

## Surface Science

### Room 120 - Session SS1-MoA

#### Innovations in Surface Science

**Moderator:** U. Heiz, University of Ulm, Germany

**2:20pm SS1-MoA2 An Accurate Parametrization for the Extended Hückel Theory (EHT): Application to the Electronic Structure and STM Imaging of the Cu(110)+c(2x2)-Si Surface Alloy, J.I. Cerdá, C. Rojas, C. Polop, J.A. Martín-Gago, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain; R. Fasel, J. Hayoz, D. Naumovic, P. Aebi, Université de Fribourg, Switzerland**  
The electronic structure of the Cu(110)+c(2x2)-Si surface alloy has been studied both experimentally and theoretically. On the experimental part, we have mainly employed Angle Resolved Ultraviolet Photoemission Spectroscopy (ARUPS) together with atom resolved images acquired with a Scanning Tunneling Microscope (STM). On the theoretical part, we have made use of a recently developed Extended Hückel Theory (EHT) parametrization scheme<sup>1</sup> in order to describe the Atomic Orbital (AO) interactions, while the Cu(110)+c(2x2)-Si system has been modelled by a surface-alloy layer stacked on top of a semi-infinite Cu(110) bulk. The corresponding electronic structure and associated STM images (for different tips) have been calculated via Green's functions techniques. Despite the simplicity of the EHT approach, we find a very good agreement with the surface specific electronic features experimentally observed: Fermi surface, Surface State Bands, Atomic corrugation in the STM images, etc. This fact evidences the good transferability of the EHT parameters between different chemical and geometrical environments.  
@FootnoteText@  
<sup>1</sup>J. Cerdá and F. Soria, Phys. Rev. B, Vol. 61 (2000) 7971.

**2:40pm SS1-MoA3 UV Free Electron Lasers and Their Applications in Surface Science, M. Marsi, Sincrotrone Trieste, Italy**  
**INVITED**  
Free Electron Lasers (FELs) are intense, monochromatic, tunable and coherent light sources that, thanks to their unique features, are opening new research opportunities in many different fields. For several years FEL's have been operating with success in the infrared; recently a considerable progress has been made in the UV region, where lasing wavelengths shorter than 190 nm have been able to be obtained, disclosing new opportunities for the study of the electronic properties of thin films and microstructures. UV FEL's are powerful instruments to probe the excited states of matter, especially when used in combination with synchrotron radiation in a pump-probe configuration. This kind of two-photon photoemission experiments, performed on Si surfaces and interfaces, have allowed a detailed study of the behavior of the non-equilibrium carrier distribution, making it possible to observe the role of interface states in the charge flow mechanism at photoexcited surfaces. Beside their use in combination with synchrotron radiation, UV FEL's have some unique features which make them particularly attractive also per se: in particular, being very intense and naturally tunable, they are ideal light sources for threshold photoelectron emission microscopy, and thus powerful instruments to study the electronic properties of nanostructures.

**3:20pm SS1-MoA5 An End Station for Synchrotron-Based Photoelectron Spectroscopy of Actinide and Other Highly Reactive Samples, D.A. Arena, J.G. Tobin, Lawrence Livermore National Laboratory; D. Shuh, Lawrence Berkeley National Laboratory; R.K. Schulze, Los Alamos National Laboratory; P. Boyd, Boyd Technologies, Inc.**

We have constructed a specialized UHV experimental chamber to allow for the convenient study of the electronic structure of actinide and other highly reactive samples using synchrotron radiation at the Advanced Light Source (ALS). This chamber, the Actinide Spectroscopy End Station (ASES), is currently equipped to perform high-resolution photoemission spectroscopy in both spin integrated and spin resolved modes. The system includes a novel sample introduction system where samples are brought on-site in small ion-pumped vacuum suitcases and introduced into the experimental chamber without exposure to the atmosphere. We have included a separate sample preparation chamber to provide for sample cleaning and gas dosing followed by a quick transport to the analysis position. The ASES is equipped with numerous isolation valves to allow for the removal and repair of individual components while maintaining the vacuum integrity of the overall system. The sample manipulator allows for both heating and liquid nitrogen cooling of the samples and the end station also contains a number of redundant systems such as multiple sample heating and temperature measurement stages so that experiments can

continue in the event of common occurrences such as a broken heating filament or open thermocouple connection. Expansion plans include the addition of a fluorescence spectrometer and a thin film deposition system. An extensive series of experiments are planned, including resonant photoemission, spin-resolved double polarization investigations, and oxidation studies of elemental plutonium and other actinide samples. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

**3:40pm SS1-MoA6 Closing the Pressure Gap: Photoemission at 5 Torr and the Premelting of Ice, D.F. Ogletree, Lawrence Berkeley National Laboratory; H. Bluhm, Lawrence Berkeley National Lab and Fritz Haber Institute, Germany; F. Requejo, Lawrence Berkeley National Laboratory; C.S. Fadley, Lawrence Berkeley National Lab and University of California at Davis; Z. Hussain, M. Salmeron, Lawrence Berkeley National Laboratory**  
Fundamental studies of surface processes and reactions at high pressure are outside the reach of many surface science techniques - the so-called "pressure gap". Scanning probe microscopy and non-linear optical probes can be used to study surface topography and vibrational excitations, respectively, but probes of electronic structure and atomic composition are hard to come by. We have recently extended x-ray photoemission spectroscopy to pressures as high as 5 Torr using a synchrotron light source and a differentially pumped electron transfer lens. One of the first applications of this method has been a study of the pre-melting of the ice surface. The new instrument will be described, and the results on ice pre-melting will be presented. Near-edge x-ray adsorption fine structure (NEXAFS) probes the density of unoccupied molecular states. In the case of water, NEXAFS is sensitive to the effects of hydrogen bonding and can therefore distinguish between water vapor, liquid water and ice. Surface sensitivity was obtained by using the O KLL Auger electron yield as a probe of x-ray absorption. Electron spectroscopy allowed the Auger yield to be extracted, since total electron yield measurements were complicated by secondary electron cascades in the gas phase. Pre-melting was investigated for ice, in equilibrium with its vapor, between -40 and 0 C (the vapor pressure of ice at the melting point is 4.6 Torr). NEXAFS results showed that a liquid-like film exists at the ice surface above -20 C, reaching a thickness of ~ 2 nm near 0 C. We also found that the presence of hydrocarbon contamination strongly influenced the pre-melting of ice.

**4:00pm SS1-MoA7 Desorption/Ionization on Porous Silicon (DIOS) Mass Spectrometry: A New Methodology for Bioanalysis, Z. Shen, J.E. Crowell, University of California, San Diego; G. Siuzdak, The Scripps Research Institute**  
DIOS-MS is a new mass spectrometry strategy based on pulsed laser desorption/ionization from a porous silicon surface. DIOS-MS is similar to matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS) in that it utilizes the same instrument; however, in DIOS-MS, porous silicon is used to trap analytes deposited on the surface and laser radiation is used to vaporize and ionize these molecules, without the presence of any matrix material. We have shown that DIOS-MS can be used for a wide range of small molecules as well as biomolecules at the femtomole and attomole level with little or no fragmentation, in contrast to what is typically observed with other direct desorption/ionization approaches. DIOS-MS offers many unique advantages including good sensitivity, low background ion interference, and high salt tolerance. We will demonstrate the application of DIOS-MS to small molecule quantitative analysis, chemical reaction monitoring, enzyme-substrate reaction and inhibition characterization, and drug metabolism study. We will also demonstrate DIOS-MS as a unique scanning approach for small-molecule high throughput analysis.

**4:20pm SS1-MoA8 Enantiospecific Properties of Chiral Surfaces, J.D. Horvath, A.J. Gellman, Carnegie Mellon University**  
Chirality is an omnipresent feature of the biochemical and biophysical world. The handedness of the important molecules that form the basis of life creates the need for enantiomeric purity in the chemicals used for pharmaceutical and other bio-active purposes. Many of the processes used for synthesis and preparation of enantiomerically pure compounds rely on the use of chiral surfaces. This represents an interesting and important new opportunity for surface science. I will describe some of the recently discovered, enantiospecific physical and chemical properties of chiral surfaces prepared from simple high Miller Index metal surfaces. The kinked step structures of such surface are chiral. As an example, the heats of adsorption of small chiral molecules such as propylene oxide (CH<sub>3</sub>CH(O)CH<sub>3</sub>) and R-3-methylcyclohexanone are sensitive to the

handedness of surfaces such as Cu(643). This has been observed using thermally programmed desorption measurements which reveal that the desorption kinetics of these chiral molecules are enantiospecific on chiral surfaces. They do not exhibit enantiospecificity on achiral surfaces such as Cu(111). Similarly, the orientation of chiral molecules on chiral surfaces can be shown to depend on the relative handedness of adsorbate and substrate. This has been shown by study of the infrared reflection absorption spectra of 2-butoxy groups on the Ag(643) surface. The intensities of the absorptions by R- and S-2-butoxy groups are dependent on the handedness of the Ag(643) substrate. Understanding and controlling these enantiospecific properties poses some extremely interesting challenges for surface chemistry and surface physics that can have broad impact in the chemical and life sciences.

**4:40pm SS1-MoA9 Can Cu-TBP Porphyrin Molecules Emit Light under an STM Excitation?**, *D. Fujita, H. Nejo, S. Yokohama, S. Mashiko, Z.-C. Dong*, National Institute for Materials Science, Japan

Photon emission on metal surfaces induced by tunneling electrons is thought to arise from the radiative decay of localized surface plasmons. While this theory is still not yet complete due to the negligence of non-local effects, the situation becomes more complicated and difficult to study when molecules are sandwiched between the tip and surface. It remains unclear how molecules couple with the electrodes and electromagnetic field to give out light. We demonstrate here a technique to produce tunneling-electron induced photon emission from Cu-TBP porphyrins on Cu(100). The emission intensity and optical spectra show not only the enhancement effects, but also new features revealing the molecular origin of light emission. The quantum efficiency is estimated to be  $10^{-4}$  photons per electron. The observation of a broad peak around 630 nm associated with molecules is particularly exciting but puzzling, since Cu-centered porphyrin molecules are known not to fluoresce under photoexcitation. This broad peak appears dramatically enhanced when the bias voltage is above 3 V, in good agreement with the high B-band absorption via optical excitation. These observations suggest that while energy absorption behavior by electrons appears in parallel with that by photons, the excitation or decay mechanism might be different in the two processes, and may thus bring up new physics. Tunneling electrons can excite surface plasmons in metal substrates, which causes the enhancement of local electromagnetic field. Excitation of molecules occurs via the resonant coupling of molecular electronic states with the localized electromagnetic modes between the tip and substrate. Light is emitted when excited molecules decay to the ground state. The decoupling of luminescent porphyrin cores from the substrate, a means to suppress the fast nonradiative energy dissipation, is found to be important for efficient light emission.

**5:00pm SS1-MoA10 A Fourier Transform-Based TOF HREELS Spectrometer**, *R.H. Jackson, L.J. LeGore, Y. Yang, P. Kleban, B.G. Frederick*, University of Maine

A major limitation of the conventional, dispersive sector, electron energy analyzer is that it is inherently a serial device, leading to long data acquisition times in high resolution electron energy loss spectroscopy (HREELS). A throughput advantage of order 500-1000 can be achieved by combining time-of-flight (TOF) methods with pseudo-random (PRBS) modulation of the back-scattered electron beam. We present the first results of this new approach to HREELS and compare with simulations of the TOF spectrometer. Although PRBS modulation techniques have been applied to a number of other areas,<sup>1,2</sup> the Poisson noise distribution arising from pulse-counting detection and the sub-nanosecond time resolution required for meV resolution in HREELS place several demands upon the chopper, detection electronics and digital signal processing software. We will discuss how the chopper, based upon the "interleaved comb" device,<sup>3</sup> limits the minimum gating time and the nominal time resolution of the spectrometer. Traditional cross correlation methods, utilized to recover the signal in PRBS modulation, obtain a throughput advantage over single pulse TOF at the expense of resolution; however, the methods are not strictly valid when the noise correlates with signal power. To overcome these limitations, we have developed maximum likelihood methods which account for the Poisson noise distribution and achieve a resolution enhancement of up to a factor of 8, relative to the nominal TOF time resolution, depending upon the signal to noise ratio. <sup>1</sup>Y. Uehara, T. Ushiroku, S. Ushioda, Y. Murata, Jap. J. App. Phys., 29 (1990) 2858-2863. <sup>2</sup>J. L. Buevoz, G. Roul, Rev. de Phys. Appl., 12 (1977) 59 7. <sup>3</sup>P. R. Vlasak, D. J. Beussman, M. R. Davenport, C. G. Enke, Rev. Sci. Instrum., 67 (1996) 68-72.

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