Tuesday Afternoon, October 26, 1999

Surface Science Division Room 607 - Session SS3-TuA

Diffusion on Surfaces

Moderator: T.L. Einstein, University of Maryland

2:00pm SS3-TuA1 Mechanisms and Energetics in Diffusion of O2-Molecules and H-atoms on Si(1x1)-7x7 Surfaces, *R.L. Lo, I.S. Hwang, M.S. Ho,* Academia Sinica, Republic of China

Using a variable temperature STM, atom and molecular dynamics on solid surfaces can be observed directly and the energetics studied in detail. It is possible to trace the path of single particle movement, measure site and path specific hopping rates and the rate parameters of individual atoms and molecules on solid surfaces as well as to probe the mechanisms. We find that on Si(111)-7x7 surface, O2 molecules adsorb on top of adatom sites while H atoms adsorb on top of rest atom sites. Diffusion and hopping of H and O2 on this surface is achieved by hopping of chemical bonds via intermediate states. We have identified the intermediate states and also derived site and path specific activation energies and frequency factors, and the potential energy curves for the hopping of O2 and H on this surface. The physical significance of these measurements will be discussed. Research supported by NSC of ROC and Academia Sinica. 1. I-S Hwang, R-L Lo and T. T. Tsong, Phys. Rev. Lett. 78, 4797 (1997). 2. R-L Lo, I-S Hwang, M-S Ho and T. T. Tsong, Phys. Rev. Lett. 80, 5584 (1998).

2:20pm SS3-TuA2 Real-Time Imaging of Step Motion on Cu(100) with the Low Energy Electron Microscope@footnote 1@, C.L.H. Devlin, S. Chiang, X.D. Zhu, University of California, Davis

The low energy electron microscope (LEEM) is capable of real-time, realspace imaging of metal and semiconductor surfaces, at the scale of tens of nanometers. We have recently used a new instrument at UC Davis to image the motion of steps on the Cu(100) surface. We have seen a number of intriguing effects at the relatively low temperature range of 100 to 300°C. Impurities pin the step positions, affecting the shapes of the steps over regions of many microns. The kink density of the steps decreases with additional sample cleaning, with the steps becoming more rectilinear. Evidence exists for several different phases on the surface as a function of temperature, as the contrast on terraces changes markedly on the scale of 10-20 nm with increasing temperature. The size of an area corresponding to a particular phase also changes. In some cases, rapid fluctuations of the contrast at the boundaries are evident as the phase shrinks. For curved steps, wave-like motions have been observed along the length of steps. Steps have also been observed to move into and out of an impurity at constant temperature. An X-ray photoemission spectrometer and a commercial variable temperature scanning microscope (VT-STM) (50-800K) have recently been added to the UC Davis LEEM system and are being used to further characterize the Cu(100) system. @FootnoteText@ @footnote 1@Funded by National Science Foundation (DMR-95-12231).

2:40pm SS3-TuA3 Diffusion and Dynamics of 2D Clusters on Crystal Surfaces, G. Rosenfeld, University of Twente, The Netherlands; L.K. Verheij, D.C. Schloesser, IGV, Forschungszentrum Jülich, Germany; G. Comsa, University of Bonn, Germany INVITED

Using fast scanning tunneling microscopy, the diffusion and shape fluctuation of nanoscale vacancy clusters on a Cu(111) surface have been studied. The diffusion constant has been determined as a function of cluster size and temperature, and the underlying atomic scale diffusion processes have been deduced.@footnote 1@ The results are discussed with respect to simple scaling theories. Via detailed analysis of cluster shapes and shape fluctuations both the anisotropy and the absolute value of the line tension, i.e., the specific free energy of cluster edges, have been determined.@footnote 2@ The experimental data yield a comprehensive set of energies believed to be representative for the diffusion and stability of 2D metal clusters on fcc(111) surfaces. @FootnoteText@ @footnote 1@ D.C. Schloesser, L.K. Verheij, G. Rosenfeld, G. Comsa, to be published @footnote 2@ D.C. Schloesser, L.K. Verheij, G. Rosenfeld, G. Comsa, Phys. Rev. Lett. 82, 3843 (1999).

3:20pm **SS3-TuA5 Sulfur's Effect on Cu(111) Surface Morphology**, *J. de la Figuera*, *K. Pohl, M.C. Bartelt, N.C. Bartelt, P.J. Feibelman, R.Q. Hwang*, Sandia National Laboratories

Numerous studies have demonstrated the dramatic effects that small amounts of an adsorbate can have on film growth and surface morphology. The origin for these effects range from kinetic limitations to thermodynamic considerations. We have recently observed that extremely small amounts of sulfur can significantly affect the smoothing of Cu(111). Cu islands of monolayer height decay several orders of magnitude faster in the presence of ~0.01 ML of sulfur as compared to the clean case. Using time-resolved STM, we have monitored the rate and morphology of the decay to identify the origin of this phenomenon. In agreement with these observations, first-principles calculations predict a dramatic change in the ratio of Cu step formation energies in the presence of a row of S atoms at the steps. Sulfur atoms bind more strongly to the A-type step. The ratio of the equilibrium lengths of the A- and B-type steps is about 1:1.1 on the clean surface, but about 2.4:1 when the step edges are S-saturated. We discuss the observed superfast island decay in terms of atomic processes at and near island edges, including S-mediated near-irreversible detachment of Cu atoms, enhanced diffusion of Cu adatoms and small clusters on the terraces, and more efficient downward transport. This work is supported by the Office of Basic Energy Sciences Division of Materials Sciences of the U.S. DOE (DE-AC04-94AL85000).

3:40pm SS3-TuA6 Influence of Adsorbates on the Self-diffusion of Pt Adatoms and the Stability of Pt Dimers, *S. Horch*, University of Aarhus, Denmark; *T.R. Linderoth*, University of Aarhus, Denmark, Sweden; *S. Helveg*, *L. Petersen*, *E. Laegsgaard*, *I. Stensgaard*, *F. Besenbacher*, University of Aarhus, Denmark

Surface diffusion of atoms is an important phenomenon in areas of materials processing such as chemical vapor deposition (CVD) and sintering. In these particular areas, the diffusion are modified by atoms adsorbed from the gas phase. Here we try to derive mechanistic insight into this effect from observations, using the Scanning Tunneling Microscope, of adsorbate promoted self-diffusion on the Pt(110)-(1x2) surface.@footnote 1@ In the case of hydrogen, we directly image an activated Pt-H complex (with H bound on top the Pt adatom) which has a diffusivity enhanced by a factor of 500 at room temperature, relative to Pt adatoms on the clean surface. The influence of other adsorbates also on the binding energy of Pt dimers is currently being investigated. @FootnoteText@ @footnote 1@ S. Horch, H. T. Lorensen, S. Helveg, E. Laegsgaard, I. Stensgaard, K. W. Jacobsen, J. K. Norskov and F. Besenbacher, Nature 398 (1999) 134.

4:00pm **SS3-TuA7 Study of Subsurface Hydrogen in Pd(111) by STM**, *M.K. Rose*, Lawrence Berkeley National Laboratory; *A. Borg*, Norwegian University of Science and Technology, Norway; *D.F. Ogletree*, *M. Salmeron*, Lawrence Berkeley National Laboratory

Using Variable Temperature Scanning Tunneling Microscopy we have studied hydrogen atoms embedded in the topmost layers of Pd(111) and the influence of these impurities on surface adsorbates. Hydrogen is imaged beneath surface three-fold hollow sites at 20K. Subsurface hydrogen atoms exhibit attractive interactions leading to aggregation into clusters. We observe diffusion of two distinct hydrogen species within the subsurface layer above 200K, with activation energies differing by approximately 10%. Significant variation in the diffusion barriers is found in the presence of surface adsorbates. Interlayer diffusion is not observed below 220K, which sets lower bounds on the surfacesubsurface and subsurface-bulk diffusion barriers and provides a benchmark for ab-initio total energy calculations. Scanning Tunneling Spectroscopy of subsurface hydrogen has been performed and the results are compared with tightbinding calculations. Adsorbed molecules interact strongly with subsurface H. In the case of CO, binding occurs preferentially at sites separated by @sr@3 lattice vectors from surface hollow sites above embedded hydrogen. For O@sub 2@, thermal dissociation proceeds adjacent to H sites. Subsurface H clusters provide nucleation sites for ordered adsorbate structures, pin adsorbate domain boundaries, and hinder adsorbate diffusion.

4:20pm **SS3-TuA8 Enhanced Interlayer Mass Transport and Dynamics of Film Smoothening on a Symmetry-broken Ag(111) Surface**, *H. Yu*, *C.-S. Jiang*, University of Texas, Austin; *Ph. Ebert*, Forschungszentrum J@um u@lich, Germany; *X.-D. Wang*, *C.K. Shih*, University of Texas, Austin

We have studied the dynamics of the film flattening process at room temperature and higher annealing temperatures of Ag films deposited at low temperature on GaAs(110) surfaces. We will present a scanning tunneling microscopy movie, which shows the evolution of the film morphology over 13 hours at room temperature. The initial surface contains a distribution of surface heights up to five monolayers. The vacancy islands at the lowest layer and the islands at the top layer both decay very rapidly with the same decay constants. The remaining islands (of a surface with three monolayers exposed) decay with a much slower

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rate and we observed a freeze of decay after about 7 hours. Consecutive annealing up to 400 K induces a further decay of the roughness, such that finally nearly only two layers are exposed. The island size increased during room temperature and consecutive annealing steps considerably and the steps align preferentially along the high symmetry directions of the twofold superstructure present on the Ag surface. These results demonstrate the existence of a considerably enhanced interlayer mass transport and a different symmetry behavior compared to those observed for Ag homoepitaxy on Ag(111) surfaces. The enhanced interlayer mass transfer is interpreted in terms of a very low Ehrlich-Schwoebel barrier.

4:40pm SS3-TuA9 Ion-Enhanced Surface Diffusion: Experiment and Simulation, *E.R. Blomiley*, *Z. Wang*, *E.G. Seebauer*, University of Illinois, Urbana

Low-energy ion enhancement of thin film deposition has become an increasingly widespread technique for lowering growth temperatures and improving film properties. Rational process optimization has remained difficult, however, because the beneficial effects of enhanced surface diffusion are often opposed by the deleterious effects of sputtering and ion embedding. Good explanations for important aspects of the governing physical processes remain lacking. We have recently reported for the first time direct quantitative measurements of low-energy (<70 eV) ionenhanced diffusion, using the Ge/Si(111) adsorption system with noble gas ions as the bombarding species. The present work extends that work to examine the effects of incident bombardment angle. Experiments with second harmonic microscopy show that below about 750°C, diffusional enhancement increases monotonically as the incident angle increases from normal toward grazing. However, above 750°C diffusional effects change nonmonotonically in a manner more akin to sputtering yields. Molecular dynamics simulations show these effects arise from ion-induced adatomvacancy pair formation.

5:00pm SS3-TuA10 The Effect of As@sub 4@ Flux on the Ga Diffusion on the GaAs(001)-(2x4) Surface, *D.W. Bullock*, *V.P. LaBella*, *Z. Ding*, *P.M. Thibado*, University of Arkansas

The activation energy for an individual Ga atom to hop across the technologically important GaAs(001) 2x4 reconstructed surface as a function of As@sub 4@ flux was measured. This study was motivated by the ongoing development of short-period III-V semiconductor superlattices for electronic and optoelectronic applications grown by molecular beam epitaxy (MBE). This study was carried out in an ultrahigh vacuum MBE system with an in situ scanning tunneling microscope (STM) to study III-V single cryst al surfaces and interfaces on the atomic scale. The diffusion measurement was achieved by measuring the number density of islands as a function of substrate temperature and As@sub 4@ flux, and comparing it to random walk computer simulations of the grow th process. The Ga atom's relative probability to stick to existing island edges and its relative diffusion anisotropy are estimated. Interestingly, it was discovered that increasing the As@sub 4@ pressure forces the Ga atoms to diffuse more isotropically. This work was funded in part by the National Science Foundation (DMR-9733994) and the Office of Naval Research (N00014-97-1-1058).

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