Monday Morning, November 15, 2004

Surface Science
Room 210C - Session SS2-MoM

Functionalization of Semiconductor Surfaces

Moderator: J.N. Russell, Jr., Naval Research Laboratory

8:20am **SS2-MoM1 Atomic-level Control of Chemical Properties of Si(100) with Dopant Impurities***, Y. Wang, **G.S. Hwang**,* The University of Texas at Austin

Atomic-level manipulation of surface chemical properties becomes necessary for the fabrication of ever smaller semiconductor devices and a wide range of future molecular devices. The electronic structure of semiconductor surfaces can be modified by surface reconstruction, defects, impurities, and adsorbates. This will in turn alter physical and chemical processes occurring on the surfaces. One could envisage atomistic control of surface reactivity by incorporating dopant impurities into the surface or subsurface. A detailed understanding of the role of dopants as possible reaction promoters or inhibitors will contribute greatly to finding a new and reliable way to construct desired organic function assembly on semiconductors for various chemical, biological, and electronic applications. Using density functional theory calculations, we have looked at the modification of Si(001) surface properties by incorporating Boron and Phosphorous atoms into the surface and subsurface layer. We have found that surface (or subsurface) dopants bring about a significant change in surface chemical properties by altering surface polarization. As a result, chemical reactions on a dopant-modified surface show a distinctively different feature from on the clean surface. In this talk, we will present i) the effect of subsurface Boron on the surface reactivity of Si(001) based on water and ammonia adsorption and ii) auto-catalyzed molecular nanostructure formation of styrene on Si(001) using Phosphorous as initiator and terminator.

8:40am **SS2-MoM2 Chemistry on Surfaces of Thin Films and at Thin Film/Silicon Buried Interface: Vinyltrimethylsilane and (hfac)Cu(VTMS) on Si(100)-2x1 and on TiCN/Si(100)***, **A.V. Teplyakov**, L. Pirolli,* University of Delaware

Surface chemistry of vinyltrimethylsilane (VTMS) and (hfac)Cu(VTMS) on Si(100)-2x1 surface covered with several nm thick TiCN films formed from tetrakis-(dimethylamino)-titanium has been investigated using multiple internal reflection Fourier-transform infrared spectroscopy (MIR-FTIR), Auger electron spectroscopy (AES) and thermal desorption mass spectrometry. The structure of the films has been analyzed using time-of-flight secondary ion mass spectrometry and atomic force microscopy. This unique combination of surface analytical techniques allows one to follow chemical and physical changes at the surface of the system, within the thin film, and at the thin film/silicon interface. VTMS was found to adsorb molecularly both on Si(100)-2x1 and on the surface of the TiCN thin film at cryogenic temperatures (100 K), while it exhibits chemisorption if dosed at room temperature. Multiple reactions involving VTMS on both surfaces occur upon thermal annealing: molecular desorption around 400 K, formation and desorption of propylene by 500 K, decomposition leading to the release of silicon-containing products around 800 K. On a clean Si(100)-2x1, surface decomposition leading to the production of silicon carbide and the release of hydrogen takes place at 800 K. This chemistry is markedly different from the previously reported behavior of VTMS on Si(111)-7x7 surface resulting in 100% conversion to silicon carbide. (hfac)Cu(VTMS) chemistry, in particular the role of the VTMS ligand and the decomposition products, has also been studied both on clean Si(100)-2x1 and on a TiCN film deposited on silicon. A comparison of these studies with previous aluminum precursor chemistry will be discussed.

9:00am **SS2-MoM3 Functionalization of Semiconductor Surfaces***, M.A. Filler, D.W. Porter,* Stanford University*; A. Kim,* KAIST, Korea*; J.A. Van Deventer, **S.F. Bent**,* Stanford University **INVITED**

The growing importance of organic materials in electronic and optical technologies motivates the development of new attachment chemistries for combining organic layers with semiconductor substrates. We have investigated methods of functionalizing semiconductor surfaces by chemically reacting organic molecules at silicon and germanium surfaces in vacuum. These surfaces present intriguing templates for chemical reactions because the nature of the (100)-2x1 reconstructed surface of silicon and germanium yields dimers that can mimic the reactivity of organic functional groups. This behavior allows for the use of a wide variety of reactions to attach organic groups to the semiconductor surface. Our studies have explored the reactivity of a range of functional groups, including alkenes and dienes, amines, alcohols, carbonyls, nitriles, and isocyanates. The results of experimental and theoretical studies of the adsorption chemistry will be described in the context of several key mechanistic themes, including electrophilic/nucleophilic chemistry and [4+2], [3+2], and [2+2] cycloaddition reactions. Approaches for using these reactions for molecular layer deposition will be introduced, and some of the challenges in organic functionalization, including formation of inter- and intradimer products as well as coverage-dependent effects, will be discussed.

9:40am **SS2-MoM5 Adsorption of Amines on Germanium and Silicon Surfaces***, P. Prayongpan, **C.M. Greenlief**,* University of Missouri-Columbia

The bonding and structure of organic molecules with semiconductor surfaces is important for a variety of potential applications. This work examines the interactions between small organic molecules; ethylamine and allylamine, with Si(100)-2x1 and Ge(100)-2x1 surfaces. Ab initio calculations are used to investigate the transition states and predicted adsorption products for the reactions between the organic molecules and a dimer cluster model of the semiconductor surfaces. The cluster models include Si@sub 9@H@sub 12@, Ge@sub 9@H@sub 12@, and a mixed cluster; Ge@sub 2@Si@sub 7@H@sub 12@. Ultraviolet and x-ray photoelectron spectroscopy are used to examine the chemical bonding of the adsorbed products. This work will examine the effect of electron donating organic molecules with semiconductor surfaces. The selectivity and reactivity of functional groups in the surfaces will be described. According to our recent experimental and theoretical studies, the adsorption products for the interaction between amine molecules with Si(100)-2x1 and Ge(100)-2x1 surfaces are temperature dependent. Low temperature adsorption favors dative bonding of the amine with either surface, whereas different adsorption geometries are observed for adsorption at higher surface temperatures.

10:00am **SS2-MoM6 Silicon Surface Chemistry of Substituted Triazines***, **S.M. Casey**, L.M. LeMond,* University of Nevada, Reno

Deposition of substituted triazines onto the Si(100) surface was examined in order to investigate the initial stages of an organic molecular beam epitaxial growth approach to carbon nitride film formation. These reactions were probed under ultrahigh vacuum conditions using thermal desorption spectroscopy, Auger electron spectroscopy, and low-energy electron diffraction. Experiments reveal that the reactions of species such as 2-amino-1,3,5-triazine are self-limiting with a saturation coverage of about one molecule per four silicon surface atoms. Computational modeling of available reaction pathways was also performed using ab initio and density functional theory approaches. The results from these computations using cluster models of the silicon surface are consistent with the results from the experimental studies, and point to stable reaction products where the incident substituted triazine molecule bridges between two adjacent (within the same dimer row) silicon surface dimers.

10:20am **SS2-MoM7 Carbonyl Chemistry at the (100)-2x1 Semiconductor Interface***, **M.A. Filler**, S.F. Bent,* Stanford University

Several recent studies of the covalent attachment of organic molecules at group-IV (100)-2x1 semiconductor interfaces reveal that even for simple compounds, complex bonding geometries that may involve multiple surface dimers are probable. In an attempt to gain further insight into the fundamental thermodynamics and kinetics of intra- and interdimer bonding pathways, we have studied the reactions of acetone and acetaldehyde on Si(100)-2x1 and Ge(100)-2x1 using a combination of infrared and X-ray photoelectron spectroscopy. For the Ge(100)-2x1 surface, infrared data of both acetone and acetaldehyde reveal a low coverage peak near 1510 cm@super -1@. Isotopically-labeled derivatives of these compounds provide evidence that this mode corresponds to an interdimer adsorption product where a carbonyl moiety donates charge to a neighboring dimer atom. Additional absorption peaks are observed near 1675 cm@super -1@ for moderate surface coverages and at 1600 cm@super -1@ near saturation, likely resulting from @nu@(C=O) and @nu@(C=C) stretching modes, respectively. These data suggest that, in addition to the previously reported ene product, carbonyl-containing compounds can react to form a C-H dissociation product where the carbonyl moiety remains intact. Results will be discussed within the context of classical organic chemistry, mainly keto-enol tautomerization, acidity, and hydrate formation.

10:40am **SS2-MoM8 Adsorption of Chiral Enantiomers of 2,3 butanediol on Si(100)**, *J.W. Kim,* Fritz-Haber-Institute der MPG, Germany*; M. Carbone,* Universita Tor Vergata, Italy*; M. Tallarida, J.H. Dil,* ***K. Horn,*** Fritz-Haber-Institute der MPG, Germany*; M.P. Casaletto,* Instituto per lo Studio die Materiali Nanostrutturati ISMN, Italy*; R. Flammini,* Istituto de Metodologie Inorganiche e dei Plasmi CNR, Italy*; M.N. Piancastelli,* Universita Tor Vergata, Italy

The adsorption of the chiral L,L- and R,R as well as the achiral R,L enantiomer of 2,3-butanediol on a Si(1 0 0) surface has been investigated by photoelectron spectroscopy. The valence band spectra show features assigned to molecular orbitals of 2,3-butanediol by comparison with calculations, and the surface states of clean Si are removed. The Si 2p reveals core-level shifts with two new components at 0.24 and 0.97 eV from the bulk, which are assigned to Si-H and Si-O bonds, respectively. The C 1s core-level spectrum consists of two major peaks separated by 1.3 eV, which are attributed to carbon atoms in -CHOH and -CH3 groups, in the molecule respectively. From the analysis of the valence band, the Si 2p, C 1s, and O 1s core-level spectra, we conclude that the 2,3-butanediol molecule undergoes a cleavage of the O-H bonds, and is bonded to the surface by the oxygen atoms. The molecule shows no further fragmentation and probably forms a six-membered ring of the O-C-C-O segment with the Si dimer atoms. By using circularly polarized x-rays we were able to observe a sizeable circular dichroism in the C1s core level emission from the different enantiomers. We discuss this finding in its potential to identify the presence of chiral centers in adsorbed molecules.

11:00am **SS2-MoM9 Self Assembly on Si(114)-(2x1): Molecular Attachment Via Alkene Functional Groups***,* ***D.E. Barlow****, A.R. Laracuente, L.A. Baker, L.J. Whitman, J.N. Russell, Jr.,* Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface oriented 19.5@degree@ between (001) and (111). Because the equilibrium surface reconstruction consists of a single domain of oriented, periodic rows of dimers, rebonded (001) steps, and non-rebonded steps, it is an ideal substrate for examining whether structure-specific reactivity can be used to create organic 1-D nanostructures on Si. We used STM and FTIR spectroscopy to study ethylene and cyclopentene chemisorption on Si(114)-(2x1) in ultra-high vacuum and to characterize the resulting degree of order at the organic-Si interface. Specifically, we examined the orientation, structure, and bonding arrangements of the adsorbates at the various sites on the Si(114) surface. STM and LEED show that well-ordered monolayers can be formed even on this heterogeneous surface. STM images show that the initial adsorption occurs preferentially along a single structural row, rather than by random occupation of multiple binding sites. Polarized transmission FTIR results are consistent with chemisorption of both ethylene and cyclopentene on Si(114)-(2x1) via [2+2] cycloaddition with preferential adsorbate orientation along the rows on the surface. The results clearly demonstrate that Si(114)-(2x1) is a suitable high index surface for organic self assembly using alkene cycloaddition chemistry.

11:20am **SS2-MoM10 Adsorption of Cata-condensed Aromatic Compounds on Si(100)***, K. Okamura, Y. Hosoi, Y. Kimura, H. Ishii,* ***M. Niwano,*** Tohoku University, Japan

We have investigated the adsorption of cata-condensed aromatic compounds on a Si(100)-2x1 surface using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR). Si samples (prisms) used for MIR-IRAS measurements were prepared from n-type Si wafers and pre-cleaned by the conventional RCA treatment. The 2x1 reconstructed surface was obtained by flashing the sample surface at about 1300 @super o@C following thermal annealing at 900 @super o@C in an UHV chamber. To dose the 2x1 surface with small aromatic compounds (benzene, naphthalene and anthracene), we introduced them into the chamber in gas phase, while larger aromatic compounds were adsorbed on the surface by vacuum evaporation. We have collected IRAS spectra of those aromatic compounds adsorbed on the 2x1 surface, and analyzed the spectra in the region of C-H stretching vibration modes. It is well known that carbon in the sp2 coordinate exhibits absorption peaks in the region of 3000-3100 cm@super -1@, and carbon in the sp3 coordinate shows peaks in the region of 2900-3000 cm@super -1@. All of the measured spectra exhibited C-H stretching vibration peaks at both regions, indicating that some of the carbon atoms of the molecule are transformed from the sp@super 2@ to sp@super 3@ coordinate to form Si-C bonds when the aromatic compounds adsorb on the surface. We observed that these aromatics adsorb on the surface in different manners depending on the surface coverage. Compared with cluster calculation based on the density functional theory method, we determined that small aromatic compounds adsorb in a relatively simple conformation at low coverage, while high-coverage produces some complicated adsorption configurations. Larger aromatic compounds exhibited two different kinds of peaks; one is due to the molecule adsorbed directly on the Si surface (chemisrption), and the other is due to that adsorbed on the monolayer-covered surface (physisorption).

11:40am **SS2-MoM11 Ideal Methyl Termination of the Si(111) Surface***,* ***T. Yamada****, M. Kawai,* RIKEN, Japan*; A. Wawro,* Polish Academy of Sciences, Poland*; S. Suto, A. Kasuya,* Tohoku University, Japan

Si(111) surface ideally terminated by methyl (CH@sub 3@-) groups with a (1x1) periodicity was realized by Grignard reaction of Cl:Si(111)-(1x1). STM discerned a well-ordered (1x1) adlattice covering the Si(111) monoatomic step/terrace features as well as 3-fold-symmetric internal structure of protrusions corresponding to the CH@sub 3@ adsorbates. Reservation of all CH@sub 3@ internal bonds and formation of C-Si bond were confirmed by HREELS.@footnote 1@ Scanning tunneling spectroscopy (STS) exhibited diode-like I-V characteristics involving a new surface-originated occupied density of state at -1.6 eV. This unique electronic structure seems to be reflected on the electrochemical behavior in aqueous solutions. Measurement of vibrational decay time by laser sum-frequency generation is now in process for the internal modes. This finding of (1x1) adstructure led us to consider about the conditions of 2-dimensional ordering of organic moieties. Due to the C-Si covalent bonding, the adsorbates can hardly be mobile and self-assembling by inter-adsorbate interaction cannot be expected. Ordering should basically be originated by one-by-one termination of surface Si, and the adspecies should be accommodated within a hexagonal (1x1) unit cell of Si(111).@footnote 2@ We plan to deposit small moieties, such as CH:::C-, N:::C- and CF@sub 3@- by novel organic reagents. We also critically consider about deposition of long-chain alkyl adsorbates usually studied for purposes of application. The anchoring part of a long alkyl moiety sticks out of the (111) unit cell, and some of the neighborhood Si atoms should be terminated by small adsorbates (such as H and fragmented hydrocarbons). We attempted to approach this problem by investigating the surfaces formed by Grignard reaction with linear-chain alkyl groups (C4 and less). @FootnoteText@ @footnote 1@ T. Yamada et al., J. Am. Chem. Soc. 125 (2003) 8039.@footnote 2@ P. Allongue et al., J. Electroanal. Chem. 550 (2003) 161.

Author Index

Bold page numbers indicate presenter