

Surface Science

Room 326 - Session SS1-MoA

Stimulated Processes at Surfaces

Moderator: J.A. Yarmoff, University of California, Riverside

2:00pm SS1-MoA1 Growth of Ordered and Disordered Arrays of Silicon Pillars During Laser-Assisted Etching, D. Mills, K.W. Kolasinski, Queen Mary, University of London, UK

We report on the formation of conical silicon pillars on a Si(111) substrate by etching with a nanosecond pulsed excimer laser in the presence of SF₆ or HCl or NF₃. The change in the silicon surface morphology was monitored as the number of shots from the XeCl (308 nm) excimer laser was varied from one to several hundred, for all experiments the energy density at the silicon surface was kept at about 1 J cm⁻². Significant changes in pillar morphology result from changing the process gas. This is a clear indication that gas-phase/plasma chemistry occurring in the laser ablation plume and plume/surface interactions are instrumental in the pillar formation mechanism. Initial surface morphology also affects pillar dimensions. Exposure of an unpolished surface results in much sharper pillars for a given number of laser shots than does exposure of the polished side. Modulation of the laser intensity profile by the effects of diffraction can be used to enhance the order of the pillars. For instance, the diffraction profile resulting from irradiation of a Gaussian shaped interface produces concentric rings of pillars. Large areas of pillars, on the order of 1 cm², have been formed by rastering the beam across the Si sample under continual laser irradiation at 20-50 Hz. Progress has also been made with the production of ordered arrays of the pillars using near field diffraction effects from fine wires and grids. Further investigation will examine the effects of varying the pressure of the process gas, the partial pressure of process gas mixtures, pre-heating of the surface with an argon ion laser, the effects of pulse repetition rate and diffraction on the pillar height, width and packing densities.

2:20pm SS1-MoA2 Defect-driven Photodesorption at UV and VUV Excimer Laser Wavelengths, L. Cramer, S.C. Langford, J.T. Dickinson, Washington State University

The optical properties of single crystal calcium fluoride make it useful lens material for the ultraviolet to vacuum-ultraviolet region, including possible use at 157 nm (7.8 eV) for high resolution microlithography. Of concern is possible degradation of these properties with prolonged exposure to laser light. Both surface and bulk modification of the material are of interest. Our interest is to obtain fundamental understanding of laser induced emissions (e.g., ions, electrons, and neutrals) from insulators with wide bandgaps (CaF₂ has a band gap of ~11.2 eV) and radiation induced surface/bulk modifications. We report and compare the measured rates of laser desorption from cleaved surfaces of CaF₂ of the observable ionic and neutral species at three excimer laser wavelengths: 157, 193, and 248 nm with pulse lengths ~20-30 ns. Mass selected time-of-flight techniques allows both species and kinetic energies to be determined. At laser fluences well below threshold for plume formation, only positive ions are observed. Ca⁺ is seen at all of the wavelengths; CaF⁺ is seen only at 157 nm. The Ca⁺ intensity vs. fluence shows essentially no dependence on wavelength. Ion energies show slight wavelength dependencies but all emissions are consistent with a multiple-photon electrostatic repulsion model. Neutral emission is dominated by Ca⁰ and the neutral energy distributions correspond to thermal distributions at relatively high temperatures (> 2500 K). Finally, we report on the role of simultaneous keV electron irradiation co-focused on the laser spot. We observe substantial increases in the laser desorbed products which we contribute to the resulting halide vacancy formation (F-centers).

2:40pm SS1-MoA3 Hot Electron Generation and Detection from Chemical Reactions on Metal Surfaces, E.W. McFarland, B. Roldan Cuenya, University of California, Santa Barbara

INVITED

Chemical reactions at metal surfaces have associated charge and energy transfer processes that are both ubiquitous and incompletely understood. There is increasing theoretical evidence that the traditional adiabatic description of reaction kinetics is limited, and that many if not most reactions on metal surfaces involve nonadiabatic elementary steps. Non-adiabatic processes in highly exothermic reactions are well known; however, for low energy reactions, experimental observation of charge carriers generated by electronic excitations during the reaction is difficult. A Schottky junction device structure consisting of an ultra-thin metal film

deposited on a semiconductor allows direct observation of electrons or holes generated during bond forming reactions at surfaces as a "chemicurrent" analogous to a diode photocurrent. Investigations of the chemical reaction induced electron current during adsorption of atomic and molecular species including, H, O, O₂, N₂O, NO₂, C₂H₄ and other hydrocarbons on Ag, Au, and Pd surfaces have revealed complex chemically induced electronic phenomena. The adsorption energies span a large range and we find a general tendency of the chemicurrent to increase with increasing energy and a distinct current amplitude and transient behavior for each species and surface. Detailed interpretation of the electronic signature for each species requires understanding of both the electron/hole excitation spectrum as well as the diode electronic characteristics. These data suggest the direct transfer of reaction energy to electronic excitations is a common feature of a wide range of surface reactions and that the unique electronic signal from such reactions might be used for improving our understanding of surface reactions and in creating new devices and sensors directly coupling chemical processes with electronics.

3:20pm SS1-MoA5 Factors Influencing Ion Yields and Angular Distributions in Electron Stimulated Desorption, N.S. Faradzhev, D.O. Kusmierek, T.E. Madey, Rutgers University

The focus of this work is on scattering processes affecting the survival probability and 'depth of origin' of low-energy ions (F⁺, F⁻) that pass through condensed ultrathin layers of polar molecules (H₂O, NH₃). The ions are generated by electron stimulated desorption (ESD) of SF₆ adsorbed on Ru(0001) at 25K. Electron stimulated desorption ion angular distribution (ESDIAD) and temperature programmed desorption (TPD) reveal predominantly molecular adsorption of SF₆ on Ru(0001) via three F atoms, with the other three pointing away from the surface. Several characteristic angular distributions of F⁺ and F⁻ (halo, hexagon) are observed as a function of temperature, coverage, and electron irradiation. Adsorption of overlayers of polar molecules, e.g. H₂O and NH₃ leads to changes in both the F⁺ and F⁻ ion intensities (attenuation and enhancement), as well as dramatic changes in the ion angular distributions. Analysis of these changes gives insight into the role of charge-transfer and elastic scattering processes during the passage of ions through ultrathin polar films. The polar coadsorbate can also influence the ESD process itself by modifying polarization energies, low-energy electron lifetimes, and potential barriers for electron tunneling.

3:40pm SS1-MoA6 Effects of Water Ice Films on Thermal Stability and Electron-activated Decomposition of CF₂Cl₂ on Metal Surfaces, N.S. Faradzhev, Rutgers University; C.C. Perry, Johns Hopkins University; D.O. Kusmierek, Rutgers University; D.H. Fairbrother, Johns Hopkins University; T.E. Madey, Rutgers University

We report the kinetics of processes, activated by low energy electrons, for an environmentally important molecule CF₂Cl₂ co-adsorbed with water ice on metal surfaces (Ru; Au) at low temperature <100K. The results are compared with similar data obtained for CCl₄. TPD, RAIRS and XPS has been utilized. TPD reveals an increase of thermal stability of molecular CF₂Cl₂ on Ru(0001) when deposited under an amorphous solid water (ASW) overlayer at 25K or adsorbed inside ASW ice matrix; dissociation is completely inhibited. Weakly-bound CF₂Cl₂ desorbs from ASW surface at ~110K, but desorption of CF₂Cl₂ trapped in the ASW matrix is impeded until the onset of ice crystallization at ~155K. All techniques indicate that ionizing radiation (electrons or X-rays) incident on CF₂Cl₂/H₂O layer leads to rapid decomposition of halocarbon, which proceeds via dissociative attachment (DA) of low energy secondary electrons. The rates of decomposition for 1ML of CF₂Cl₂ and CCl₄ are similar on the metal surface and increase in the ASW ice environment indicating a possibly important role of a polar medium in halocarbon dissociation. The highest decomposition cross-sections are observed for submonolayer halocarbon coverage on a water ice surface: 1.0x10⁻¹⁵ cm² for CF₂Cl₂ and 2.5x10⁻¹⁵ cm² for CCl₄. The cross-sections are identical for halocarbon adsorbed on an ice surface and caged in a water matrix. The initial dominant radiation-induced process in adsorbed CF₂Cl₂ is C-Cl bond cleavage. For CF₂Cl₂ in ASW, fragments and reaction products include Cl⁻ and F⁻, H₂O, COF₂, and CO₂; for CCl₄ in ASW, COCl₂ and C₂Cl₄ are also seen. Product distributions, the kinetics of halocarbon damage,

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and subsequent reaction pathways are qualitatively independent of the radiation source.

4:00pm SS1-MoA7 Water Enhanced Decomposition and Nanometer Scale Structure Formation Generated by Radiative Exposure of Solid Surfaces, *K. Nwe, S.C. Langford, J.T. Dickinson*, Washington State University

Novel nanometer scale structures on insulating inorganic materials with wide bandgaps can be generated by simultaneous exposure of surfaces to electron and laser beams plus low pressure water vapor. Dramatic synergisms are observed on ionic single crystal surfaces due to bond weakening which arises from localized chemisorption. We are able to modify single crystal surfaces of alkali halides and calcium phosphates/carbonates either at the single atomic layer level or, with higher intensities, at the level of several microns. These modifications are due to electronic excitations leading to decomposition of the crystal. Arrays of cones and fractal structures with unique optical properties can readily be generated. Alkali halide and nitrate surfaces exhibit strongly angular dependent "black" surfaces which are generated in a self-organized fashion. The high absorption is due to the high tortuosity of the surface (a "stealth" surface). We also quantify that in the presence of water vapor, the rates of both laser and electron beam induced decomposition/desorption increase by as much as an order of magnitude. We present AFM evidence that this is a highly localized, defect mediated mechanism. We suggest that point defect clusters lead to atomic dimension step structures (e.g., kinks) that peel off due to bond weakening from sorbed water derived radicals. Supporting evidence from spectroscopic and microscopic data on exposed surfaces will be presented.

4:20pm SS1-MoA8 Electron-stimulated Reactions in Thin Amorphous Solid Water Films on Pt(111), *G.A. Kimmel, N.G. Petrik*, Pacific Northwest National Laboratory

The electron-stimulated production of D_2 from amorphous solid D_2O deposited on Pt(111) is investigated as a function of film thickness. The D_2 yield has two components with distinct reaction kinetics. Using isotopically layered films of H_2O and D_2O demonstrates that the D_2 is produced in reactions that occur at both the Pt/amorphous solid water (ASW) interface and the ASW/vacuum interface, but not in the bulk. The energy for the reactions, however, is absorbed in the bulk of the films and electronic excitations migrate to the interfaces where they drive the reactions. At the Pt(111) surface, the electronic excitations cause dissociation of water molecules at the interface, leading to the build-up of adsorbed hydrogen atoms. A model based on the diffusion of electronic excitations to either interface accounts for the principle experimental observations.

4:40pm SS1-MoA9 Temperature-Dependent Thresholds for Ion-Stimulated Surface Diffusion: Experiments with Second Harmonic Microscopy, *Z. Wang, E.G. Seebauer*, University of Illinois at Urbana Champaign

Ion-surface interactions at low energies (<100 eV) characterize an increasingly diverse array of material processing steps in ion beam assisted deposition (IBAD), plasma enhanced deposition, reactive ion etching (RIE), and other applications. The governing kinetic phenomena are often tacitly considered to lie at one of two poles: physical effects where momentum matching dominates, and chemical effects involving thermal activation of atomic bonds according to Arrhenius expressions. Here we report surface diffusion measurements demonstrating behavior that lies at neither pole. Optical second harmonic microscopy is used to image diffusion of Ge and In adsorbed on Si(111) under low-energy noble-gas ion bombardment. Both adsorbates exhibit a surprising new form of tradeoff between substrate temperature and the energy threshold at which ion influences become manifest. Molecular dynamics simulations suggest that the effect originates from changes in surface point defect concentrations. Instantaneous nonuniformities in net surface potential induced by thermal vibrations provide a mechanism by which ions can affect these concentrations nonlinearly. The effects generally increase the rate of mass transport across the surface except for Ge above the Si(111)-(7x7) to (1x1) phase transition, where ion-induced changes in charge-mediated complexation of mobile species with surface defects slows the diffusion.

5:00pm SS1-MoA10 Femtosecond Photo-generated Carrier and Reaction Dynamics on a Chlorinated Silicon Surface: Reaction Yield Calculation by Rate Equation of Adsorbed Chlorine, *S. Harachi, F. Sasaki*, National Institute of Advanced Industrial Science and Technology, Japan

We have studied the mechanism of a photo-induced reaction of Si/Cl system especially in the low fluence region, which is a promising candidate

for an extremely low-damage etching. The following procedures were employed in the femtosecond pump probe experiment to obtain the photo-generated carrier dynamics during the reaction. First, the variation of surface second-harmonic (SH) intensities generated by probe light, which directly reflects surface chlorine coverage, has been measured during a photo-induced reaction. Here both incident lights respectively produces two reaction factors of carrier generation and instantaneous surface vibration. However the pump beam of 3.1 eV photon energy mainly produces carrier generation, and the probe light of 0.95 eV photon energy mainly produces instantaneous surface vibration. In addition, the pump power is set just under the reaction threshold, so the reaction must be induced only when the carrier generation by pump beam and the surface vibration by probe light simultaneously occur on the surface. After obtaining the variation of surface chlorine coverage during a photo-induced reaction, the reaction yield is calculated by using a first and second-order rate equation of the surface chlorine atoms. Second, the reaction yield is calculated for several delays between two beams, and the obtained reaction yield dependence on the delay time reflects the femtosecond photo-generated carrier dynamics. The dynamics can be described by first and second-order kinetics, and both results show no significant difference but the almost equal excitation peak at around 0.4 ps. Here the excitation time constant in the obtained carrier dynamics is 0.1-0.2 ps and tends to decrease with increasing the power of each excitation lights. On the other hand, we have found two relaxation time constants of 0.2-1.0 ps and 1.5-10.0 ps, and both short and long relaxation time constants tend to increase with increasing the excitation power.

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