Monday Afternoon, November 13, 2006

Surface Science
Room 2004 - Session SS2-MoA

Functionalization of Semiconductor Surfaces

Moderator: S. Bent, Stanford University

2:00pm **SS2-MoA1 Comparative Molecular Surface Functionalization of Silicon Surface Structures**, *D.E. Barlow, S.C. Erwin, A.R. Laracuente, L.J. Whitman,* ***J.N. Russell,*** Naval Research Laboratory

Methods and chemistries to covalently attach organic molecules to single crystal semiconductor surfaces are the subject of considerable interest. While past functionalization studies on silicon have focused primarily on the (001) surface, the Si(114), oriented 19.5° between (001) and (111), has an equilibrium surface reconstruction comprised of parallel rows of dimers, rebonded atoms, and tetramers, with all the rows oriented along the same crystallographic direction. These structures make Si(114) an ideal surface for elucidating relationships between surface structure and organic reaction mechanisms on silicon. We have investigated cyclopentene and ethylene chemisorption on Si(114) using transmission Fourier transform infrared (FTIR) spectroscopy, scanning tunneling microscopy (STM) and density-functional-theory (DFT) calculations. The FTIR spectra are consistent with di-sigma bonding. A detailed analysis of the strong angular and polarization dependence of the ethylene C-H stretching mode intensities indicates it chemisorbs with the C-C bond axis parallel to the structural rows oriented along the [(1)10] surface 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 and DFT results, these structures can be identified as [2+2] cycloaddition products, bridged rebonded atoms, and [4+2] cycloaddition products, respectively. The order of surface site reactivity is found to be rebonded atoms > dimers > tetramers. We found each ethylene/Si(114) adsorption structure has a characteristic C-H vibrational signature, which we used to identify the ethylene molecules that are chemisorbed on the step edges of the 4° off-axis (single domain) Si(001) surface.

2:20pm **SS2-MoA2 Adsorption of Ethanethiol, Ethanol, and Mercaptoethanol on Ge(100)-2x1**, ***J.S. Kachian****, S.F. Bent,* Stanford University

The adsorption of ethanethiol, ethanol and mercaptoethanol on Ge(100)-2x1 at 310 K was investigated to gain a fundamental understanding of bonding in these systems for use in practical applications surrounding semiconductor passivation. Vibrational spectra of the products of these three reactions obtained via multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy in ultrahigh vacuum suggest that the products are formed via dissociation of the X-H bond, where X represents the electronegative atom(s)-O and/or S--in the adsorbate. It is believed that these reactions are preceded by a dative-bonded state in which the electronegative atom of the adsorbate donates a lone pair of electrons to the down atom of a germanium dimer. Density functional theory was used to investigate this pathway, and potential energy surfaces and frequency spectra obtained by calculation support the postulated mechanism. The results will be discussed in the context of relative reactivity of S versus O groups. Further, these results can be applied towards the analysis of larger molecules, which contain reactive centers in addition to that of a thiol or alcohol group. Of particular interest is the thiol-containing amino acid cysteine. This molecule, which introduces competition between thiol, amino and carboxyl moieties, is largely responsible for the formation of disulfide bonds in proteins, thus leading to stable three-dimensional protein structure. Understanding the reactivity of the thiol moiety in the context of a biologically relevant molecule brings the concept of nanoscale biosensors one step closer to reality.

2:40pm **SS2-MoA3 The Cycloaddition of Organic Molecules to the Si(100)c(4x2) Surface: Microscopic Mechanism and Tunneling Properties of Single Molecules**, ***J. Yoshinobu,*** University of Tokyo, Japan **INVITED**

Chemical modification of Si surfaces has attracted much attention from the view point of coating, sensors, molecule-based microelectronics and so on. The cycloaddition of organic molecules to the Si(100) surface is the most important family of chemical reactions for the modification of the Si surface as well as Lewis acid-base reaction, because the stable Si-C covalent bonds are formed between molecules and the surface. In the cycloaddition, the asymmetric dimer on the reconstructed Si(100) surface plays an important, in which a partial charge transfer occurs from a down dimer atom (Sd) to an up dimer atom (Su). The chemical nature of Sd and Su is electrophilic and nucleophilic, respectively; the asymmetric dimer may act as a zwitter ion. In this talk, first, we show some examples of regioselective cycloaddition reaction between asymmetric alkene molecules and the asymmetric dimer on Si(100)c(4x2) using low-temperature STM. The regioselective cycloaddition product may be controlled by a precursor state. Next, scanning tunneling spectroscopy (STS) results of a single adsorbed molecule will be presented. In some cases, interesting features are observed in I vs.V characteristics, which may be due to adsorbate derived local electronic states.

3:20pm **SS2-MoA5 Passivation of Germanium and Silicon Surfaces with Oxide, Hydrogen, Chlorine, and Methyl**, ***S. Rivillon Amy****, Y.J. Chabal,* Rutgers University*; F. Amy, A. Kahn,* Princeton University

Chemical passivation of semiconductor surfaces represents an important part of front end processing for CMOS and other microelectronics applications. The industry has been based primarily on silicon (Si) technology due to the remarkable properties of its oxide, but there is a need to explore higher mobility substrates such as germanium (Ge). Although Si and Ge are both group IV semiconductors, it is well-known that their chemical properties differ dramatically. In particular, Ge has a variety of rather unstable oxides and cannot be chemically passivated as easily as Si. The focus of this talk is on comparing the passivation of germanium surfaces with oxide, hydrogen, chlorine, and methanol to that of the corresponding species on silicon, which have been well characterized. The main characterization techniques to monitor the chemical state of the surface are infrared absorption spectroscopy (IRAS) and X-rays photoelectron spectroscopy (XPS). Besides the formation of much more complex and less stable oxides on Ge, we confirm that H-termination of Ge in HF solutions is much more delicate and invariably leads to atomically rough surfaces with predominance of dihydrides on Ge(100) and trihydrides on Ge(111). To compensate for variation in "native" oxide thickness, a procedure involving H@sub2@O rinsing, oxidation by H@sub2@O@sub2@ immersion and dilute (10 vol%) HF (or HCl) etching has been developed, which reliably leads to H- (or Cl-) termination. XPS data confirm the presence of chlorine (Ge-Cl and Ge-Cl@sub2@) on Ge(100) surface. The stability of both H- and Cl-terminated surfaces is similar: poor in air but stable in clean N@sub2@ environment. The results of methanol adsorption on Ge and Si surfaces illustrate the propensity for Ge to bind with C, which constitutes a clear drawback for microelectronics applications.

3:40pm **SS2-MoA6 Photochemical Functionalization and Chemical Patterning of Gallium Nitride Thin Films with Biomolecular Layers**, ***H. Kim****, P. Colavita, K. Metz, B.M. Nichols, B. Sun, J.J. Uhlrich, X. Wang, T.F. Kuech, R.J. Hamers,* University of Wisconsin at Madison

Gallium nitride is a particularly intriguing semiconductor for sensing applications because it can be grown as a thin crystalline film and because the high ionic character of GaN causes the intrinsic surface states to be near the respective band edges, where they have less impact on the interfacial electronic properties. We have investigated the functionalization of gallium nitride (0001) surfaces with well-defined molecular and biomolecular layers. After cleaning in a hydrogen plasma, GaN surfaces were reacted photochemically with organic alkenes bearing protected amine groups using ultraviolet light. Using a simple contact mask to control the UV light, we demonstrate the ability to directly pattern chemical groups onto the surface with a spatial resolution of <12 microns. After linking to the surface, the molecules groups were deprotected and used to link DNA oligonucleotides to the GaN surface. Measurements using fluorescently labeled complementary and non-complementary sequences showed that the DNA-modified GaN surfaces exhibit excellent selectivity, and repeated cycles of hybridization and denaturation show good stability. These results demonstrate that GaN can be used as an alternative substrate for molecular and biological sensing applications.

4:00pm **SS2-MoA7 Achieving a Low Surface Recombination Rate Despite a High Surface Defect Density: the Role of Charge Carrier Concentration**, ***D.J. Michalak****, N.S. Lewis,* California Institute of Technology

Low interfacial electron-hole recombination rates are essential for low-noise electronic devices and high-efficiency solar energy converters. This interfacial recombination rate is dependent on both the electrical trap state density, N@sub T@, and the concentrations of electrons, n@sub s@, and holes, p@sub s@.@footnote 1@ Reports of low recombination rates have often been attributed to a low N@sub T@,@footnote 2@ without a measurement of n@sub s@ and p@sub s@, partly because the importance of n@sub s@ and p@sub s@ has not been fully recognized and partly because an accurate evaluation of n@sub s@ and p@sub s@ can be difficult. In this work, surface recombination rates of stable silicon/liquid junctions, observed using a contactless rf photoconductivity technique, were compared with n@sub s@ and p@sub s@ values obtained from Mott Schottky analysis. Our results demonstrate that recombination rates can only be correlated with N@sub T@ when n@sub s@ = p@sub s@. Otherwise, the recombination rate was always low due to a large n@sub s@ or p@sub s@ even in the presence of a large N@sub T@. The full impact of this work was further realized through a study of the recombination rates of H-Si immersed in solutions of 48% HF, 40% NH@sub 4@F, or buffered HF (BHF) because such measurements are often performed for in situ monitoring of the surface quality during wafer processing steps. Our results demonstrate that only HF contacts can be used for in situ monitoring because n@sub s@ = p@sub s@. For NH@sub 4@F or BHF contacts, low recombination rates were observed only because n@sub s@ is much larger than p@sub s@, and no information about N@sub T@ can be inferred from these measurements. @FootnoteText@ @footnote 1@ Hall, R.N., Physical Review 1952, 87, (2), 387, and Shockley, W., and Read, W.T., Physical Review 1952, 87, (5), 835-842.@footnote 2@ Msaad, H., et al., J. Electron. Mater. 1994, 23, (5), 487-491, and Yablonovitch, E. et al., Phys. Rev. Lett. 1986, 57, (2), 249-252.

4:20pm **SS2-MoA8 Reaction of Amino Acids on the Ge(100) Surface***, **S.J. Jung,*** Korea Advanced Institute of Science and Technology (KAIST)*; J.S. Kachian,* Stanford University*; S. Kim,* Korea Advanced Institute of Science and Technology (KAIST)*; S.F. Bent,* Stanford University

The adsorption of amino acids on the Ge(100) surface was investigated with multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy, scanning tunneling microscopy (STM) and density functional theory. All amino acids consist of a carboxylic acid (-COOH) and an amino (-NH@sub 2@) functional group attached to the same tetrahedral @alpha@-carbon atom. Amino acids are distinguished by the different R-groups attached to the @alpha@-carbon. The simplest amino acid is glycine, with an H as the R-group. Our MIR-FTIR results indicate that for glycine, the principal surface product is formed by OH dissociation of the carboxylic acid group. This result is consistent with calculations, which indicate that the OH dissociation product is the most thermodynamically stable. More than one surface product is evident in the spectra, however, with the results suggesting products containing nitrogen dative bonds. Based on the understanding of glycine, the effect of the side chain can be probed in more complex amino acids. Histidine (C@sub 6@H@sub 9@N@sub 3@O@sub 2@), a basic amino acid, has an imidazole group as the R-group. STM results reveal the ordering of histidine molecules on the Ge(100) surface. At saturation coverage, the STM images show globally ordered arrays consisting of dumbbell shape features that are independent of the direction of the underlying dimer rows of the Ge (100) surface. We will present the adsorption structures and discuss the role of adsorbate-adsorbate intermolecular interactions based on the experimental results and ab initio calculations of glycine. The studies of glycine and histidine allow us to understand the competitive tendencies of the amine and carboxylic acid functional groups in amino acids and also identify the reactivity of the moieties present in the side chain. These results provide a basis for future studies of amino acid polymers, i.e. proteins, which can be used in biocompatible materials of the future.

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