

Thursday Afternoon, October 18, 2007

Surface Science

Room: 611 - Session SS2+EM+TF-ThA

Organics and Carbon Films on Silicon

Moderator: A.A. Baski, Virginia Commonwealth University

2:00pm **SS2+EM+TF-ThA1 Reactivity of n-type/p-type H:Si(111) for Photoadsorption of CH₃Br**, *T. Yamada*, RIKEN, Japan, *H. Ozawa*, The University of Tokyo, Japan, *H.S. Kato*, RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

Ultraviolet photo-assisted adsorption of CH₃Br gas was examined on hydrogen terminated Si(111)-(1x1) surfaces of n-type (P-doped, resistivity 7-10 Ωcm) and p-type (B-doped, 10-40 Ωcm) substrates. After treatment of Si substrates at 1x10⁻⁵ Pa of CH₃Br pressure with simultaneous irradiation by high-pressure Hg lamp (100W) for 10 min - 3 hours at room temperature, high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) were applied to detect the adsorbate. On n-type H:Si(111), hydrocarbon adsorbates were observed, and on p-type H:Si(111), Si-Br stretching signal (450 cm⁻¹) was exclusively detected. To survey the mechanism of reaction, we divided this adsorption process into UV irradiation in ultrahigh vacuum (UHV) and following CH₃Br introduction without UV. Although a small amount of hydrocarbon contaminant was deposited on both n-type and p-type substrates during UHV UV irradiation, the post-adsorption of CH₃Br resulted in increase of only hydrocarbons on n-type, and only Br on p-type. This result indicates that the irradiation of UV on H:Si(111) promoted photo-assisted desorption of H and leaves hydrogen vacancies, namely, dangling bonds. The difference of adsorption product between the n-type and p-type should be associated with the electronic structure of substrate modified with dopant atoms. We performed molecular-orbital calculations of various H-terminated Si(111) model clusters (sized from 32 Si atoms to 400 Si atoms) with H vacancies on the surface and a few Si atoms replaced with P or B atoms, on the basis of density functional theory (DFT). It was demonstrated that the orbital protruding over the dangling bond was the highest filled electronic orbital on P-doped cluster, whereas on B-doped, it was the lowest unoccupied orbital. This result did not change if we change the number of dangling bonds or dopant atoms. Although this approximation is too rough because of orders-of-magnitude higher dopant level than the real substrates, the result matches the classical formalism of semiconductor band bending near the surface. We further performed DFT calculations on the dangling bond coordinated with a CH₃Br molecule. The dangling bond on n-type/p-type substrate attracts the CH₃ group/Br atom, respectively. It was recognized that the effects of dopant are crucial for the adsorption selectivity of surface dangling bonds towards organic molecules.

2:20pm **SS2+EM+TF-ThA2 Effects of Dative Bond Formation on Si(114) Reaction Pathways**, *D.E. Barlow*, Nova Research, Inc., *S.C. Erwin*, *A.R. Laracuate*, *L.J. Whitman*, *J.N. Russell, Jr.*, Naval Research Laboratory

Si(114)-(2x1) is a stable high-index surface with a single domain-like surface reconstruction composed of parallel rows of dimers, rebonded atoms, and tetramers.¹ We have used transmission FTIR, STM, and DFT to compare the reactions of ethylene and acrylonitrile at the Si(114)-(2x1) tetramer sites. These sites have a diene-like structure, allowing us to investigate the potential Diels-Alder reactivity of an unusual Si surface structure.² In particular, we have investigated the effects of conjugated, electron-withdrawing substituents on the dieneophile. For organic reactions, such substituents typically increase the reaction rate, often by several orders of magnitude. Ethylene reacts as the dieneophile in a Diels-Alder reaction at the tetramer site with a reaction probability of ~10⁻². Surprisingly, however, we find that acrylonitrile does not undergo the Diels-Alder reaction at the tetramer sites. Rather, exposure of the clean Si(114) surface to acrylonitrile leads to three distinguishable ketenimine (-C=C=N-) structures in the FTIR spectra. Polarized transmission FTIR results indicate the presence of ordered ketenimine arrays, with strong registry to the Si(114) surface and site-dependent orientation. We have distinguished the acrylonitrile adsorption structures at the tetramer sites from those at the dimer and rebonded atom sites by analyzing site-dependent heterofunctionalized Si(114) surfaces on which we have first passivated a large portion of rebonded atom and dimer sites with ethylene, allowing the acrylonitrile to preferentially react with the remaining tetramer sites. From the polarized FTIR spectra, we conclude that the -C=C=N- structures are aligned parallel

to <110> at the rebonded atom and dimer sites, but perpendicular to <110> at the tetramer sites. The differing ethylene and acrylonitrile reactivities on Si(114) further emphasize the variable reaction pathways possible for dative bonding on reconstructed Si surfaces.

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

² D. E. Barlow, et al., *J. Phys. Chem. B* 110, 6841 (2006).

2:40pm **SS2+EM+TF-ThA3 Surface Chemistry of Silicon: Making the Connection to Molecules**, *J.M. Buriak*, *D. Wang*, *Y. Qiao*, *J. Chai*, University of Alberta, Canada **INVITED**

The chemistry of semiconducting surfaces is a field of intense interest, not only for the prospect of exciting cutting edge applications, but also from a fundamental perspective.¹ Control over the surface reactivity of silicon and other semiconducting materials is critical for interfacing new molecular devices on chips and other nanotechnological applications, and to perhaps replace oxide overlayers as feature sizes on transistors become smaller than 50 nm. In this talk, we will attempt to provide a preliminary reactivity 'road map' towards understanding the organometallic surface chemistry of silicon that, interestingly, can vary greatly from that of silicon-based molecules. For example, by using the silicon surface as an electrode, electrochemistry can drive reactions that have no obvious parallels with molecular chemistry. As a result, molecules as diverse as alkynes and tetraalkylammonium salts can serve as organic sources to prepare organic monolayers directly on silicon, bound through Si-C bonds.² We will also discuss our latest results concerning the patterning of silicon surface reactivity on the nanoscale (features sizes <30 nm); both conjugated organic monolayers and monodisperse metallic nanocrystallites can be interfaced directly to the surface of silicon for a variety of applications.

¹ Buriak, J. M. "Organometallic Chemistry on Silicon and Germanium Surfaces", *Chemical Reviews*, 2002, 102, 1271-1308.

² Wang, D.; Buriak, J. M. "Trapping Silicon Surface-Based Radicals", *Langmuir*, 2006, 22 6214-6221.

3:40pm **SS2+EM+TF-ThA6 Liquid Methanol Reaction with H-terminated Silicon Surfaces**, *D.J. Michalak*, University of California, Berkeley, *S. Rivillon Amy*, Air Products and Chemicals, Inc., *A. Esteve*, LAAS, France, *Y.J. Chabal*, Rutgers University

The reaction of hydrogen-terminated Si(111) and oxide terminated silicon surface with neat anhydrous liquid methanol (CH₃OH) has been studied with high resolution Fourier transform infrared spectroscopy (FTIR) to determine several factors regarding the surface chemistry. First, a high temperature reaction of atomically smooth H-Si(111) surfaces in neat anhydrous CH₃OH liquid produces methoxylated surfaces that are virtually free of subsurface oxidation. At long reaction times (t > 3h), the surface saturates with Si-OCH₃ sites covering ~30% of a monolayer, with a residual ~70% comprised of Si-H sites. The virtually-oxide free surface facilitates two important conclusions. First, surface reaction mechanisms involving the insertion of oxygen atoms in the subsurface Si-Si back bonds can be ruled out. Because subsurface oxidation often presents deleterious surface electrical trap states, the absence of significant oxidation also holds important implications for the use of alcohol-terminated precursors in the functionalization of surface chemistry for use in electronics devices. Second, the vibration modes of the clean surface are very sharp and allow a more careful analysis of surfaces that contain subsurface oxidation. Specifically, it has been observed previously that, despite the presence of subsurface oxidation on some methoxyl-terminated surfaces, no evidence for subsurface oxygen atoms has been observed directly below Si-H sites. This is surprising from the standpoint that the surface still retains nearly 60-70% unoxidized Si-H sites. It was proposed that the oxidation may reside underneath Si-OCH₃ sites. In this work, comparison of partially oxidized surfaces with the virtually oxide-free surfaces demonstrates that the presence of blue shifted Si-OCH₃ vibrational modes is correlated with the presence of subsurface oxidation. This assignment is corroborated by studies performed on oxide-terminated surfaces that present similar, but blue shifted modes to those observed on the oxide-free H-Si(111) surface. Thus, this work demonstrates that while virtually oxide-free surface can be made, there is a large selectivity towards the formation of oxide underneath atop Si-OCH₃ sites relative to the Si-H sites, which retain almost exclusively unoxidized backbonds. Finally, mechanisms for the formation of oxide are presented with regard to these new results.

4:00pm **SS2+EM+TF-ThA7 Dissociative Electron Attachment Induced Growth of Thin Graphite Films or Graphene on Si(111)-7x7**, *D. Oh*, *H. Abernathy*, *N. Sharma*, *P.N. First*, *M. Liu*, *T.M. Orlando*, Georgia Institute of Technology

There is currently keen interest in developing good strategies for the growth of a few layers of graphite or graphene on substrates such as Si. We are

exploring the use of low-energy electron induced dissociation of adsorbed benzene, naphthalene and phenylacetylene in the production of graphite/graphene films with good lateral heterogeneity. In this study, benzene, naphthalene or phenylacetylene is chemisorbed onto reconstructed Si(111)-7×7 surfaces. These adsorbates are fragmented via low-energy electron bombardment at energies which are dominated by dissociative electron attachment resonances. In general, the incident electron beam can be captured by low-lying π^* states of the chemical precursors and can lead to controlled dissociation and the formation of reactive radicals and negative ions. These fragments can then react to form a network structure of predominantly sp^2 hybridization. The deposited carbon overlayer is examined with Auger electron spectroscopy, Raman spectroscopy and scanning tunneling microscopy. The quality of the deposit and the viability of this non-thermal growth strategy will be discussed.

4:20pm **SS2+EM+TF-ThA8 Adsorption Irregularities of 1,3-Cyclohexadiene and Naphthalene on Silicon(100) Investigated by STM, DFT and an Extended Frontier Orbital Analysis, P.M. Ryan**, CRANN, Trinity College Dublin, Ireland, *L.C. Teague*, National Institute of Standards and Technology, *J.J. Boland*, CRANN, Trinity College Dublin, Ireland

We consider the reactions of 1,3-cyclohexadiene (1,3-CHD)^{1,2} and Naphthalene on Si(100) and examine possible origins for the surface adsorption selectivity evident from STM measurements. The major adsorption products for both molecules are identified by STM. DFT calculations are carried out in order to examine the energetics of the major products and their associated structural analogs. The calculations reveal that the theoretical product distributions based on thermodynamics alone, for both systems, differ significantly from the experimental ones. We explain, using an extended frontier orbital analysis, that secondary orbital interactions which can discriminate between certain concerted reactions and are unavailable at the Γ point due to symmetry considerations become feasible at other κ points in the surface Brillouin zone. We propose that these interactions play a role in the kinetics of the adsorption process and may account for the observed reaction selectivity.

¹ Teague, L.C. and J.J. Boland, STM Study of Multiple Bonding Configurations and Mechanism of 1,3-Cyclohexadiene Attachment on Si(100). *Journal of Physical Chemistry B*, 2003, 107(16): p. 3820-3823.

² Teague, L.C., D. Chen, and J.J. Boland, DFT Investigation of Product Distribution Following Reaction of 1,3-Cyclohexadiene on the Si(100)Surface. *Journal of Physical Chemistry B*, 2004, 108(23): p. 7827-7830.

4:40pm **SS2+EM+TF-ThA9 CNTs on a Si(100) Surface: Dry Deposition, STM/STS, and Contacts, B. Naydenov**, Trinity College Dublin, Ireland, *J.J. Boland*, Trinity College Dublin and CRANN, Ireland

We present a cryogenic STM study of carbon nanotubes (CNTs) deposited on Si(100) surfaces. Imaging and spectroscopic results by means of LT-STM will be demonstrated and analyzed. Using STM-manipulations, contacts (different metals) with the CNTs are formed and characterized. Aspects of the CNTs purity, preparation, and interaction with the substrate will be discussed.

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