Wednesday Morning, October 27, 1999

Surface Science Division Room 607 - Session SS2+AS+PS-WeM

Ion-Surface Interactions I

Moderator: L. Hanley, University of Illinois, Chicago

8:20am SS2+AS+PS-WeM1 Trapping and Desorption of Energetic Cu Atoms on Cu(111) and (001)Surfaces at Grazing Incidence, *D.E. Hanson*, *A.F. Voter*, *J.D. Kress*, Los Alamos National Laboratory; *X.-Y. Liu*, Motorola, Inc.

Cu is widely used as an interconnect in semiconductor chips. It is deposited by ionized physical vapor deposition on sub-micron features that have sidewalls nearly parallel to the incident ion beam. Molecular dynamics (MD) simulations have shown that, for angles of incidence (with respect to normal) up to 20 degrees, the sticking probability is unity for all energies; the impact atom penetrates and loses all of its kinetic energy to the surface. As the impact angle increases, the probability for the impact atom to reflect increases, reducing the sticking probability. Surprisingly, for angles above 70 degrees, the sticking probability increases with impact angle. We have performed MD simulations of Cu atoms impacting both Cu(111) and (001) surfaces at grazing incidence and find that this unexpected increase in sticking probability is a consequence of trapping (or surface skipping). An energetic Cu atom (10 ¾ E ¾ 100 eV) can become trapped by the mean attractive potential above the surface, oscillating normal to the surface. While in this trapped state, it can traverse hundreds of Å as it dissipates energy to the surface. Until the atom either desorbs or comes to rest, it experiences an average energy loss rate that is piecewise linear, typically comprised of two or more roughly linear (dE/dt = constant) regions. The process can be characterized by two parameters: the desorption probability at each oscillation and an average energy loss rate (per oscillation) that is independent of energy. These parameter values are the same for both the (111) and (001) surfaces. A phenomenological model based on these parameters is presented, and the predictions of sticking probability, average energy transfer to the surface, and total distance traveled along the surface, agree with full MD simulations. The dependence of the desorption probability on the surface temperature, was also studied.

8:40am SS2+AS+PS-WeM2 Dynamics of NO@super +@ Abstraction of Oxygen on Al(111), *M. Maazouz*, *P.L. Maazouz*, *D.C. Jacobs*, University of Notre Dame

Energetic collisions between molecules and surfaces can activate a number of reaction processes, such as electron transfer, activated dissociative chemisorption, dissociative scattering, atom abstraction, and sputtering. The branching into each of these channels can be affected by the initial internal energy (electronic, vibrational, and rotational) and collision energy of the molecule. Reactive collisions of NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v=1) with oxygen-covered Al(111) are explored across a range of hyperthermal energies (5-80 eV). A laser forms the incident ions from the neutral NO via resonance-enhanced multiphoton ionization (REMPI). This produces NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v) in a selected vibrational level (v=0-6) of the ground electronic state. Scattered products include O@super -@, NO@super -@, and NO@sub 2@@super -@. The latter product arises from an atom abstraction channel and is the main focus for the present study. The NO@sub 2@@super -@ formation shows a strong dependence on the oxygen coverage and the NO@super +@ primary energy. Detailed reaction mechanisms leading to NO@sub 2@@super-@ emergence will be discussed.

9:00am SS2+AS+PS-WeM3 Oxygen Negative Ion Emission from Al(100) Bombarded by Li@super+@ Ions, J.A. Yarmoff, W.K. Wang, B.-L. Young, B.C. Corbitt, University of California, Riverside; Z. Sroubek, Academy of Sciences of Czech Republic

The intensity of oxygen negative ions sputtered from metal surfaces (V, Mo, Cu) by rare gas ions is known to increase by up to 3 orders of magnitude when the surface work function is lowered by alkali metal adsorption. A resonant charge transfer process from the surface bands to the oxygen affinity level is apparently responsible for the negative ion formation, and such a process is strongly dependent on the surface potential. We have measured the intensities and kinetic energy distributions of O@super-@ sputtered from Al(100) via bombardment by 200 eV Li@super+@ ions. In contrast to experiments with rare gas ions, the O@super-@ intensity is found to be relatively independent of the work

function changes induced by Cs deposition (@DELTA@@phi@ = - 3 eV). For O@super-@ kinetic energies above 20 eV there is no increase in the yield, and it increases by only a factor of 2-3 at lower O@super-@ kinetic energies. The energy distribution depends exponentially upon the O@super-@ kinetic energy, and has a cutoff at about 120 eV. These results suggest that the yield of oxygen particles sputtered from clean Al(100) by Li@super+@ is already nearly completely ionized due to the local potential perturbation caused by the projectile. Thus, a further lowering of the surface potential by the deposition of alkali adsorbates has little effect. This is clear evidence of the localized nature of the resonant charge exchange process, and the first evidence that such a local effect can be induced by the primary particle.

9:20am SS2+AS+PS-WeM4 Matrix Dependent He+ Neutralization by Adsorbates: An ISS Study of S and Cl on TiO@sub 2@(110), W. Hebenstreit, E.L.D. Hebenstreit, U. Diebold, Tulane University

We have studied the adsorption of S and Cl on TiO@sub 2@(110) with lowenergy He@super +@ ion scattering spectroscopy (ISS) , X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). Because of its high surface sensitivity, ISS is ideally suited to determine the chemical composition of surfaces. While it is well known that quantification of ISS spectra is influenced by trajectory-dependent blocking, the element-specific neutralization of the probing ion is generally assumed not to be matrix dependent. We found that the neutralization of He+ ions (400 - 2450 eV, scattering angle 139°) scattered on Cl or S (adsorbed on TiO@sub 2@(110)), depends strongly on sample pretreatment and adsorption site. Cl (~ 1 ML) and S (~ 2/3 ML) give rise to pronounced peaks in ISS spectra when adsorbed on the sputtered TiO2 sample (1 keV Ar@super +@, flux 1.5 10@super 16@ cm@super -2@), but both species cannot be detected after adsorption at RT on the annealed, stoichiometric TiO@sub 2@(110) surface (coverage ~ 1/3 ML). STM shows that the adsorbates are located on the rows of 5-fold coordinated Ti atoms. When dosed at 573 K, S adsorbs at the position of bridging oxygen atoms, where it forms a (1x3) superstructure. In this case S becomes "visible" again for ISS. All spectra (on sputtered and annealed substrates) show a decrease in the O and Ti ISS signal due to blocking induced by the adsorbates. Subsurface positions of the adsorbates in the "invisible cases" can be excluded by STM. The difference in neutralization is due to different electronic structures of the substrate surface: (a) semiconducting with a 3 eV band gap when annealed; (b) metallic due to defect states and oxygen deficiency after sputtering. In case of S located at the position of bridging oxygens, neutralization is affected by the different local bonding.

9:40am SS2+AS+PS-WeM5 Hyperhhermal Ion - Surface Interactions, J.W. Rabalais, University of Houston INVITED

The chemical and physical phenomena accessible by means of low energy ion beams on surfaces will be discussed. Such energetic reactive ions can stimulate selected physical and chemical processes, such as film deposition, growth, synthesis, and shallow implantation within a nonequilibrium UHV environment. The 'low energy' or 'hyperthermal' range is considered to be 5 eV to a few keV. The lower limit is of the order of chemical bond energies. In this limit, chemical bonding interactions become significant, the binary-collision approximation (BCA) becomes questionable, and inelastic interactions can alter the ion trajectories. In the high energy limit, the sputtering yield becomes equivalent to or higher than the beam flux, classical ion trajectory simulations using the BCA provide a satisfactory description of the collision events, and the impinging ions are implanted in the subsurface layers. Mass-selected ion beam deposition (IBD) allows independent control over parameters such as ion energy and type, ion fluence and dose, substrate temperature, and background gases. The advantages of IBD for stimulation of chemical reactions, control of film stoichiometry, low temperature epitaxy, good film-substrate adhesion, and for growth of materials with metastable structures, isotopic purity, and high densities will be contrasted with the disadvantages, such as production of defects, imperfections, and amorphous materials and the limited thicknesses of IBD films. Examples of the use of mass- and energyselected beams for hyperthermal surface reactions, film growth, synergism between ion energy and substrate temperature, and shallow implantation will include: Si+ ion homoepitaxy, the growth SiO2 from pulsed Si+ and O+ beams, low energy Ti+ beams for growth of titanium silicide on silicon and mixed Ti-Al oxides on sapphire (a-Al2O3), growth of diamond-like carbon, growth of Ag(111) on a Ni(100) surface, and survival probabilities of scattered TiClx cluster ions.

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10:20am SS2+AS+PS-WeM7 Dissociation and Energy Distribution Processes in XY@super -@(CO@sub 2@)@sub n@ (XY = ICl, I@sub 2@, and Br@sub 2@) Collision onto Silicon Surface, S. Koizumi, Genesis Research Institute, Inc., Japan; H. Yasumatsu, A. Terasaki, T. Kondow, Toyota Technological Institute, Japan

Collisional dissociation induced by impact of a cluster anion, ICl@sup -@(CO@sub 2@)@sub n@ (n = 0 - 20), onto a silicon surface were studied by measuring the branching fractions of the ICl@sup -@ dissociation and the translational energies of the product anions as functions of n and the collision energy (per ICl@sup -@) of ICl@sup -@(CO@sub 2@)@sub n@ in an apparatus consisting of a tandem time-of-flight mass spectrometer. It was found that the branching fraction of the ICl@sup -@ dissociation did not change with n at the collision energies of 30 - 70 eV. Molecular dynamics simulation showed that the impinging core ion, ICl@sup -@, tends to orient with the molecular axis of the core ion being at the angle of 55 ° with respect to the surface normal, whereas in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ (X = Br, I) collision, the molecular axis of the X@sub 2@@sup -@ core ion being in parallel to the surface plane. This finding together with prominent wedge effect in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ collision leads us to conclude that the CO@sub 2@ molecules do not work as 'wedge' in the ICl@sup -@(CO@sub 2@)@sub n@ collision because of the unfavorable orientation of the incoming cluster anion. No discernible cage effect could also be related to the orientation. The translational energies of the product anions were interpreted in terms of energy redistribution of the collision energy among the degrees of freedom of the cluster anion and the surface atoms involved in the collision. It was also found that the I and Cl product ions reach quasiequilibrium with the surface from the measurement of these translational energy distributions.

10:40am SS2+AS+PS-WeM8 Angle Resolved Measurements of Ions and Neutrals Scattered from HOPG Surfaces upon Hyperthermal Glancing Incidence Irradiation with Large Polyatomic Ions: Charge Changing and Impact Orientation Phenomena, *M. Hillenkamp, J. Pfister, M. Kappes,* University of Karlsruhe, Germany; *R. Webb,* University of Surrey, United Kingdom

We have scattered a series of polyaromatic hydrocarbons and various fullerenes from graphite at hyperthermal kinetic energies (100-5000eV) under glancing incidence (75 degrees with respect to the surface normal). Resulting cations, anions and fast neutrals have been studied with a secondary time-of-flight mass spectrometer/detector rotatable about the scattering plane. The corresponding angular distributions have been compared to those obtained upon irradiation of HOPG with He@super +@ and Xe@super +@ ion beams under otherwise identical conditions. Molecular projectiles were typically studied as either singly or multiply charged parent cations. In addition to dominant neutralization, we also observe the scattering of smaller amounts of both cations and anions (parents and fragments). We discuss the relative yields of charge states in terms of charge transfer rate theories as well as in terms of postcollision decay processes (e.g. delayed electron loss). In comparing the surprisingly narrow (and near Gaussian) angular distributions determined for fast neutrals from fullerene scattering with those recorded for xenon, we find that while Xe is specularly scattered over the full energy range studied, fullerenes are scattered subspecularly - with the deviation from specular angle increasing with increasing collision energy. Molecular dynamics simulations with Brenner potentials suggest that this effect results from a combination of the comparatively long (>300 fesec) "turnaround " time of the molecular projectile and a significant perpendicular deformation of the layered target on the collision time scale. For the topologically much more anisotropic polyaromatic hydrocarbon projectiles we find structured fast neutral angular distributions suggestive of a simple dependence between impact orientation and scattering angle

11:00am SS2+AS+PS-WeM9 Surface Structure Determination by Angle-Resolved Mass Spectroscopy of Recoiled Ions, G.S. Herman, Pacific Northwest National Laboratory

Low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) are powerful techniques for the determination of surface composition and structure. The combination of time-of-flight methods with an electrostatic time focussing analyzer has recently resulted in a new technique - massspectroscopy of recoiled ions (MSRI).@footnote 1@ The MSRI technique has an advantage over LEIS and DRS in that it has much higher massresolution and sensitivities. Results related to the exchange of @super 18@O into samples will be presented to illustrate the high mass-resolution. Furthermore, recent results indicate that in the angle-resolved mode, structural determinations can be performed. Angle-resolved MSRI (AR- MSRI) results will be presented for CeO@sub 2@(001) and TiO@sub 2@(001)-Anatase films grown on SrTiO@sub 3@(001) substrates by molecular beam epitaxy and chemical vapor deposition, respectively. The experimental data are fit to calculations using the scattering and recoiling imaging code based on the binary collision approximation.@footnote 2@ The ideal CeO@sub 2@(001) surface is polar and predicted to be unstable. However, LEED results indicate that a sharp (1x1) pattern can be obtained. The structural model determined by AR-MSRI consists of an oxygenterminated surface with a half monolayer of oxygen removed. This structure is consistent with a model based on the reduction of the surface dipole moment. The TiO@sub 2@(001)-Anatase surface has only recently been experimentally investigated in much detail. LEED measurements indicate that the surface undergoes a (1x4) reconstruction after a sputter and anneal cycle. A comparison between experiment and theory for several models for this reconstruction will be presented. @FootnoteText@ @footnote 1@ K. Eipers-Smith, K. Waters, and J.A. Schultz, J. Am. Ceram. Soc. 76, 284 (1993). @footnote 2@ V. Bykov, C. Kim, M.M. Sung, K.J. Boyd, S.S. Todorov, and J.W. Rabalais, Nucl. Instr. And Meth. In Phys. Res. B 114, 371 (1996).

11:20am SS2+AS+PS-WeM10 Depth Information in Direct Recoiling Peak Shapes: Simulations from Model Surfaces, *M. Tassotto*, Oregon State University; *P.R. Watson*, Oregon State University, U.S.

Direct recoil spectrometry (DRS) has been used in the past to study adsorbate surface structures, chemisorption processes, and average orientations of molecules at surfaces. In these studies, DRS has experimentally been proven to be very surface sensitive. Information on surface structure and composition is primarily based on the analysis of DR peak intensities from the time-of-flight (TOF) spectra. These DR peaks frequently exhibit long tails to higher TOF which often overlap with neighboring peaks. It is common practice to obtain intensities from TOF spectra by integrating the DR peak areas over narrow time windows. Unfortunately, quantitative analysis is complicated by a lack of accurate background removal and only the use of relative intensity variations is possible. In this study, the MARLOWE computer code has been applied to calculate the trajectories of atoms recoiling from both simple and more complex model surfaces (diamond and alkane polymers, respectively) while the depth from which recoiled particles originated was recorded. The DR peak itself as well as the long TOF tail to lower energies contain depthrelated information. Near the peak maximum recoils originate from mainly the first atomic layer, supporting the high surface sensitivity of DRS. The initial portions of the tail of the peak provide an approximate atomic depth profile but at longer TOF the tail contains recoils that were produced by several mechanisms from a wide variety of depths. The trajectory calculations have been converted to actual TOF spectra which allows comparison with experimental data from the literature. Here it is important to account for varying detector efficiencies as well as broadening of the simulated DR peak due to the finite pulse width of the ion beam. The MARLOWE calculations make DR peak deconvolution possible. This leads to accurate background removal in determining atomic ratios.

11:40am SS2+AS+PS-WeM11 Hyperthermal-energy Ion Scattering on Si(100), C.L. Quinteros, S.I. Tzanev, D.C. Jacobs, University of Notre Dame

Ion-surface scattering experiments on a Si(100) surface are presented, introducing a new gas/surface experimental system with unique capabilities. Using a Colutron type source, an ion beam with energies between 5-300 eV can be generated. The ions are extracted, accelerated, mass-selected by a Wein filter, decelerated and focused on the surface target. Scattered ions and neutral products are mass- and energy-resolved with a fully rotatable, differentially-pumped detector that includes an ionization source for detection of neutrals, a cylindrical electrostatic analyzer for energy selection, and a quadrupole mass spectrometer for mass selection of the energy-filtered particles. Incident angles between 0-90° and scattering angles between 0-150° can be accessed by independent rotation of the sample manipulator and the detector. A complement of surface analysis techniques (LEED, Scanning Auger Electron Spectroscopy, X-Ray Photoelectron Spectroscopy, and a Kelvin Probe) monitor surface modifications resulting from ion-beam exposure. The surface sample can be cooled to 80K through a liquid nitrogen reservoir or resistively heated to 1000K. The hyperthermal energy range spans from thermal energies (<1eV), where chemical interactions produce inelastic scattering events, to the low energy regime (1-5 keV), where predominantly elastic scattering occurs. We present scattering results for a series of different projectiles on Si(100) that bridge these two energy regimes. The charge state and energy distributions of the scattered products are reported as a function of collision energy and scattering angle.

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