Tuesday Afternoon, October 3, 2000

Surface Science
Room 209 - Session SS2-TuA

Stimulated Processes and Excitations

Moderator: T.E. Madey, Rutgers, The State University of New Jersey

2:00pm **SS2-TuA1 Ultra-Fast Dynamics Measurements of One- and Two-Dimensional Surface State Electrons on Stepped Cu(775)**, *X.J. Shen, H. Kwak,* ***D. Mocuta****, S. Smadici, R.M. Osgood, Jr.,* Columbia University

Dynamical questions regarding surface state electrons on metallic surfaces can best be answered in the time domain using ultra-fast nonlinear probes. Of particular interest is the effect of controlled nano-size features on the femtosecond scale dynamics of surface states. In this connection, we have employed the momentum- and time-resolved two photon photoemission technique to study the dispersion and lifetimes of these states on a prototypical nano-structured surface, stepped Cu(775). Here we report on a newly observed one-dimensional surface state (0.27 eV below Fermi level) and an image-like unoccupied state on stepped Cu(775). Both states are dispersive along the step direction but are localized in the direction perpendicular to the steps. The origin of the states is attributed to the step-edge potential confinement and to an Anderson localization mechanism. The lifetime of n=1 electrons on the regular step array of Cu(775) has been measured as a function of their translational momentum, k@sub //@. At the terrace normal, this lifetime is equal to that for flat Cu(111), i.e., t = 16±2 fs. The lifetime decreases symmetrically with k@sub //@ about k@sub //@ = 0 for electrons moving parallel to the step orientation. This is in good agreement with a theoretical calculation of k@sub //@ dependent n=1 lifetime done on Cu(111) by Echenique, et al.@footnote 1@ In contrast, the lifetime is asymmetric in k@sub //@ for the direction perpendicular to the step edges. The asymmetric behavior is attributed to direction-dependent coupling between image and bulk states, leading to a decrease in lifetime of the electrons climbing the steps and an increase for descending electrons. The overlap between the unoccupied localized state and the n=1 image state at k@sub //@ = 0.2 Å@sup -1@ results in an increase in the measured lifetime at this value of the momentum. @FootnoteText@ @footnote 1@J. Osma, I. Sarria, E. V. Chulkov, J. M. Pitarke, and P. M. Echenique, Phys. Rev. B59, 10591 (1999).

2:20pm **SS2-TuA2 Electron-Stimulated Oxidation of Al(111)**, ***V. Zhukov****, I. Popova, J.T. Yates, Jr.,* University of Pittsburgh

The electron stimulated dissociative adsorption of O@sub 2@ on Al(111) has been studied at surface temperatures from 90 to 300 K. A rastering electron beam technique has been used to deliver electrons with energies from ~1 to 200 eV to the aluminum surface during O@sub 2@ exposure. Experimental evidence for the presence of an O@sub 2@ precursor was found for the oxidized Al(111) surface at low temperature. Precursor adsorption energy of 70-80 meV was estimated from the temperature variation of the oxide growth rate, stimulated by 100 eV electrons. The effect was found to be proportional to the primary beam current. A threshold electron energy of 7 ± 0.5 eV for the electron stimulated oxidation was observed when utilizing electrons with variable energies. This threshold value is in agreement with the 6.8 eV electron attachment cross-section resonance for the gaseous O@sub 2@ species. In contrast to the significant increase of oxidation rate on the oxide-precovered aluminum surface, no effect of electrons was found on the initial stages of oxide growth on the clean Al(111) surface over the temperature range studied. This suggests that the O@sub 2@ precursor is stabilized on oxide clusters.

2:40pm **SS2-TuA3 Ion-Influenced Nucleation and Surface Diffusion: A Computational Study**, ***Z. Wang****, E.R. Blomiley, E.G. Seebauer,* University of Illinois, Urbana-Champaign

Ion-beam assisted deposition (IBAD) has been used to improve material properties for a wide variety of semiconductors, metals and oxides. In many applications, beneficial effects derive from ion-induced surface diffusion, while deleterious effects derive from ion-induced damage to the substrate. Process optimization involves finding a kinetic balance between these opposing effects, which in turn demands useful rate expressions. We have recently demonstrated experimentally both the enhancement and inhibition of surface diffusion by low-energy ions in the case of Ge/Si(111). We have simulated this system via molecular dynamics, and have developed a fairly nuanced picture of the interplay between sputtering, knockin, and vacancy formation on the surface and within the bulk. Our simulations show marked thresholds for both ion energy and substrate temperature, with a previously unknown conservation law relating these two parameters: E + bT = constant. The physical significance of the proportionality constant b we derive is discussed. The ideas deriving from these simulations are then applied to continuum simulations of ion-influenced nucleation during IBAD, with the goal of explaining why ions sometimes increase nucleation densities and other times decrease them.

3:00pm **SS2-TuA4 Surface Modification of CaF@sub 2@ for Improved Heteroepitaxy**, ***A. Bostwick****, B.R. Schroeder, S. Meng,* University of Washington*; E. Rotenberg,* Lawrence Berkeley National Laboratory*; M.A. Olmstead,* University of Washington

Fluorite (CaF@sub 2@) is a candidate epitaxial insulator for three dimensional circuits. However, heteroepitaxial growth of semiconductors and metals on CaF@sub 2@(111) surfaces is inhibited by CaF@sub 2@s low surface energy. We have investigated use of electron irradiation and surfactant incorporation to alter the surface energy balance and promote laminar growth of silicon and related materials on CaF@sub 2@(111). We report here photoelectron diffraction studies of the interaction of electrons and arsenic with CaF@sub 2@(111) surfaces. Irradiation of CaF@sub 2@ with 40 eV electrons creates fluorine vacancies in the film, raising the fluorite surface energy. The resultant defects are extremely reactive. Exposure of this surface to arsenic passivates the surface to oxygen and water contamination. We find As@sub 4@ does not stick to pristine CaF@sub 2@(111) between room temperature and 600C, but sticks only in the presence of surface defects. Room temperature exposure results in As on the fluorite surface. At elevated temperature, however, arsenic diffuses into CaF@sub 2@. It occupies two ordered sites, neither of which is a bulk fluorine site. As-stabilized, irradiated CaF@sub 2@ is more stable than either pristine or irradiated CaF@sub 2@ with regard to photon-stimulated desorption of fluorine. Deposition of Si on unirradiated CaF@sub 2@ results in an amorphous film at room temperature, but sticking is inhibited at high temperature. Si deposition on As-terminated CaF@sub 2@, on the other hand, leads to laminar growth of Si at 550C. The As acts as a surfactant, floating to the top of the Si film.

3:20pm **SS2-TuA5 Consequences of Electron Irradiation of Hydrated Crystals: Self Organized Nanometer Cone Formation**, ***S.C. Langford****, M. Dawes, J.T. Dickinson,* Washington State University

Radiation effects on hydrated single crystals are poorly understood. We find that dense arrays of conical structures, with aspect ratios on the order of 200, are produced by exposing single crystal brushite (CaHPO@sub4@.2H@sub2@O) to energetic electrons (2 keV). By exposing thin brushite platelets bonded to the surface of a metal heater to energetic electrons, the surface temperature can be controlled independently of electron dose. This work shows that cone formation requires surface temperatures of 400-600 @degree@C. The cones are directed along the direction of the incident electrons, and often display a cap-like structure that may play a role in cone production. Cone formation is accompanied by the development of a distinctive orange luminescence during electron irradiation, presumable due to electronic defects. The waters of hydration in this material may play a role in cone development by enhancing ion mobility in the heated material. Characterization of surfaces covered with conical structures has been performed by TEM, EPS, and IR spectroscopy.

3:40pm **SS2-TuA6 Femtosecond Measurements of Surface-State-Electron Dynamics on Nanostructured Ni Surfaces**, ***S. Smadici****, X.J. Shen, D. Mocuta, R.M. Osgood, Jr.,* Columbia University

Ultra-fast nonlinear optical probes have recently been shown to enable time-resolved measurements of electron dynamics on metal surfaces. While most measurements have been on flat surfaces, we have recently begun an investigation of the ultra-fast dynamics for electrons confined in surface metallic nano-structures. Here we will describe our femtosecond, momentum- and time-resolved two-photon photoemission measurements of electron lifetimes and dispersion curves on systems with controlled nano-size features obtained by Ag deposition on stepped Ni(977) and Ni(111). Ag deposition reduces the Ni work function and permits the observation of surface and image states at the accessible pulse energies. We will present measurements of the dispersion for the occupied surface state and the unoccupied n=1 image state located ~3Å above the metal surface. We report on band-folding of the Ag induced surface state on Ni(977), with a controllable bandwidth, caused by the periodic step potential. As the Ag coverage is increased the width of the allowed band increases as predicted by a Krönig-Penney model which is appropriate to the periodic potential on this Ag-decorated surface. The n=1 state lifetime measurements on the Ag/Ni(977) system showed a downward trend with increasing parallel momentum. This result is similar to that observed by us

on Cu surfaces@footnote 1@ and is consistent with theoretical results indicating the increased importance of elastic and inelastic scattering at higher k@sub //@. The n=0 surface state lifetime showed an unexpected similar behavior when moving away from the terrace normal direction with a variation of ~10 fs over a change of k@sub //@ of 0.2Å@super-1@. This result is explained in terms of a resonant excitation of the n=2 image state, with the detector sampling a mixture of two different photoemission channels. @FootnoteText@ @footnote 1@.X. J. Shen, H. Kwak, A. M. Radojevic, S. Smadici, D. Mocuta, and R.M. Osgood, Jr., submitted to Phys. Rev. Lett.

4:00pm **SS2-TuA7 Theory of Single Molecule Vibrational Spectroscopy and Microscopy**, ***N. Lorente***, *M. Persson,* Chalmers/Gothenburg University, Sweden

A recent breakthrough in Surface Science has been the experiments demonstrating vibrational spectroscopy and microscopy of single molecules by inelastic electron tunneling using a scanning tunneling microscope.@footnote 1@ Based on density functional theory and a many-body generalization of Tersoff-Hamann theory, we have developed a theory and calculational method for this new spectroscopy.@footnote 2@ We apply our theory to acetylene on copper and explain why only the carbon-hydrogen stretch modes are observed in terms of elastic and inelastic contributions to the tunneling conductance. The calculated values for the changes in tunneling conductance induced by these stretch modes and their spatial images are in good agreement with experiments. We find that the symmetry of the adsorbate-induced states makes the inelastic signal for the anti-symmetric stretch mode to dominate over the signal for the symmetric one. This result is in agreement with experiment and shows that the symmetries of the lowest unoccupied molecular states has an important influence on the spatial dependence of the vibrationally inelastic tunneling.@footnote 3@ @FootnoteText@ @footnote 1@ B. C. Stipe, M.A. Rezaei, and W. Ho, Science 280, 1732 (1998). @footnote 2@ N. Lorente and M. Persson, (submitted to Phys. Rev. Lett.). @footnote 3@ N. Lorente, M.Persson, L.J. Lauhon, and W. Ho, (to be submitted).

4:20pm **SS2-TuA8 Transient Currents as a Tribological Probe**, ***J.V. Wasem***, *S.C. Langford, J.T. Dickinson,* Washington State University

When conductors contact and slide on insulator surfaces charge transfer between the surfaces allows one to measure instantaneous transient currents (TC). We have instrumented a vacuum tribological apparatus with high sensitivity normal, lateral, and TC pick-up using metal and semiconductor stylii. Performing single pass wear track formation tests on polymer and ceramic substrates, we observe striking correlations between the mechanical and electrical signals. In particular, the TC exhibit fluctuations with a rich temporal/frequency spectrum, for example during stick-slip events. Through correlations with SEM images of the substrate we are able to relate spatial microscopic damage and corresponding TC behavior. The TC reveals details of the micromechanics during wear on microsecond time scales. Studies on Fomblin Zdol lubricated hard drive surfaces reveals charge transfer events that correspond to free electrons going to the lubricant. Yates et al. have previously shown that electron attachment to such polyperfluoroethers can cause decomposition of the polymer. Thus, our studies can provide quantitative values and rates for the charge deposited which can then be used to predict lubricant lifetimes from measured attachment cross-sections.

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