Thursday Morning, October 28, 1999

Surface Science Division Room 604 - Session SS3+AS+NS-ThM

Novel Surface Probes & Technique Enhancement Moderator: B.E. Koel, University of Southern California

8:20am SS3+AS+NS-ThM1 Determination of Sticking Probability and Transition State Energy by Line-of-Sight Detection: Halocarbons on Cu(111), A.S.Y. Chan, C.A. Clifford, R.G. Jones, University of Nottingham, UK We have used a new technique, Line-of-Sight Sticking Probability (LOSSP) to study the reactions of chloroform and 1-bromo-2-chloroethane (BCE) on Cu(111). The sticking probability measurements were made by applying a thermally randomised pressure of the halocarbon above the surface and detecting the reflected flux as a narrow beam of molecules flying in line-ofsight from the centre of the sample surface to the mass spectrometer.@footnote 1@ The general reaction undergone by both halocarbons on the copper surface is: M(gas) -> M(phys) [1] M(phys) -> M(gas) [2] M(phys) -> chemisorbed halogens + gas phase product [3]. By measuring the sticking probability as a function of temperature, we are able to obtain the energies of the transition state M(phys) towards decomposition, which for the non-activated adsorption system of BCE on Cu(111) is ~13 kJ/mol below zero, and for the activated adsorption of chloroform on Cu(111) is ~4 kJ/mol above zero. (Zero energy is defined as the energy of the molecule at an infinite distance from the surface. @FootnoteText@ @footnote 1@ R G Jones and C J Fisher; Surface Science 424 (1999)127.

8:40am SS3+AS+NS-ThM2 Demonstration of Angle Resolved Augerphotoelectron Coincidence Spectroscopy from a Solid: First Results from the Cu(111) Surface, D.A. Arena, R.A. Bartynski, Rutgers University; D. Cvetko, L. Floreano, A. Morgante, F. Tommasini, Laboratorio Nazionale TASC-INFM, Italy; A. Attili, A. Ruocco, G. Stefani, Universita' di Roma, Italy; L. Marassi, P. Luches, Universita' di Modena, Italy; S. Iacobucci, CNR-IMAI, Montelibretti, Italy

We report the first successful angle-resolved Auger-photoelectron coincidence spectroscopy (AR-APECS) measurements from a solid. These measurements were made at the ALOISA beamline at the ELETTRA synchrotron radiation center in Trieste, Italy. This novel analysis chamber is equipped with seven hemispherical electron energy analyzers mounted on two independent rotatable frames; the arrangement allows for the efficient exploration of different kinematical conditions for the emitted pair of electrons. We measured the angular distribution of Cu L@sub3@VV Auger electrons from the Cu(111) surface in coincidence with Cu 2p@sub 3/2@ photoelectrons emitted at selected angles; these angles correspond to maxima and minima in the photoelectron diffraction (PED) pattern. When the 2p@sub 3/2@ core level is at a PED maximum, the Auger pattern is indistinguishable (within statistics) from the noncoincidence distribution. In contrast, if the 2p@sub 3/2@ photoelectrons are at a PED minimum, the coincidence Auger angular distribution shows additional structure as compared to the noncoincidence pattern. This observation may arise because the two coincidence conditions access different intermediate states. The effects of the lattice may be more pronounced in the Auger angular pattern collected in coincidence with photoelectrons on the PED maximum while the Auger angular distribution acquired in coincidence with the photoelectrons on the PED minimum may exhibit more "atomic-like" behavior. Alternatively, the difference may be a consequence of different probing depths on and off the PED maximum, and hence the sampling of different scattering sites. Experiments to discriminate between these possibilities are currently underway. This work is supported by NSF-DMR 98-01681 and NATO-CRG 97-0175.

9:00am SS3+AS+NS-ThM3 Multiple Atom Resonant Photoemission: A New Tool for Determining Near-Neighbor Atomic Identities and Bonding, A.W. Kay, UC Davis and LBNL; E. Arenholz, LBNL and UC Berkeley; B.S. Mun, UC Davis and LBNL; J. Garcia de Abajo, LBNL; C.S. Fadley, UC Davis and LBNL; R. Denecke, Z. Hussain, M.A. Van Hove, LBNL

A newly discovered resonance photoemission process between neighboring atoms in multielement samples will be presented. Experimental evidence for the effect and possible applications will be considered. In several metal oxides, including MnO, Fe2O3, and La0.7Sr0.3MnO3, we have observed an enhancement in the core-level photoelectron peak intensity associated with one element in the sample (e.g. O 1s) while the excitation energy is tuned through an energetically deeper absorption edge of a second element (e.g. Mn 2p or Fe 2p or La 3d). At the edges of this second element, a 40-100% enhancement in the peak intensity (as an area above inelastic background) of the first element is observed. Furthermore, this peak intensity enhancement exhibits a dependence upon photon energy that closely, but not identically, follows the x-ray absorption coefficient of the second atom. This is evidence of an interatomic or multi-atom resonance photoemission (MARPE) process, that is related to but distinctly different from the much-studied intraatomic or single-atom resonance photoemission (SARPE). Theoretical calculations based on extensions of previous intratomic resonance models have yielded encouraging agreement with our experimental results. The MARPE effect is expected to provide a direct method for determining the atomic identities (atomic numbers) of near-neighbor atoms to the excited atom, as well as providing a new technique for studying bonding and magnetism in molecules, at surfaces, buried interfaces, and perhaps bulk materials provided that secondary fluorescence detection of the resonance can be utilized.@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the U.S. Department of Energy, Office of Energy Research, Basic Energy Sciences Division, Materials Science Division, and the Miller Institute (Berkelev)

9:20am SS3+AS+NS-ThM4 Incident Beam Diffraction in Electron Stimulated Desorption, *M.T. Sieger*, *G.K. Schenter*, *T.M. Orlando*, Pacific Northwest National Laboratory

The use of electron beams to remove surface-bound atoms and molecules (electron-stimulated desorption, or ESD) is a topic of interest for many disciplines, from semiconductor device processing to astrophysics. We have been studying the role of scattering and diffraction of the incident electron in the initial state of the desorption process. We report calculations and experiments demonstrating that total ESD yields show fine-structure with incident electron direction, consistent with quantum-mechanical scattering and interference of the electron in the initial state of the desorption process. In a time-independent picture interference of the incident plane wave with waves scattered from the crystalline lattice forms an electron standing wave (ESW), having spatially localized maxima and minima in the incident electron density. Whether a particular point on a surface experiences a maximum or minimum depends on the wavelength of the electron, the direction of incidence relative to the crystal axes, and the locations of nearest neighbor atoms. Since the probability of excitation is proportional to the incident electron density at or near the site of the "absorber" atom (the site of the inelastic scattering event), the total ESD rate should depend upon the local atomic structure and the k-vector of the incident wave. The total desorption yield, when measured as a function of incident direction at constant energy, shows oscillations with the symmetry of the absorber bonding site. Since every inequivalent atomic bonding site has a unique pattern of oscillation electron standing wave stimulated desorption (ESWSD) measurements can in principle uniquely determine the bonding geometry of the absorber. We present experimental measurements for chlorinated Si surfaces.

9:40am SS3+AS+NS-ThM5 Direct Atomistic Observation of Structural Dynamics in Surfaces and Interfaces by Time-Resolved High-Resolution Transmission Electron Microscopy, *T. Kizuka*, Nagoya University and Japan Science and Technology Corporation, Japan INVITED Atomic processes of mechanical interaction and gas-phase epitaxial growth

were directly observed in situ by time-resolved high-resolution transmission electron microscopy at spatial resolution of 0.1 nm and time resolution of 1/60 s. Nanometer-sized tips of gold and silicon approached, and were contacted, bonded, deformed and fractured inside a 200 kV electron microscope using a piezo-driving. Contact boundaries of a few atomic columns width in gold, silicon/silicon-oxide/silicon tunnel junctions, and quantum dots of silicon/gold-cluster/silicon were produced.@footnote 1@ A few layers near the surfaces and contact-boundaries were responsible for the bonding and separation processes. Atomic scale contact or non-contact type surface-scanning similar to that in scanning probe microscopy was performed by the same method.@footnote 2@ The mechanical removal of one atomic layer was also demonstrated.@footnote 3@ New kinds of atomic scale mechanical tests, such as friction test, compressing, tensile and shear deformation tests were proposed. Gold was vacuum-deposited on (001) surfaces of magnesium oxide inside the electron microscope. Atomic process of epitaxial growth was in-situ observed cross-sectionally. Various types of growth phenomena, such as 'embryo' formation, structural fluctuation, repeated process of truncation and construction of a corner in one gold cluster, secondary nucleation and coalescence, were analyzed in real-space.@footnote 4@ @FootnoteText@ @footnote 1@T. Kizuka, Phys. Rev. Lett., 81 (1998) 4448. @footnote 2@T. Kizuka et al., Phys. Rev., B55 (1997) R7398. @footnote 3@T. Kizuka, Phys.

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Rev. B57 (1998) 11158. @footnote 4@T. Kizuka et al., Phys. Rev. B56 (1997) R10079.

10:20am SS3+AS+NS-ThM7 Ionization Mechanisms of Water in High Interfacial Electric Fields, *D.L. Scovell*¹, University of Washington, U.S.A; *V.K. Medvedev, C.J. Rothfuss, E.M. Stuve,* University of Washington

High surface fields (Ã1 V/Å) drive many important processes, such as electrochemistry and field emission. The behavior of water in these fields is important because water is the primary component in electrochemical processes and a major contaminant in the vacuum surrounding field emitter arrays in flat panel displays. It is usually assumed that water amplifies the field at the electrode surfaces, but little is known about how water affects the electric field distribution. Field emitter tips lend themselves to the study of the dielectric properties of water because they produce fields as high as 5 V/Å. To better understand the effect of high electric fields on water, numerical analyses have been conducted to model the electric field distribution around a water-covered emitter tip. The calculations include the field-dependence of the relative permittivity of the water adlayer. The model predicts that the dominant field occurs at the vacuum interface in thin water layers and at the metal surface in thick layers. In very thick layers the field at the tip surface is predicted to be greater than the applied electric field. This response is analogous to that assumed for a traditional electrode/electrolyte interface. Experiments have been conducted to verify the predicted trends for thin water layers. In these experiments water was adsorbed onto a platinum field emitter tip under field-free conditions in ultrahigh vacuum. Ionization was examined by isothermal ramped field desorption (RFD) performed as a function of temperature and water layer thickness. The experimental results are consistent with the predicted trends. This work was supported by the Office of Naval Research.

10:40am SS3+AS+NS-ThM8 Free Electron Laser Nanospectroscopy Interface Applications, *G. Margaritondo*, Ecole Polytecnique Fédérale, Switzerland; *A. Cricenti*, Consiglio Nazionale delle Ricerche, Italy; *N.H. Tolk*, Vanderbilt University; *R. Generosi*, *P. Perfetti*, Consiglio Nazionale delle Ricerche, Italy; *I.D. Aggarwal*, U.S. Naval Research Laboratory

We present the first result of a major effort to investigate the lateral fluctuations of properties of solid interfaces on a microscopic scale. The key elements were the use of a small-tip optics fiber and its coupling with a scanning module; in this way, we achieved and verified the condition of near-field microscopy -- including a lateral resolution much below the wavelength value. Our discussion includes a presentation of the first scanning near-field optical microscopy images obtained with a free electron laser infrared sources and data on small and microscopic-scale fluctuations of semiconductor interface barriers.

11:00am SS3+AS+NS-ThM9 Imaging and Charge Transport Measurements using Dual-Probe Scanning Tunneling Microscopy, *H. Grube*, *J.J. Boland*, University of North Carolina

Scanning tunneling microscopy has evolved into a valuable tool for the study of semiconductor and metal surfaces. However, the single probe geometry of STM limits its application to local and static measurements of the local density of states.@footnote 1@ Incorporation of a second electrically and mechanically independent STM tip within nanometers of the first enables measurements of surface properties that conventional STM cannot perform.@footnote 2,3,4@ Our DP-STM has been characterized by placing both tips in close proximity on a sample surface and obtaining images from each tip showing its local surface environment and the other probe. We discuss the challenges encountered of DPSTM and the feasibility of charge transport measurements on a variety of systems including carbon nanotubes. @FootnoteText@ @footnote 1@ G. Binnig et al., Phys. Rev. Lett., 49 (1), 57 (1982)@footnote 2@ Q. Niu, M. C. Chang and C. K. Shih, Phys. Rev., B 51 (8), 5502 (1995)@footnote 3@ J. M. Beyers and M. E. Flatte, Phys. Rev. Lett., 74 (2), 306 (1995)@footnote 4@ J. M. Beyers and M. E. Flatte, J. Phys. Chem. Solids., 56 (12), 1701 (1995)

11:20am **SS3+AS+NS-ThM10 The Miniature Cylindrical Mirror Analyzer: A New Tool For Surface Analysis**, *K. Grzelakowski*, Focus Polska Sp. Z o.o., Poland; *M.S. Altman*, Hong Kong University of Science and Technology, P.R. China

The design and performance of a new miniature cylindrical mirror analyzer (CMA) are presented. The CMA comprises outer and inner cylinders, integral on-axis electron gun, and detector system consisting of ring aperture and channeltron, all mounted on a 2.75" flange. Entrance angle,

sample-to-detector distance, and polar cone angle were chosen, in consideration of second order focussing effects, that optimized analyzer transparency and resolution. Fringe field correction at the ends of the CMA is made by means of six rings precisely separated by sapphire insulators. The electron gun is a one-lens electrostatic system equipped with XYdeflector for beam adjustment and scanning. A CeB6 low temperature cathode operating at up to -2.0keV delivers emission current up to 100 mA. The energy range of analyzed electrons can be varied between 0 eV to 2.0 keV. The flange mounting also incorporates a high precision Z-motion for optimization of the working distance. The control electronics and software permit operation of the instrument in pulse and phase sensitive detection modes. Results obtained for a W(001) surface with this new miniature CMA demonstrate an energy resolution of 0.08%, which is comparable to larger 6" and 8" flange mounted instruments. The very small size of the mini-CMA permits its use in small or crowded ultra high vacuum chambers or where only 2.75" ports are available, thereby increasing flexibility in surface analysis.

11:40am SS3+AS+NS-ThM11 Investigations of Surface Reactions on Thin Film-Supported Catalysts Using Microhotplate Arrays, R. Walton, R. Cavicchi, S. Semancik, M. Class, J. Allen, J. Suehle, National Institute of Standards and Technology

This presentation describes the use of microhotplate arrays and electrical measurements for efficiently investigating surface reactions on supported metal catalysts under varied temperature and gas exposure conditions. Each ~100 µm x 100 µm microhotplate platform used in our work includes functionality for rapid control and measurement of film temperature (thermal time constant ~ 1 ms) and for probing of gas-induced changes in a film's electrical properties. Arrays of individually addressable microhotplates are well suited for directly comparing catalytic layers of different composition, loading, and degree of dispersion. The results we present are relevant to both gas sensing and catalysis. Specifically, fourelement arrays were used to evaluate reactions on Pt, Pd, and Cu catalyst particles (formed by annealing 25-100 Å layers) supported on tin oxide. Electrical conductivity was used to monitor changes in the electron density of the thin film catalysts caused by surface reactions in air of H@sub 2@, CO and CH@sub 3@OH, respectively, at film temperatures ranging from 20 to 500 °C. Each of the catalysts interacts with these reactants in air to produce changes in film conductivity that we relate to factors including surface oxygen concentration, reaction rates, catalyst loading, and catalyst fouling. As a further example of this approach, we also illustrate the use of microhotplates to explore the conditions of thermal cycling and partial pressures under which CO oxidation oscillations occur on Pt particles supported on SnO@sub 2@.

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