Friday Morning, October 29, 1999

Surface Science Division Room 604 - Session SS3+EM-FrM

Reactions on Semiconductors Moderator: S.F. Bent, Stanford University

8:20am SS3+EM-FrM1 A Comparative Study of [2+2] Cycloaddition Reactions of Organic Alkenes on Group IV Semiconductor Surfaces, *R.J. Hamers, J.S. Hovis, S.C. Coulter,* University of Wisconsin, Madison; *C.M. Greenlief,* University of Missouri, Columbia

Organic alkenes such as cyclopentene can bond to Si(001) and Ge(001) surfaces to produce monolayer organic films that are chemically homogeneous and structurally ordered. The bonding of these molecules to the dimerized Si, Ge, and C (diamond) surfaces is analogous to a class of ring-forming reactions known in organic chemistry as [2+2] cycloaddition reactions. While the bulk reactions involve the reaction of two alkene groups to form a four-member ring, the surface reactions involves two electrons from the organic alkene and two electrons from the ? orbital of the surface Si=Si, Ge=Ge, or C=C dimers. Solution-phase reactions of organic compounds via [2+2] processes are forbidden by orbital symmetry considerations and are therefore extremely slow. In order to better understand the nature of the analogous surface reactions, we have used infrared spectroscopy, scanning tunneling microscopy, X-ray photoelectron spectroscopy, and quantum chemistry methods to investigate the adsorption of cyclopentene and other simple alkenes on Si and Ge(001) semiconductor surfaces. Our results show that reactions of simple alkenes on Si(001) and Ge(001) surfaces are facile, producing ordered monolayers. Ab initio calculations for Si, Ge, and C clusters indicate that the reactions on Si and Ge surfaces are facile because of the ability of these surface dimers to tilt, facilitating a low-energy, low-symmetry pathway to adsorption on these surfaces. This talk will summarize our recent experimental and computational studies aimed at understanding the nature of cycloaddition reactions of organic alkenes on Group IV semiconductor surfaces. @FootnoteText@ This work was supported in part by the U.S. Office of Naval Research and the National Science Foundation.

8:40am SS3+EM-FrM2 Novel Organic Monolayer Films on Si(100): Theoretical Studies of Cylocaddition Chemistry, J.A. Barriocanal, D.J. Doren, University of Delaware

A class of cycloaddition reactions will be described that can be used to attach monolayer organic films to Si(100). These reactions, known as 1,3-dipolar additions, can be performed with organic molecules containing a wide variety of organic functional groups. Examples include nitro compounds (R-NOO), azides (R-NNN) and their sulfur and phosporous analogs. Density functional theory calculations for prototypical cases show that the molecules chemisorb with negligible activation barrier. As in traditional organic synthesis, having a variety of functional groups that react in a similar way allows some control over the final product by proper choice of the reagent. A complication, in many cases, is that the product of the initial reaction is not the thermodynamic product, and rearrangements, based on density functional theory calculations, will be discussed. Potential applications and comparisons to available experimental work will also be described.

9:00am SS3+EM-FrM3 Formation of Si/Thiophene Hybrid System in UHV by a Hetero Diels-Alder Cycloaddition Surface Synthetic Strategy, Y. Cao, G.Q. Xu, National University of Singapore, Singapore

The formation of organic monolayer on semiconductor surfaces has great device applications in biosensors, field effect transistors as templates for the epitaxial layer growth on semiconductors. In this work, the covalent coupling of thiophene monolayer on a semiconductor surface has been attained by a facile way at room temperature in UHV. We demonstrate here a hetero Diels-Alder cycloaddition reaction strategy for chemical modification of a well-defined Si(111)-7x7 surface with thiophene molecules. The concerted [4+2] cycloaddition reaction of thiophene with adjacent rest atom-adatom pair, resulting the formation of a 2,5dihydrothiophenelike cycloadduct on Si(111)-7x7, has been clearly demonstrated by combined STM and HREELS spectroscopic studies. Documented as the least reactive diene in Deils-Alder cycloaddition reaction due to its high aromaticity, however, the cycloaddition reaction of thiophene on Si(111)-7x7 is facile even under UHV conditions. In addition, the reactivity of thiophene toward the rest atom-adatom pairs on Si(111)-7x7 can be theoretically explained by correlation of the the HOMO and LUMO energy of thiophene molecule and the surface band level for the empty and filled states on Si(111)-7x7. The feasibility of such procedure provides a better understanding of the chemical reactions proceed through semiconductor surfaces, more significantly, offers a potential new methodology for functionalization the semiconductor surfaces with desired control.

9:20am SS3+EM-FrM4 Kinetics of Abstraction of Monohydride and Dihydride D from Si(100) Surfaces, A. Dinger, C. Lutterloh, J. Küppers, Universität Bayreuth, Germany

The interaction of H(D) atoms with Si(100) surfaces and the abstraction of D adsorbed in the monohydride and dihydride phases on Si(100) by H was studied with thermal desorption spectroscopy and direct product rate measurements. H/D atoms were produced in W tube sources heated at 2000 K. H/D atom exposure to clean Si(100) surfaces at 380 K and 640 K lead to the formation of dihydride and monohydride phases with the characteristic desorption peaks at 690 K and 810 K. In addition, after application of high atom fluences, H@sub 2@ (D@sub 2@) peaks were seen at 910 K which are interpreted as a consequence of etching. Etch products were monitored in desorption and during reaction. H atom exposure to monohydride D covered surfaces at 640 K revealed HD and D@sub 2@ as gaseous products. At a saturated monohydride surface about 6% of the adsorbed D occurred in D@sub 2@ products. The kinetics of HD formation is not in accordance with the operation of an Eley-Rideal mechanism. This is most clearly apparent at small D coverages since then the HD rate is constant at decreasing D coverage. Abstraction of D from dihydride phases at 380 K exhibit an Eley-Rideal phenomenology in the HD rates, however a small contribution of D@sub 2@ products (<1%) illustrate that another mechanism also acts in abstraction of D from the dihydride. The results can be explained by the operation of hot-atom mechanisms, in which the probabilities of hot-atom sticking and reaction determine the kinetics of gaseous products formation.

9:40am SS3+EM-FrM5 The Adsorption and Thermal Decomposition of Dimethylamine Adsorbed on Si(100), S.M. Casey, C.P.A. Mulcahy, A.J. Dennis, University of Nevada, Reno

Dimethylamine (DMA) adsorption on the Si(100)-(2x1) surface has been studied using Auger electron spectroscopy (AES), low-energy electron diffraction, and temperature-programmed reaction spectroscopy (TPRS). It is shown that at room temperature DMA chemisorbs on this surface with a saturation coverage of about 0.5 monolayers. These experiments also show evidence for multilayer formation in this adsorbate system. For doses above the saturation dose level, intact DMA molecules begin to adsorb on top of the surface-bound adsorbate layer. TPRS data show that the decompostion of DMA adsorbed on the Si(100) surface proceeds via two different mechanisms in the monolayer vs. multilayer coverage regimes. The adsorbates directly bound to the surface are shown to decompose via reactions that form gaseous hydrogen and hydrogen cyanide products, while the intact multilayer DMA species decompose to form hydrogen and imine dehydrogenation products. Evidence for formation of both the cyclic ethylenimine species and the straight-chained N-methylmethanimine species in this multilayer regime is presented. Kinetic analysis of the TPRS data shows that the heats of desorption for the two products of the surface-bound adsorbate decomposition (hydrogen and hydrogen cyanide) are much higher than the heats of desorption for the products of multilayer decomposition. AES results show that repeated decomposition of DMA on Si(100) leads to the slow deposition of carbon- and nitrogen-based films, although the thermal deposition efficiency is relatively low and the overall stoichiometry of the resulting films could not be clearly established.

10:00am SS3+EM-FrM6 Reactivity of Diamond (100) towards Cycloaddition Chemistry, G.T. Wang, S.F. Bent, Stanford University; J.S. Hovis, R.J. Hamers, University of Wisconsin, Madison; J.N. Russell, Jr., J.E. Butler, Naval Research Laboratory; M.P. D'Evelyn, General Electric

Diamond has a number of extreme material properties that make it an ideal candidate for a wide range of applications, including electronic devices, electron emitters, multispectral windows, and heat sinks. Similar to Si(100) and Ge(100), the diamond (100) surface undergoes a 2x1 reconstruction in which pairs of atoms are bonded into dimers via a strong sigma bond and a partial pi bond. Recent studies on 2x1 reconstructed Si(100) and Ge(100) have shown that the pi bond of the surface dimers can react with unsaturated hydrocarbons via [2+2] and [4+2] (Diels-Alder) cycloaddition reactions, forming covalently attached ring structures. In this study we investigate the viability of the diamond (100) surface to undergo cycloaddition reactions with cyclopentene and 1,3-butadiene using multiple internal reflection infrared spectroscopy and ab initio quantum

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chemistry calculations. While cyclopentene can react with the surface only via a [2+2] cycloaddition (which is formally forbidden for concerted reactions by symmetry considerations), 1,3-butadiene can potentially react via a [2+2] or [4+2] cycloaddition due to its conjugated double bond. It was found that both cyclopentene and 1,3-butadiene reacted with the diamond (100) surface at room temperature, although significantly larger exposures of cyclopentene may be attributable to 1,3-butadiene bonding via a lower-barrier [4+2] pathway not available to cyclopentene. Comparison of cycloaddition reactivity on diamond (100) versus Si(100) and Ge(100) provides insight into the mechanism of these reactions on semiconductor surfaces. These results also demonstrate the viability of organic synthetic routes for modifying the diamond surface.

10:20am SS3+EM-FrM7 Surface Infrared Spectroscopy of CH@sub x@ Adsorbates during GaAs OMVPE, J.R. Creighton, K.C. Baucom, Sandia National Laboratories

We have used surface infrared spectroscopy (SIRS) to identify the adsorbates present on GaAs(001) during organometallic vapor phase epitaxy (OMVPE) and atomic layer epitaxy (ALE). The key advantage of SIRS, as compared to reflectance-difference spectroscopy (RDS) and related UVvis reflectance techniques, is that the interpretation of infrared spectra is much more straightforward and less ambiguous. One example of the rich spectral information derived with SIRS is seen during the trimethylgallium (TMGa) ALE cycle. During the initial stages of TMGa exposure, methyl groups (CH@sub 3@) bonded to both gallium and arsenic can be detected and differentiated. With time, the methyl-arsenic species disappear and methylene (CH@sub 2@) species (the precursors to carbon incorporation) begin to cover the surface. During low-temperature OMVPE we also detect a significant methyl group coverage, and these results will be compared to the other in-situ optical measurements, e.g. RDS, at similar growth conditions. (Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.).

10:40am SS3+EM-FrM8 Ab initio Study of Adsorption and Decomposition of NH@sub 3@ on Si(100)-(2x1), Y. Widjaja, M. Mysinger, C. Musgrave, Stanford University

Deposition of silicon nitride thin films has become a key technology in the microelectronics industry. In silicon nitride deposition, NH@sub 3@ is typically used as the nitriding agent because of its high sticking coefficient and reactivity. In this study, we investigate the atomistic mechanisms for NH@sub 3@ adsorption and initial decomposition on the (2x1) reconstructed Si(100) surface using B3LYP density functional theory (DFT) and by utilizing the cluster model. We present a detailed investigation of the effects of cluster size on the reaction energetics. We find that the Si@sub 9@H@sub 12@ (1-dimer) cluster model does not describe the NH@sub 3@(a) adsorption state well due to the delocalized nature of the electron transfer in forming the NH@sub 3@(a) dative bond. We find that the Si@sub 21@H@sub 20@ (3-dimer) cluster is necessary to fully capture these non-local effects. The 3-dimer model is able to satisfactorily reproduce the results of larger cluster models. We then use the 3-dimer cluster model to study the adsorption and decomposition reactions of NH@sub 3@ on the Si(100)-(2x1) surface. Ammonia is found to adsorb on the down atom of buckled silicon dimers with no activation barrier. This adsorption is exothermic with an adsorption energy of 29 kcal/mol. This adsorption is then followed by dissociation to form NH@sub 2@(a) + H(a)with a low activation energy. Our calculated recombination desorption energy of 51 kcal/mol is found to be in good agreement with the TPD experimental result of 47 kcal/mol. In addition, we also calculate the vibrational spectra of the dissociated species. We find our results to be in good agreement with the experimental HREELS spectra.

11:00am SS3+EM-FrM9 Reactions of Substituted Aromatic Hydrocarbons with the Si(001) Crystal Surface, S.C. Coulter, J.S. Hovis, M.D. Ellison, R.J. Hamers, University of Wisconsin, Madison

The surface chemistry of small aromatic molecular systems chemisorbed on the single domain Si(001)-(2x1) face has been investigated using Infrared and X-ray Photoelectron Spectroscopy. Both the [2+2] and the [4+2] Diels-Alder cycloaddition processes are possible. Substitued aromatic hydrocarbons, including toluene, benzonitrile and ortho-, meta- and paraxylene, have been studied to provide clues as to their possible steering effects into a favored bonding geometry. Our data indicates that these reactions are complex and, in some cases, involve multiple bonding configurations. Detailed analysis of the infrared spectra and comparisons with known compounds have been used to help identify the surface products and to provide new understanding of substituent effects during molecular bonding at silicon surfaces.

11:20am SS3+EM-FrM10 Thermal Hydrogen Reactions with Boron-doped Si(100) Surface, B. Gong, The University of Texas at Austin; S.K. Jo, Kyung Won University, South Korea; J.G. Ekerdt, The University of Texas at Austin The reactions of hydrogen with boron-doped Si(100) have been studied with temperature programmed desorption, high resolution electron energy loss spectroscopy and low energy electron diffraction. Recent studies by our group have illustrated that in the boron concentration range from 0.002 to 0.1 monolayer (ML), SiH@sub 2@ (@beta@@sub 2@) formation is greatly suppressed at 400 K. This inability of the H-passivated Si(100) to undergo the 3x1 reconstruction is associated with the subsurface boroninduced bond strain and silicon dimer vacancy defects. At higher boron coverages (0.2-0.5 ML), H@sub 2@ desorption data show a new, broad desorption peak (@beta@@sub 3@) at ~ 400 K in addition to SiH (@beta@@sub 1@) and SiH@sub 2@ states. The @beta@@sub 1@ and @beta@@sub 2@ desorption energies are unchanged by boron. The new H@sub 2@ desorption peak is related to trihydride formation (SiH@sub 3@) on silicon sites that are associated with second layer boron atoms. Both SiH@sub 3@ and @beta@@sub 3@-H@sub 2@ desorption increase with increasing boron coverage. We propose that the enhanced silicon growth rate found during in situ boron doping is related to the new H@sub 2@ desorption channel that has its origin with SiH@sub 3@ formation. Extensive H-induced surface etching is also seen on intrinsic Si(100) surfaces at 180 K. SiH@sub 4@ desorption at ~600 K has been used as an indicator of H-induced etching, where SiH@sub 3@ forms as a result of H atoms breaking Si-Si back bonds; SiH@sub 2@ formation precedes the formation of the SiH@sub 3@ etch product. This surface etching is sharply reduced on lightly boron-doped Si(100) surfaces, which is in good agreement with the result that low coverage boron prevents SiH@sub 2@ formation on Si(100).

11:40am SS3+EM-FrM11 Impact of Surface Structure on the Arsine Adsorption Kinetics on GaAs and InP (001), *Q. Fu*, *L. Li*, *C. Li*, *D. Law*, *R.F. Hicks*, University of California, Los Angeles

Arsine adsorption on the gallium-rich GaAs (001) (4x2) reconstruction and on the indium-rich InP (001) (2x4) reconstruction has been studied by internal-reflection infrared spectroscopy and scanning tunneling microscopy. It was found that AsH@sub 3@ adsorption on the (4x2) follows an autocatalytic mechanism, with the rate proportional to the fraction of occupied and vacant sites. By contrast, AsH@sub 3@ adsorption on the (2x4) follows a Langmuir adsorption mechanism, with the rate depending only on the fraction of vacant sites. We attribute these differences in the reaction kinetics to the impact of the semiconductor surface structure on the adsorption mechanism. The GaAs (4x2) reconstruction is terminated with 3 gallium dimers per unit cell, while the InP (2x4) contains one In-P heterodimer, and 4 In dimers per unit cell. An arsine molecule dissociatively adsorbs onto the group III dimers and transfers hydrogen to a group V dimer site. On the GaAs (4x2), only a few of these latter sites are present, and more are created by adsorption, so the reaction is autocatalytic. Conversely, on the InP (2x4), the latter sites are readily available, and Langmuir adsorption occurs. The decomposition mechanisms of arsine on these surfaces will be discussed in detail at the meeting.

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