

# Tuesday Afternoon, October 16, 2007

## Surface Science

Room: 611 - Session SS2-TuA

## Excitations at Surfaces

**Moderator:** G.A. Kimmel, Pacific Northwest National Laboratory

2:00pm **SS2-TuA2 Electronic Excitation and Bond Dissociation via Transient Anion Formation at the Surfaces of Molecular and Biomolecular Solids**, *L. Sanche*, University of Sherbrooke, Canada  
**INVITED**

Electrons with energies in the range 0-30 eV can induce at interfaces and surfaces specific reactions which are relevant to applied fields such as nanolithography, dielectric aging, radiation waste management, radiation processing, astrobiology, planetary and atmospheric chemistry, surface photochemistry, radiobiology, radiotherapy and ballistic electronics. The action of low energy electrons (LEE) at the surface of molecular and biomolecular solids has been investigated with model systems consisting of pure or doped thin molecular films. Some of the results will be presented at the conference. In these experiments a target film is deposited on a metal or semi-conductor substrate and bombarded by a LEE beam under ultra high vacuum (UHV) conditions. Backscattered electrons are energy analysed to determine the energy and characteristics of electronic excited states at the surface of the molecular solid. Bond dissociation is analysed by mass spectrometry (MS); i.e., we determine the energy, mass and intensity of the neutral fragments and ions emanating from the films vs electron energy. The products remaining in the films are analyzed in situ by X-ray photoelectron and electron energy loss spectroscopies; they can also be removed from the UHV system and analyzed by HPLC and LC/MS. By comparing the results of the theory and different experiments, it is possible to determine fundamental mechanisms that are involved in the processes induced by LEE. Such mechanisms involve the formation of transient anions which play a dominant role in the fragmentation of all molecules investigated and dipolar dissociation which produces an anion and a cation. The transient anions fragment the parent molecules by decaying into dissociative electronically excited states or by dissociating into a stable anion and a neutral radical. These fragments usually initiate other reactions with nearby molecules, causing further chemical damage. The damage caused by transient anions is dependent on the molecular environment. This research is financed by the CIHR.

2:40pm **SS2-TuA4 An Atomic Seesaw Switch by Tunneling Carrier Injection on Ge (001)**, *K. Tomatsu, K. Nakatsuji, T. Iimori*, University of Tokyo, Japan, *Y. Takagi, Riken Harima, Japan, H. Kusuhabara, A. Ishii, Tottori University, Japan, F. Komori*, University of Tokyo, Japan

Reversible switching of electronic conduction through atom manipulation is one of the main subjects of nanoscience. However, different conducting pathways have not been clearly observed with atomic resolution. Here, we demonstrate the correlation between the change of surface atomic position by tunneling carrier injection and that of the reflection of one-dimensional (1D) surface-state electrons on the Ge (001) surface with a low density of heterogeneous Sn-Ge dimers.<sup>1</sup> On the clean Ge(001) surface, two atoms form a buckled dimer, and bonding  $\pi$ - and antibonding  $\pi^*$ -states localize on upper and lower atoms of the dimer. The Ge dimers align in the [110] direction and form a dimer row. The  $\pi^*$ -electron behaves like a 1D free electron along the dimer row. It has been shown that the buckling orientation of the Ge dimer can be reversibly controlled by surface bias voltage of STM.<sup>2</sup> This conformation change is induced by inelastic scattering of injected carriers from the STM tip to the surface under the electric field due to the bias voltage. When Sn atoms are deposited on the clean Ge(001) surface at room temperature, buckled dimers originating from the Sn atoms are formed at the Ge dimer position in the surface.<sup>3</sup> We identify the dimer as a heterogeneous Sn-Ge dimer by reversing its buckling orientation with STM and observing the change of the STM images at 80 K. An atomic seesaw switch is realized for the 1D  $\pi^*$  electrons in the Ge dimer-row direction by using the STM to reversibly flip the buckling orientation of a single Sn-Ge dimer in the dimer row. When the Sn atom of the heterogeneous dimer is at the lower position, the 1D electrons are reflected and a standing wave of this state is observed in the  $dI/dV$  image. Whereas, when it is at the upper position, the 1D electrons pass through the heterogeneous dimer, and no standing wave is observed. In this state, the lower atom of the dimer is Ge, and the  $\pi^*$  state of the dimer is little different

from that of the Ge-Ge dimers. These are confirmed using first-principles calculations.

<sup>1</sup>K. Tomatsu, K. Nakatsuji, T. Iimori, Y. Takagi, H. Kusuhabara, A. Ishii, F. Komori; Science 315, 1696, 2007.

<sup>2</sup>Y. Takagi, Y. Yoshimoto, K. Nakatsuji, F. Komori; Phys. Rev. B75, 115304, 2007.

<sup>3</sup>K. Tomatsu, K. Nakatsuji, T. Iimori, F. Komori; Surf. Sci. 601, 1736, 2007.

3:00pm **SS2-TuA5 Detection of Hydrogen During Low-Energy (5-50 eV) Electron Bombardment of Acetylene Adsorbed on Si(111) Surfaces**, *K.R. Shepperd, T. Li, P.N. First, T.M. Orlando*, Georgia Institute of Technology

The interaction of hydrocarbons with Si surfaces is a topic of wide interest. This is generally related to the technological importance of SiC and the growing interest in graphene. In an effort to grow SiC interfaces and graphene overlayers, we have investigated the interaction of  $C_2H_2$  ( $C_2D_2$ ) with Si(111) surfaces and the low-energy electron-beam induced chemistry of this adsorbate-substrate system. We monitor the production and release of hydrogen using sensitive and selective resonance enhanced multiphoton ionization laser detection schemes. We have measured the threshold energy and the yield vs. incident electron energy. We discuss the structure in the yields vs. energy in terms of direct dissociative excitations and dissociative electron attachment. We also have investigated the remaining carbon deposit using Auger electron spectroscopy, scanning electron and scanning tunneling microscopy. Initial results indicate facile formation of SiC at low coverage but no clear signature of graphene.

4:00pm **SS2-TuA8 Mechanism of Negative Ion Formation during the Laser Ablation of Alkali Halides**<sup>1</sup>, *J.T. Dickinson, K. Kimura, S.C. Langford*, Washington State University

Pulsed excimer laser radiation produces a variety of surface and near surface defects in the alkali halides that contribute to particle emission. Quadrupole mass spectrometry during pulsed 248-nm laser irradiation of cleaved LiF, NaCl, KCl, and KBr shows intense emissions of positive alkali ions at fluences well below the threshold for visible plume formation. We argue that these ions are emitted directly from surface defect sites when nearby electron traps are photoionized. In this work, we describe somewhat weaker emissions of negative alkali ions with kinetic energies similar to that of the positive ions. Measurements of induced charge on a metal sheet mounted behind a thin sample show that the surface develops a positive charge during the laser pulse. Thus the direct emission of negative ions at these low fluences is not expected. In previous work, we have shown that the cloud of positive alkali ions is accompanied by enough electrons to compensate much of the positive charge. These electrons are electrostatically confined to the ion distribution to produce a mixed charge cloud. Although these electrons are available for electron attachment processes, detailed measurements on KCl show no  $Cl^-$  at our level of sensitivity, despite the presence of the neutral Cl, with its high electron affinity. We attribute the lack of  $Cl^-$  to the absence of spatial overlap between neutral Cl and the charge cloud. Since the detected neutral K and Cl have similar velocity distributions, negative ion formation by electron attachment to neutral K desorbed directly from the surface is similarly difficult. These considerations suggest that  $K^-$  is formed by double electron attachment to  $K^+$ . Measurements of the total ion and electron emissions imply that the electron and ion densities immediately after the laser pulse are sufficient to account for the production of the observed negative alkali ions by collisional electron-ion and electron-neutral recombination. Although electron attachment is frequently observed among the products of ablation at high fluences, it is remarkable that the conditions required for double electron attachment are attained at the low fluences probed in this work. Further study of the behavior of charged emissions in this well-studied system is required to clarify how these conditions develop.

<sup>1</sup>This work was supported by the US Department of Energy under Grant DE-FG02-04ER-15618.

4:20pm **SS2-TuA9 Dissociative Attachment of Adsorbed Methyl Halides by Dielectric Layer Image State Electrons**, *E.T. Jensen*, University of Northern British Columbia, Canada

We have studied the transfer of low-energy electrons through thin films of n-hexane ( $C_6H_{12}$ ) on a Cu(110) substrate. The band structure of the thin n-hexane layers allows relatively long-lived image states to be formed at the hexane-vacuum interface.<sup>1,2</sup> In our experiments, these image states are occupied by sub-vacuum level photoelectrons from the Cu(110) substrate that are generated by a near-UV laser, and tunnel through the n-hexane film into the image states. These image state electrons can couple to the unoccupied electron affinity levels of coadsorbed  $CH_3X$  ( $X=Br, I$ ). Dissociative electron attachment (DEA) of the  $CH_3X$  is detected by the fission of the C-X bond, with the  $CH_3$  fragment escaping into the vacuum and subsequently detected by a quadrupole mass spectrometer. The

intermediary role of the image states in this DEA process is determined from the coverage dependencies of the CH<sub>3</sub> fragment yields and the distinctive translational energy distribution of the CH<sub>3</sub>- the image state electrons constitute a nearly monochromatic electron source for DEA of the CH<sub>3</sub>X.

<sup>1</sup>M.W. Cole, Phys. Rev. B 3 (1971) 4418.

<sup>2</sup>K. Nagesha and L. Sanche, Phys. Rev. Lett. 81 (1998) 5892.

4:40pm **SS2-TuA10 Photo-induced Surface Functionalization of Carbon Surfaces: The Role of Photoelectron Ejection**, *P.E. Colavita, B. Sun, K.-Y. Tse, R.J. Hamers*, University of Wisconsin-Madison

Carbon based materials are attractive for a wide range of applications, from biomaterials to fuel cells; however their effective use often requires controlling the surface chemistry to incorporate recognition moieties or reactive centers. The high stability of carbon also makes it a challenging material to functionalize; recently, the use of ultraviolet light (254 nm) to initiate functionalization of carbon surfaces has emerged as a way to obtain carbon/organic interfaces with tailored properties. We have investigated the mechanism of covalent grafting of amorphous carbon surfaces with functional organic molecules using the photochemical reaction of terminal alkenes. Measurements comparing the reactivity of different n-alkenes bearing different terminal groups at the terminus opposite the olefin showed pronounced differences in reactivity. We characterized the rate and final coverage of the resulting organic layers using X-ray Photoelectron Spectroscopy (XPS) and Infrared Reflection Absorption Spectroscopy (IRRAS). Ultraviolet Photoelectron Spectroscopy (UPS) and photocurrent measurements suggested that the reaction involves photoelectron emission from the carbon surface into the liquid phase. Density functional calculations show a strong correlation between the electron affinity of the alkenes and the observed reactivity. The specific terminal group opposite to the olefin was found to play an important role in the stabilization of excess negative charges on the molecule, thus explaining the strong dependence of reactivity on the particular terminal group. These findings suggest that the reaction involves injection of photoelectrons into the alkene acceptor levels, leading to the formation of radical anions in the liquid phase. Finally, we demonstrate that the grafting of marginally reactive alkenes can be enhanced by seeding the surface with a small amount of good electron accepting groups. These results provide fundamental new insights into the role of electronic excitations in controlling rates and mechanisms of olefin reactions at surfaces. While demonstrated here for amorphous carbon, these results may also be significant for the UV initiated grafting of olefins on other semiconductors.

5:00pm **SS2-TuA11 Electron Stimulated Reactions in Thin Water Films Adsorbed on TiO<sub>2</sub>(110)**, *N.G. Petrik*, Pacific Northwest National Laboratory, *C.D. Lane, T.M. Orlando*, Georgia Institute of Technology, *G.A. Kimmel*, Pacific Northwest National Laboratory

The electron-stimulated desorption of molecular water from TiO<sub>2</sub> (110) surface was investigated as function of coverage (0-5 ML), incident electron energy (5-100 eV), and other parameters. The two main water adsorption sites - 5-fold coordinated Ti<sup>4+</sup> ions and bridge-bonded oxygens (BBO)- have significantly different cross-sections for electron-stimulated desorption, but similar cross-sections for electron-stimulated dissociation. Isotopic layering experiments show that both desorption and dissociation of water adsorbed on the Ti<sup>4+</sup> sites is suppressed by deposition of water molecules on the BBO sites. The results suggest that electronic excitations in water molecules adsorbed on the Ti<sup>4+</sup> sites can produce reactions (desorption or dissociation) in water molecules on the BBO sites. The experimental observations are discussed in terms of specific structural characteristics of thin water films on TiO<sub>2</sub> (110).

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