

## Surface Science

### Room 328 - Session SS3-TuA

#### Organic Functionalization of Semiconductor Surfaces

**Moderator:** J.J. Boland, Trinity College Dublin, Ireland

2:00pm **SS3-TuA1 Adsorption of Substituted Butadienes on Si(100), L.C. Teague**, University of North Carolina at Chapel Hill, Ireland; *J.J. Boland*, Trinity College Dublin, Ireland

Current interest in the addition of small organics to the Si(100) surface is driven by their potential applications in "bottom-up" fabrication methods. The ability to strategically place and/or manipulate individual molecules into functional structures on surfaces has potentially important implications for molecular electronics.<sup>1,2</sup> Although several studies have focused on these types of reactions, it is evident from our previous work with 1,3-cyclohexadiene (1,3-CHD)<sup>3</sup> that these reactions are more complicated than originally assumed. STM studies of other organics such as 2,3-dimethyl-1,3-butadiene (DMBD) and 2,3-dimethoxy-1,3-butadiene (DMeOBD) on Si(100) can provide additional information about cycloaddition reactions. Both systems are similar to 1,3-CHD in that they are systems of 4 $\pi$  electrons, therefore possessing the same reaction possibilities as 1,3-CHD, however they are chain-like rather than ringed structures. Reaction products for DMBD and DMeOBD can be characterized in the same manner as those of 1,3-CHD, i.e., via the location of the remaining C=C bond in the adsorbed molecule. We present a study of the reactions of DMBD and DMeOBD on Si(100), and contrast both the appearance and attachment geometry for reaction products of DMBD and DMeOBD with those of cyclic molecules like 1,3-CHD. Several initial differences between 1,3-CHD products and those of DMBD and DMeOBD are reported, including the presence of dimer buckling induced on the surface after exposure to DMBD and DMeOBD. Different attachment geometries available to chain-like molecules such as DMBD and DMeOBD are shown to account for the dimer buckling observed on the surface. <sup>1</sup>Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature*, 2000, 406, 48; Bent, S. F. *Surf. Sci.* 2002, 500, 879, and references therein. <sup>2</sup>Whitesides, G. M.; Love, C. J. *Sci. Am.* 2001, 285, 39. <sup>3</sup>Teague, L. C.; Boland, J. J. *J. Phys. Chem. B* 2003, 107, 3820.

2:20pm **SS3-TuA2 Surface Chemistry of Conjugated Heteroatomic Compounds on Diamond and Silicon (100), J.N. Russell**, Naval Research Laboratory; *M.P. Schwartz*, University of Wisconsin; *D.E. Barlow, J.E. Butler*, Naval Research Laboratory; *M.P. @ag D@Evelyn*, GE Global Systems; *R.J. Hamers*, University of Wisconsin

Diamond and silicon (100)-2x1 surfaces are comprised of dimers linked by a  $\sigma$  bond and a highly-strained  $\pi$  bond, but there are notable differences in their structure and chemical reactivity. Using multiple internal reflection infrared spectroscopy, the surface chemistry of conjugated heteroatomic compounds was examined on diamond and silicon (100). Acrylonitrile chemisorbed on diamond via a [2+2] cycloaddition reaction, resulting in a product spectrum similar to that of chemisorbed CD@CH=CH@sub 2@. In contrast, acrylonitrile reacts through the nitrile group on Si(100). Cyclohexanedione, which easily tautomerizes into a keto-enol in the gas phase, maintains the enol structure when adsorbed on diamond, but chemisorbs on silicon as the diether, i.e. the [4+2] reaction product. We will examine the role of ring strain, electron donating and withdrawing groups, and dimer tilt on the adsorption probability and structure of the chemisorbed species.

2:40pm **SS3-TuA3 Reaction of Acetyl Chloride on Ge(100)-2x1: Formation of a Surface-bound Carbonyl, M.A. Filler, S.F. Bent**, Stanford University

Since the introduction of vacuum-based organic functionalization of group-IV semiconductor surfaces, there has been considerable interest in attaching molecules beyond the initial monolayer. However, functional groups that are expected to be reactive in second layer reactions, such as amines and ketones, also react directly with the bare semiconductor surface. It is therefore necessary to protect these groups during the deposition of the initial layer or use a molecule where other pathways can kinetically compete and leave the reactive moiety intact. To this end, we have studied the reaction of acetyl chloride on Ge(100)-2x1 at 300K with infrared spectroscopy, temperature programmed desorption, and density functional theory. Infrared spectra show a strong  $\nu(\text{C}=\text{O})$  stretching peak near 1680  $\text{cm}^{-1}$  and no vibration modes in the  $\nu(\text{Ge}-\text{H})$  region indicating that Cl dissociation to produce a surface-bound

carbonyl is the dominant reaction pathway. TPD results provide additional evidence of this surface product; ketene evolves near 525K while at higher temperatures H@sub 2@, HCl, and GeCl@sub 2@ desorb. DFT calculations predict that the barrier to Cl dissociation is only 1 kcal/mol above a chlorine dative-bonded state and is considerably smaller than that of any other reaction pathway. All of this data is strong evidence for a Cl dissociation reaction leaving a surface-bound carbonyl, which is expected to be more reactive toward second layer attachment chemistries and possibly enable layer-by-layer deposition of ultrathin organic films.

3:00pm **SS3-TuA4 Diethyl Ether Reactions with the Si(100) Surface, S.M. Casey**, University of Nevada, Reno

The interactions of diethyl ether with the Si(100) surface have been examined computationally, using ab initio and density functional theoretical techniques, as well as experimentally, using Auger electron spectroscopy and thermal desorption spectroscopy. This surface appears to be relatively inert with respect to reaction with the ether functional group. The reaction paths available to diethyl ether on Si(100) can be contrasted to the interactions of this surface with alcohols and amines, both of which can undergo facile addition reactions upon interacting with this surface. The interactions of ether molecules containing additional, more reactive functional groups, such as a C=C bond, with the silicon surface will also be discussed.

3:20pm **SS3-TuA5 Modification of Silicon Surfaces: Toward Functional Organic and Bioorganic Interfaces, B. Fabre**, National Research Council of Canada; *G.P. Lopinski*, National Research Council of Canada, Canada; *D.D.M. Wayner*, National Research Council of Canada

**INVITED**

Over the last decade there has been increasing awareness of the opportunities presented by the convergence of surface science and organic chemistry. This work is underpinning the development of revolutionary concepts for the design of molecular scale devices and for the integration of solid state, inorganic structures with biologically active interfaces. Although the reactions of organic molecules with silicon surfaces are not new, this area which traditionally has been dominated by physical scientists has increasingly been influenced by organic and bioorganic chemists. This organic perspective has brought new levels of complexity of structure and function and greater understanding of the molecular basis of reactivity. Much of the work so far has focused on exploring the scope of the chemistry and on understanding the structure and quality of the organic-silicon interfaces. An example is the reaction of hydrogen-terminated silicon with styrene that proceeds as a chain reaction on the silicon surface. We have developed simple chemical approaches to introduce essentially any chemical function at the ends of Si-alkyl monolayers. Most recently, we are developing strategies to pattern silicon surfaces with biologically active molecules such as proteins and DNA as well as with conducting polymers (polythiophene). A few simple devices have been prepared using electrochemically grafted polythiophene as a top contact. I will describe the preparation as well as the electrochemical and electrical characterization of these simple metal-insulator-semiconductor structures

4:00pm **SS3-TuA7 Investigation of the Adsorption of Acetic Acid on Ge(100)-2x1, J.A. Van Deventer, M.A. Filler, S.F. Bent**, Stanford University

The modification of group-IV semiconductor surfaces has been an active area of research over the past several years because a greater understanding of semiconductor surface reactivity may lead to applications in nanopatterning, biological recognition, and molecular electronics. In the present work, we investigate the reaction of acetic acid and related isotopes on Ge(100)-2x1 at 300K using infrared spectroscopy and density functional theory. This reactive system is noteworthy because it combines the carbonyl and alcohol functional groups studied in previous investigations into one bifunctional molecule, allowing competition and selectivity to be studied in detail. IR spectroscopy following chemisorption of acetic acid shows a strong absorption at 1664  $\text{cm}^{-1}$  in the  $\nu(\text{C}=\text{O})$  region and two large peaks at 1962 and 1925  $\text{cm}^{-1}$  in the  $\nu(\text{Ge}-\text{H})$  region. We attribute these features to intradimer and interdimer O-H dissociation products. DFT calculations suggest that these O-H dissociation products are likely to occur through one of two oxygen dative-bonded states. Interestingly, the more stable dative-bonded precursor state is the result of a stabilized ring formed by electron donation from the nucleophilic dimer atom to the nearby hydroxyl hydrogen atom of the adsorbed molecule. The kinetic barrier to reaction of this pathway is calculated to be 3.09 kcal/mol above the dative-bonded state, leading to a final product that lies 39.52 kcal/mol below the vacuum level. The O-H dissociation product is both kinetically and

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thermodynamically favorable compared to the other pathways, such as  $\alpha$ -CH dissociation and  $[2+2]$  C=O, available to the molecule.

4:20pm **SS3-TuA8 Electron Beam Effect of Diethylsilane on Si (100) Surfaces Investigated by TPD and LISD**, *P. Wang, J. Lozano, K. Kimberlin, J. Craig*, Bradley University

Various coverages, from 0.03 to 5.0 L, of diethylsilane (DES) on Si (100) surfaces at 100 K were bombarded by 600 eV electrons and the effect of electron on DES/Si(110) system was investigated by using Temperature Programmed Desorption (TPD) and Laser Induced Stimulated Desorption techniques. Laser photons from Nd:YAG were used in LISD technique. TPD and LISD spectra were immediately taken after each dosing and compared to the spectra after the system was irradiated by 600 eV electrons. Desorption of physisorbed species of mass 2, 28 and 59 species was seen at 130 K after coverages of DES larger than 0.07 L. However, mass 2 and 28 species were also thermally desorbed at 810 and 770 K, respectively. Desorption peak areas of mass 2, 28, and 59 with and without electron/photon bombardment were investigated as functions of coverage and electron/photon fluences. It was found that the carbon hydrides were removed from surface after both electron and laser photon radiation. The concentration changes in desorption species in TPD and LISD beam dissociation effects as well as beam induced state will be discussed.

4:40pm **SS3-TuA9 Adsorption of Naphthalene on a Si(100)-2x1 Surface Investigated by Infrared Absorption Spectroscopy**, *K. Okamura, H. Ishii, Y. Kimura, M. Niwano*, Tohoku University, Japan

Recently, adsorption of organic molecules on a Si surface has attracted a lot of interest in relation to possible application to organic-inorganic hybrid devices. Understanding of the adsorption process is required for the control of the structural and electrical properties of the interface between organic and inorganic materials. In this study, the adsorption of the naphthalene molecule, with two benzene-like rings fused together, onto the Si(100)-2x1 surface was investigated using infrared adsorption spectroscopy in the multiple internal reflection geometry. To determine the most preferred adsorption structure of naphthalene on Si(100)(2x1) at room temperature, we have carried out cluster calculations based on the hybrid density-functional theory (DFT), and compared the calculated C-H vibration frequencies with the experimental ones. The central result is that naphthalene adsorbs in different manners depending on the surface coverage of naphthalene, which is the same trend as observed for the adsorption of benzene on Si(100)(2x1). At low coverage the molecule adsorb in the bridging manner between two adjacent dimers. On the other hand, at high coverage the molecule adsorb on the Si surface so as to reduce the repulsive interaction between two adjacent naphthalene molecules adsorbed on the same dimer row. We discuss the reason why the adsorption structure depends on surface coverage, in comparison with the results of cluster calculations.

5:00pm **SS3-TuA10 Vapor-phase Adsorption Kinetics of 1-Decene on H-terminated Si(100)**, *M.R. Kosuri, H. Gerung, Q. Li, S.M. Han*, University of New Mexico; *B.C. Bunker, T.M. Mayer*, Sandia National Laboratories

We have investigated in situ and in real time the vapor-phase self-assembly of 1-decene on Si, using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The adsorption of 1-decene on hydrogenated Si(100) results in an alkane terminated hydrophobic surface. The sessile drop water contact angle after the self-assembly of 1-decene is  $107 \pm 2^\circ$ . The absolute saturation coverage of decane is approximately  $3.2 \times 10^{14}$  cm<sup>-2</sup> based on the IR absorbance of C-H stretching vibrational modes near 2900 cm<sup>-1</sup>. We also report the adsorption rate constant of 1-decene on hydrogenated Si(100) at 160 °C under 30 mTorr of vapor-phase 1-decene. The adsorption rate constant based on a Langmuir isotherm is  $1 \pm 0.1$  Torr<sup>-1</sup>min<sup>-1</sup>. The estimated thickness of the decane monolayer, determined by X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry, is approximately 16 Å. Monitoring the decane monolayer over a period of 2 months using XPS has shown that the silicon surface underneath the decane monolayer gets oxidized with time, leading to the degradation of the decane layer.

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