylene diisocyanate leads to a spontaneous urea coupling reaction between the surface-bound amine and highly reactive isocyanate functional group. Three bands at 1665, 1512, and 1306 cm-1 are characteristic of a urea linkage and provide evidence of the coupling reaction. The coupling procedure can be repeated in a binary fashion to create covalently bound ultrathin films at room temperature and, in the present work, we demonstrate the successful growth of four layers. In addition, we have found that an initial exposure of 1,4-phenylene diisocyanate to Ge(100)-2x1 produces an isocyanate-functionalized surface which, upon exposure to ethylene diamine, also forms urea linkages. This layer-by-layer deposition method provides a strategy with which to design and produce precisely tailored organic materials. @FootnoteText@ @footnote 1@ Kim, A.; Filler, M. A.; Kim, S.; Bent, S. F.; J. AM. CHEM. SOC. 2005, 127, 6123-6132

9:40am **SS2-ThM5 Alkylation of Silicon and Germanium Surfaces***, **S. Rivillon**, Y.J. Chabal,* Rutgers University

Chemical modification of semiconductor surfaces is used to modify the surface properties and to provide new functionality. In particular, the formation of self-assembled monolayers (SAM) can lead to a broad range of applications such as micromechanical systems (MEMS), biosensors, lithography, and growth of alternative dielectrics without an interfacial oxide. To date, most work has been performed on silicon surfaces for which wet chemical cleaning methods have been well developed. In this talk, we focus on the alkylation of H- and Cl-terminated Ge surfaces, with close comparison to results of similar treatments on Si surfaces. Using infrared absorption (IR) spectroscopy, we have show that while HF-etched Si(100) and Ge(100) are atomically rough, the distribution of hydride species is different: hydrogen-terminated Si(100) exhibits mono-, di- and tri-hydride species, while H-Ge(100) only exhibit Ge-H and Ge-H@sub2@ species. The stability of both semiconductor surfaces to air is also different: for H-Si(100), oxygen is slowly incorporated into the substrate, forming O@sub3@-Si-H; for H-Ge(100), little oxidation takes place. Instead, hydrocarbons react with the hydrogen forming Ge@sub2@=CH@sub2@. This propensity of the Ge surfaces for alkylation has been used and comparison with silicon indicates that methoxylation takes place more rapidly on Ge surfaces.

10:00am **SS2-ThM6 Correlation of Surface Electronic Structure with Organic Reactivity on Si(114)***, **D.E. Barlow**, A.R. Laracuente, L.J. Whitman, J.N. Russell,* Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface oriented 19.5° between (001) and (111). The equilibrium surface reconstruction is comprised of parallel rows of dimers, rebonded atoms, and tetramers, with all the rows oriented along the same crystallographic direction.@footnote 1@ The different Si(114) structural motifs within each row have distinct electronic structures, making this surface an ideal template for studying the relationship between adsorption site geometry (including symmetry), local electronic structure, and chemisorption of organic molecules on clean silicon surfaces. In this study, we have experimentally characterized the effects of charge transfer, @pi@ bonding, orbital symmetry, and di-radical reaction pathways on the cycloaddition chemisorption of ethylene on Si(114)-(2x1). Transmission FTIR spectroscopy was used to confirm the basic chemical structure and orientation of the chemisorbed ethylene. The results indicate a di-@sigma@ bonded product with a C-C bond axis preferentially oriented along the row direction. Using atomic-resolution STM, we identified three common adsorption structures located at the dimer, rebonded atom, and tetramer sites. In correlation with the FTIR results, these structures can be identified as [2+2] cycloaddition products, bridged rebonded atoms, and [4+2] cycloaddition products, respectively. The order of site reactivity is found to be rebonded atoms > dimers > tetramers. Reasons for this reactivity trend will be discussed.

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[1] **Morton S. Traum Award Finalist**

@FootnoteText@ @footnote 1@S. C. Erwin, A. A. Baski, and L. J. Whitman, Phys. Rev. Lett. 77, 687 (1996).

10:20am **SS2-ThM7 Contact Formation with a Single Molecule: 1,3-cyclohexadiene on the Si(100) Surface***, B. Naydenov, L.C. Teague, P. Ryan, **J.J. Boland,*** Trinity College Dublin, Ireland **INVITED**

We have studied the contact formed between a 1,3-cyclohexadiene (1,3-CHD) molecule on Si(100) and a Pt STM probe tip at 5 K. DFT studies indicate that the STM images obtained are the result of a specific probe-molecule interaction. This is confirmed by measurements of local barrier heights acquired at different probe-molecule separations and the associate change in the vibrational spectra measured at each separation. On this basis, we provide a detailed analysis of the physical and chemical interactions that accompany contact formation in this molecular system.

11:00am **SS2-ThM9 Surface Functionalization of Si(100)2x1 by Halogenated Ethylenes: Formation of C2-dimer, Vinylene, Vinylidene, and their Halogenated Derivatives***, K.T. Leung, **X.J. Zhou,*** University of Waterloo, Canada

Our recent studies on halogenated ethylenes on Si(111)7x7 and Si(100)2x1 have demonstrated the importance of a competing insertion mechanism to the commonly observed cycloaddition mechanism for Si surface functionalization. The combination of the C=C bond with Cl atoms provides interesting molecular platforms for investigating various novel effects involving different molecular symmetries and structures, Cl content and structural chemistries. The adsorption of these chlorinated ethylenes and their subsequent thermal chemistries on Si single-crystal surfaces can be used to generate ordered arrays of novel adspecies, including tetra-@sigma@ bonded C2 dimer (>C=C<), di-@sigma@ bonded vinylene (-HC=CH-) and vinylidene (>C=CH@sub 2@), and mono-@sigma@ bonded vinyl (-HC=CH@sub 2@) adspecies as well as their chlorinated homologs. We also show that purification of one of these C=C containing arrays could be achieved by simple manipulation of the annealing temperature or by post-exposure of H atoms. @FootnoteText@ * Work supported by the Natural Sciences and Engineering Research Council of Canada.

11:20am **SS2-ThM10 Infrared Spectroscopy Study of Adsorption of Maleic Anhydride on Si(100)***, Y. Kimura, H. Ishii, **M. Niwano,*** Tohoku University, Japan

The adsorption of maleic anhydride on Si(100)-2Ã-1 has been investigated using infrared absorption spectroscopy (IRAS) in the multiple internal reflection (MIR) geometry. Previously, it has been suggested on the basis of HREELS data that at low coverages the adsorption of maleic anhydride occurs through cycloaddition of the C=C bond to the dangling bonds of Si-Si dimers, and at high coverage, maleic anhydride dissociatively adsorbs on the Si(100) surface. In the latter case, the dissociated hydrogen is bound to the Si surface atoms to form the Si-H bond, and the remaining fragments are bound to the Si surface atoms via a single Si-C linkage with retention of C=C double bond. In this study, we observe that an intense absorption peak appears at 2125 cm-1, while the peak due to the C=O stretching vibration is relatively weak. Previously the 2125-cm-1 peak has been assigned as being due to the Si-H stretching vibration mode. However, this peak is positioned at a slightly higher frequency than the monohydride peak that shows up around 2080 cm-1. Furthermore, we observe that the 2125-cm-1 peak appears even when the Si(100) surface is dosed with deuterium-substituted maleic anhydride. From these observations, we suggest that upon adsorption the five-membered ring of maleic anhydride is broken to generate the C=C=O bond and the dissociated molecule is bound to the surface Si atoms via the C-O-Si linkage. Ab initio cluster calculations indeed predicts that the C=C=O bond exhibits a vibration mode around 2120 cm-1. The present results indicates that maleic anhydride dissociatively adsorbs on the Si(100) surface in a rather complicated manner.

11:40am **SS2-ThM11 Formation of Unsaturated Hydrocarbon Moieties on Hydrogen-terminated Si(111) by Grignard Reaction***, **T. Yamada,** K. Shirasaka, M. Noto, H.S. Kato,* RIKEN, Japan*; M. Kawai,* RIKEN and The University of Tokyo, Japan

Unsaturated hydrocarbon moieties, such as CH@SUB 2@=CHCH@SUB 2@-, CH:::C-,CH@SUB 3@CH=CHCH@SUB 2@- and CH@SUB 2@=CH- was deposited on hydrogen-terminated H:Si(111) by using the corresponding Grignard reagents (CxHyMgBr or CxHyMgCl) dissolved in tetrahydrofuran, followed by rinsing in CF@SUB 3@COOH solution. The product adsorbates were examined by vibrational methods with HREELS and internal multiple infrared reflection-absorption spectroscopy. It is anticipated that the unsaturated bonds within moieties may directly react with H:Si(111)@footnote 1@ and may be destroyed besides the desired bond shifting of C-Mg to C-Si. The CH@SUB 2@=CHCH@SUB 2@:Si(111) adsorbate was detected as the H-C= stretching and out-of-plane bending signals after the reaction in CH@SUB 2@=CHCH@SUB 2@MgBr/THF at 35°C for 5 min. The uptake of hydrocarbon moieties was 10% of surface Si with the remainder of originally terminating H atoms. The existence of C-Si stretching signal was revealed by using D:Si(111). Similarly in the cases of CH:::C- and CH@SUB 3@CH=CHCH@SUB 2@-, the unsaturated bonds were reserved. The double bond within CH@SUB 2@=CH- adsorbate was never observed, presumably because the C=C part would be close enough to the H-Si sites to undergo the direct adsorption. A notable result for better understanding of mechanism is that Grignard deposition just need one single H-Si site with no need for adsorption of MgX species in all cases. This was examined by isotope labeling in the rinsing procedure. Reservation of unsaturated bonds provides an approach to functionalized hydrocarbon moieties by addition reactions. Addition of NH@SUB 2@-, OH- or -COOH groups is prospective in surface modification with biochemical polymers with well-controlled adsorbate structure.@footnote 2@ @FootnoteText@ @footnote 1@M. R. Linford et al., J. Am. Chem. Soc. 117 (1995) 2145.@footnote 2@T. Yamada, et al., J. Chem. Phys. 121 (2004) 10660.

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