Tuesday Afternoon, October 3, 2000

Semiconductors
Room 306 - Session SC+EL+OF-TuA

Organic Chemistry on Semiconductor Surfaces

Moderator: J.E. Crowell, University of California, San Diego

2:00pm **SC+EL+OF-TuA1 Novel Reactions of Organic Molecules for Controlled Modification of Semiconductor Surfaces*, D.J. Doren,*** University of Delaware **INVITED**

Recent theoretical work on reactions of organic molecules with semiconductor surfaces will be described. The focus will be on several mechanisms that allow molecules to react with low activation barriers on (100) surfaces of Si, Ge and diamond. Cycloaddition reactions are the most thoroughly understood reactions of organic molecules on these surfaces, having been studied extensively by both theory and experiment. This work has established several families of molecules that readily chemisorb. However, in several cases, there are competing side reactions. The origins of this competition, and some approaches to controlling selectivity tbrough the choice of precursor molecule, will be discussed. Finally, a reaction that attaches an organic molecule to the surface by dissociation (as opposed to cycloaddition) will be described.

2:40pm **SC+EL+OF-TuA3 Peter Mark Memorial Award Address*, S.F. Bent*[1]**, Stanford University **INVITED**

Tailoring the surface properties of semiconductor materials through organic modification is one means of providing new functionality to the semiconductor surface, incorporating properties such as passivation, lubrication, optical response, molecular recognition, or biocompatibility. Chemical modification also has tremendous utility for the controlled synthesis of organic/semiconductor interfaces for numerous electronic and optical applications, including the coupling of organic-based devices to silicon-based microchip technology. In this presentation, I will discuss different organic attachment strategies used to functionalize semiconductor surfaces in a dry processing environment. Unsaturated molecules, such as alkenes or dienes, can be attached by cycloaddition reaction across the Si-Si dimer at the Si(100)-2x1 surface; the reaction occurs at the surfaces of Ge and diamond, as well. Amine groups provide another reactive functionality for surface attachment. The relative reactivities of cycloaddition, N-H bond dissociation, and nitrogen lone pair interactions at the Si(100)-2x1 surface will be described using a series of pyrrole compounds. The use of protecting groups to manipulate the surface reaction pathway will be demonstrated. The potential for these different classes of attachment reactions to impact future applications will also be discussed.

3:20pm **SC+EL+OF-TuA5 Structure of Cyclopentene Adsorbed on InP (001)-(2x1) Surface*, Q. Fu*,** *C.H. Li, D.C. Law, M.J. Begarney, R.F. Hicks,* University of California, Los Angeles

It has been a growing interest in engineering ordered, defect free organic thin films on semiconductor substrates for the next generation miniature electronic devices. Using metalorganic vapor phase epitaxy, we have successfully grown indium phosphide (2x1) surface terminated with a complete layer of phosphorous dimers. On InP (2x1) surface, a dangling bond on each phosphorous dimer is filled with a single electron, which makes it an ideal substrate for growing organic films through reactions with @pi@-bond of unsaturated molecules. Here, we have characterized the molecular structure of cyclopentene adsorbed on the InP (2x1) surface by scanning tunneling microscopy, internal-reflectance infrared spectroscopy, reflectance difference spectroscopy, and molecular cluster calculations. It is found that the exposed phosphorous dimers are the adsorption sites for the unsaturated organic molecule. Two adsorption configurations were identified: one with the C@sub 5@H@sub 8@ molecule sitting on top of a P dimer, and another one with the C@sub 5@H@sub 8@ molecule bridging across two neighboring P dimers. At the meeting, we will present a comparison of cyclopentene adsorption characteristics on InP (001)-(2x1) versus Si (100)-(2x1).

3:40pm **SC+EL+OF-TuA6 Formation and Reaction of Organic Layers on Germanium: Reaction of 1,5-cyclooctadiene with the Ge(100) Surface***, P. Prayongpan, D.S. Stripe,* ***C.M. Greenlief,*** University of Missouri, Columbia

Organic alkenes can bond to Ge(100) surfaces to produce monolayer organic films that are chemically homogeneous and structurally ordered. The bonding of these molecules to the Ge(100)-(2x1) reconstructed surface 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 analogous surface reaction involves two electrons from the organic alkene and two electrons from the surface Ge=Ge dimers. Here, the formation of ordered organic layers on Ge(100) substrates is examined by the reaction of 1,5-cycloocatadiene with Ge(100). This molecule reacts with the Ge dimers leading to a [2+2] cycloaddition reaction product. A combination of ab initio calculations and surface sensitive experimental techniques are used to probe the interactions. Surface modification of the organic layers is also explored. The reaction of the organic layers with atomic hydrogen and a series of alcohols will be discussed.

4:00pm **SC+EL+OF-TuA7 A Comparative Study of the Bonding of N-Containing Heterocyclic Molecules to the Si(001) Surface*, X. Cao*,** *S.K. Coulter, H. Liu, J. Liu, R.J. Hamers,* University of Wisconsin, Madison

Recent studies of a variety of unsaturated hydrocarbons has lead to increased interest in understanding the factors controlling bonding of more complex organic molecules to silicon surfaces. By understanding the propensity for heterocyclic molecules to bond into various possible configurations, we are able to gain insight into the factors controlling selectivity in molecule-surface bonding. We have studied the adsorption of pyrrole and its partially-unsaturated analog, 3-pyrroline, onto the Si(001)-(2x1) surface using Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning tunneling microscopy (STM). At 300 K, XPS spectra of pyrrole show a single, sharp N(1s) level, while FTIR spectra show that the molecule retains the high-frequency peaks that are characteristic of aromatic molecules; isotropic labeling studies show that attachment occurs through the N atom via cleavage of the N-H bond. These results show that pyrrole retains its aromatic character after bonding to the surface. In contrast, XPS and FTIR data for 3-pyrolline shows that it can bond through the N atoms or through its C=C bond via the surface equivalent of a [2+2] cycloaddition reaction. This study shows that molecules with aromatic rings show a strong preference for retention of this aromaticity, while molecules without aromaticity have more diverse chemical bonding configurations. Implications for understanding the attachment of other N-containing molecules to surfaces will be discussed.

4:20pm **SC+EL+OF-TuA8 Reaction of Pyrrole and Pyrrole Derivatives on Si(100)-2x1*, G.T. Wang*,** *C. Mui, C.B. Musgrave, S.F. Bent,* Stanford University

The ability to covalently bond to semiconductor surfaces organic layers with custom-tailored functionality could have applications in a number of areas, including lithography, molecular electronics, sensors, and low k dielectric materials. Previous studies have shown that the Si(100)-2x1 surface dimer can react with unsaturated hydrocarbons, forming covalently bound [4+2] Diels-Alder and [2+2] cycloaddition products at the surface. Amines have shown promise as alternative candidates for layer-by-layer growth and the model amine ammonia is known to react with silicon via N-H dissociation across the surface dimer. The use of more complex amines for surface modification requires an understanding of how various functional groups in the amine affect its reactivity and bonding configuration with the surface. In this study, the interaction of pyrrole and pyrrole derivatives, including saturated and unsaturated secondary and tertiary amines, with the Si(100)-2x1 surface under ultra-high vacuum is investigated via multiple internal reflection infrared spectroscopy, Auger electron spectroscopy, temperature programmed desorption studies, and ab initio quantum chemistry calculations. The results show that the nitrogen lone pair plays an important role in the reaction of amines with the Si(100) surface. In particular, the stable room temperature molecular adsorption of methylpyrrolidine through its lone pair is permitted due to the presence of a protecting methyl group, while its unprotected analogue, pyrrolidine, proceeds to covalently bond to the surface through N-H dissociation. Additionally, results examining the reaction of the Si(100) surface with a model amide (N-methylacetamide), which contains both carbonyl and amine functionalities through a peptide unit and hence could serve as a bifunctional unit for layer-by-layer growth, are presented.

4:40pm **SC+EL+OF-TuA9 Attaching Aromatic Molecules to the Si(001) Surface via Oxygen and Sulfur Tethers*, S.K. Coulter*,** *M.P. Schwartz, J. Liu, R.J. Hamers,* University of Wisconsin, Madison

Phenol, benzenethiol and phenyl disulfide have been used as model systems to compare the bonding of chemically-similar aromatic molecules to the Si(001)-2x1 surface through different Group VI tethers. The behavior of these substituted aromatic hydrocarbons on the Si(001) surface has

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[1] **Peter Mark Memorial Award Winner**

been investigated using Fourier transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). Both FTIR and XPS indicate that phenyl disulfide bonds exclusively through the sulfur substituent groups. Phenol and benzenethiol molecules bond predominately through their oxygen/sulfur substituent groups, although a small minority may chemisorb on the surface via ring attachment. Thermal studies indicate that the molecules attached to the surface via sulfur or oxygen tethers are stable to temperatures above 550 K. STM studies show that these molecules attach directly to the silicon dimer and, in the case of phenyl disulfide, form ordered rows of aromatic rings.

5:00pm **SC+EL+OF-TuA10 Chemical Reactions on the Diamond(100) Surface: First-principles Theory and Comparisons to Experiment***, **D.R. Fitzgerald**, D.J. Doren,* University of Delaware

Density functional theory calculations have been used to investigate the structures, energetics, and reaction pathways of the [4+2] and [2+2] cycloaddition reactions of butadiene with the C(100)-2x1 surface. One-dimer and three-dimer cluster models were used to represent the surface. Vibrational spectra of the product species were also calculated. Activation free energies suggest that the [4+2], or Diels-Alder mechanism, will be kinetically favored. The presence of adjacent unreacted surface dimers affects the orientation of the cycloaddition product. The adsorption of hydrogen on the surface has also been studied. Cluster size is seen to have a large effect on the vibrational spectrum of the adsorbed hydrogen. Theoretical results are compared to recent experiments.

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