Thursday Afternoon, November 5, 1998

Surface Science Division Room 308 - Session SS1-ThA

Surface Diffusion

Moderator: G.L. Kellogg, Sandia National Laboratories

2:00pm SS1-ThA1 A Novel Real-time Technique for Monitoring Adatom Surface Diffusion and Island Nucleation, *P.M. DeLuca*, *S.A. Barnett*, Northwestern University

The surface diffusion coefficient of Ga adatoms, along with twodimensional (2D) island nucleation and coarsening were measured in realtime on vicinal GaAs(001) 2x4 surfaces using specular ion current measurements (SICM). In this new technique, 3 keV Ar ions were incident upon the surface at a glancing angle (typically 1° to 3°), and the specularly scattered ion current measured. Since specular scattering requires a locally-flat surface, surface defects cause a decrease in the scattered ion current, providing a measure of average adatom and/or step-edge density. The time dependence of the Ga adatom population was measured during and after the deposition of 0.1 monolayers of Ga on vicinal GaAs(001)2x4. The scattered ion current dropped with an exponential dependence upon opening the Ga shutter and increased exponentially upon closing the shutter, in good agreement with a simple model for adatom diffusion across terraces to step edges. Diffusion coefficients, D, were obtained using the measured adatom lifetimes,@tau@, and the 70Å terrace width, x, (the miscut was 2.3 ° towards (1 1 0)) in the expression D=x2/@pi@ 2 @tau@, yielding D=(8.89x10-10 cm@super 2@/sec) exp (0.74/kT) for an As@sub 4@ ambient over the temperature range 450 to 570°C. For larger Ga coverages and/or lower substrate temperatures, deviations from simple exponentials and much longer time constants were observed, suggesting that 2D islands had nucleated. The island nucleation and coarsening behaviors will be described.

2:20pm SS1-ThA2 Direct Measurement of Adsorbed Si Dimer Dynamics on Siloga) I M. Cominalli B. S. Sugrtantrukar, Sandia National Laboratories

Si(001), J.M. Carpinelli, B.S. Swartzentruber, Sandia National Laboratories Silicon atom deposition onto a clean, well-ordered Si(001) crystal surface results in the formation of adsorbed dimers. This presentation details the use of atom-tracking scanning tunneling microscopy to determine the detailed energetics of such species in a variety of local environments at elevated temperatures (~ 100°C). Dimer diffusion along a buckled A-type step edge is found to be weakly asymmetric, indicating that the adsorbed dimer does not strongly perturb the underlying substrate bonding. A dimer adsorbed onto the middle of a terrace is attracted at only a single lattice site to a 2+1 defect in an adjacent diffusion channel, pinpointing the probable location of subsurface contamination responsible for defect formation. Additionally, a linear dependence between the activation barrier for diffusion and perpendicularly applied electric field magnitude is measured. These results provide valuable insight into the bonding and interaction of dimers with surface features prevalent during homoepitaxial growth. The quantitative measure of lattice-site specific energy parameters not only serves as input to realistic simulations, but also enables the validation and refinement of such calculations. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

2:40pm SS1-ThA3 Ion-Induced Surface Diffusion of Ge on Si(111), E.G. Seebauer, R. Ditchfield, University of Illinois, Urbana

In thin film deposition, bombardment of the surface with low-energy (10-100 eV) ions during growth has been shown to improve film quality in a variety of applications. In many cases, the improvement is attributed to enhancements in surface diffusion of the depositing species. However, such effects have never been quantified in a direct way, and the mechanisms for energy transfer from the ions to the mobile atoms remain unclear. Here we report for the first time the direct quantification of ioninfluenced surface diffusion, using Ge on Si(111) as the adsorption system and second harmonic microscopy as the measurement probe. The effects are significant and fall into two regimes of temperature. Below about 700 C, the activation energy E@sub diff@ remains unaffected, but the preexponential factor D@sub o@ increases. The increase varies as the square root of ion energy and mass (going from He to Ar to Xe), culminating in a factor of 10 increase for Xe near 60 eV. Simulations by molecular dynamics reproduce this effect nearly quantitatively, and point to an increase in the average jump length due to billard-ball-like collisions as the governing mechanism. At higher temperatures, both E@sub diff@ and D@sub o@

decrease dramatically, again according to a square-root energy and mass dependence. E@sub diff@ falls by 75%, while D@sub o@ falls by 8 orders of magnitude. Molecular dynamics simulations again reproduce the effects, and point to ion-mediated changes in the number of mobile adatoms as the governing mechanism. In both temperature regimes, the effects set in only above a threshold energy of about 15 eV.

3:00pm SS1-ThA4 Schwoebel Barriers on Stepped Pt(111)@footnote 1@, P.J. Feibelman, Sandia National Laboratories

The ab-initio Schwoebel barrier calculated for downward self-diffusion across A-type steps on Pt(111) is E@super S@(A) ~ 0.02 eV. This is too small to be consistent with the notion that lowering E@super S@(A) is how O promotes layer-by-layer epitaxy on Pt(111). Geometric arguments explain why E@super S@(B), the Schwoebel barrier at B-type steps, is more than an order of magnitude larger than E@super S@(A), a result in conflict with the observation of three-dimensional Pt islands on Pt(111) bounded by A-type steps. The first-principles downward-transport barriers are vindicated by new observations of Pt growth morphology, in which the CO background has been greatly reduced. @FootnoteText@ @footnote 1@ Work supported by the U. S. Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company for the U. S. Department of Energy.

3:20pm SS1-ThA5 Diffusion and Island Formation of Water Molecules on Ice Ih Surfaces, E.R. Batista, H. Jonsson, University of Washington INVITED We present theoretical calculations of the deposition, adsorption, diffusion, and island formation of water admolecules on the basal face of ice Ih. The calculations are based on both pairwise additive interaction potentials as well as a polarizable model. The sticking coefficient is found to be near unity for vapor deposition, but drops to 0.9 for incident energy of 1.5 eV and 60 degree angle of incidence. At low coverage, an admolecule prefers to sit at non-crystallographic sites (i.e. not fitting into the ice lattice) with a large binding energy. Since ice Ih is proton disordered, there is a range of binding energies, and for some local environments the binding energy is on the order of (and even larger than) the cohesive energy. The proton disorder also results in a range of activation energies for diffusion. After mapping out a large number of diffusion barriers using the Nudged Elastic Band method, a kinetic Monte Carlo calculation of the diffusion at 140 K was performed. At short time, the mean squared displacement has anomalous scaling with time as is common for diffusion on random lattices. From the long time scaling a diffusion barrier is obtained which is not inconsistent with recent upper bound found by Brown and George. The simulated diffusion is also reasonably consistent with earli! er estimates of the diffusion leng th by Mason. Paths and energy barriers for the formation of small islands have also been studied. It is found that islands up to and including pentamer are non-crystallographic, but the hexamer is crystallographic. The dominant activation energy barrier to the formation of the hexamer is the admolecule diffusion barrier.

4:00pm **SS1-ThA7 H and O promoted Self-Diffusion of Pt(110)**, *S. Horch*, *S. Helveg*, *I. Stensgaard*, *E. Laegsgaard*, *F. Besenbacher*, Aarhus University, Denmark

The surface self-diffusion of Pt adatoms on the Pt(110)-(1x2) surface is studied using variable-temperature Scanning Tunneling Microscopy. Exposing the surface to Hydrogen or Oxygen leads to an enhancement of the mobility of the adsorbed Pt adatoms. Atomically resolved STM movies provided the first experimental evidence that in the case of H this is due to the existence of H-Pt ad-dimer skyhooks diffusing several orders of magnitude faster than normal Pt adatoms. These movies allow us to analyse the lifetime distribution of these ad-dimers which gives a surprisingly high binding energy of about 0.8 eV. Nevertheless, only a small fraction of all Pt adatoms form these ad-dimers at the same time. A tentative model will be presented to explain these findings and compare them to the case of O.

4:20pm SS1-ThA8 Adsorption of N on Fe(100): Diffusion and Adatom-Adatom Interactions Studied with Scanning Tunneling Microscopy, *M.O. Pedersen*, *L. Österlund*, *E. Laegsgaard*, *I. Stensgaard*, *F. Besenbacher*, University of Aarhus, Denmark

The dynamics and adsorbate-adsorbate interactions of N adatoms on a Fe(100) surface have been studied using variable temperature Scanning Tunneling Microscopy (STM). By recording a sequence of STM images as a film, we can track the individual N atoms at low coverage, and study their mobility. From these STM films, the diffusion constant of the N atoms can be derived, and by varying the sample temperature from 299 K to 323 K, a

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diffusion barrier of 0.92 eV \pm 0.04 eV and a prefactor of D@sub 0@ = 2.4 10@super -3@ cm@super 2@/s are found. This value of the diffusion barrier is in good agreement with the diffusion barrier calculated using Density Functional Theory.@footnote 1@ From the STM images, the N adatom pair correlation function can also be deduced, from which an ensemble interaction potential can be found. Measuring the ensemble interaction potential at two different coverages (0.034 ML and 0.10 ML), allows us to quantify the entropic contributions and thus find the direct pair interaction potential between the N atoms. As expected, the nearest neighbour interaction is found to be strongly repulsive, whereas the next nearest neighbour interaction is attractive. From the STM images, the N atoms are found to adsorb in the four-fold hollow site, confirming previous LEED experiments. Due to the attractive interactions between the N adatoms, island nucleation is observed, even at sub-monolayer coverage. @FootnoteText@ @footnote 1@J.J. Mortensen, L.B. Hansen and J.K. Norskov, private communication

4:40pm SS1-ThA9 Novel Diffusion Channel Parallel to Steps: CO on Pt(111), X.D. Xiao, J.-W. Ma, M.M.T. Loy, The Hong Kong University of Science and Technology, China

Surface diffusion parallel to steps for CO on Pt(111) has been studied by an optical diffraction technique. With a large accessible dynamic range for diffusion coefficient measurement from 10@super -12@ to 10@super -8@ cm@super 2@/sec, we could cover a wide range of temperatures from 120 to 320 K, within which non-Arrhenius processes can be unambiguously identified. For steps along [110] direction (B-type steps in the present experiment) with a density of one-step/30-atoms, it was found that diffusion at low temperatures are controlled by terrace diffusion and at high temperatures controlled by diffusion along step edges. At 0.3 ML CO coverage, the terrace diffusion was measured with an activation energy of 4.2 kcal/mol and a prefactor of 6x10@super -7@ cm@super 2@/sec. The diffusion along step edges was measured with an activation energy of 10.9 kcal/mol and a prefactor of 0.2 cm@super 2@/sec. It is this large prefactor that compensates the respect high activation barrier for step edge diffusion to take control at high temperatures. As we change the step direction to along [112], a novel diffusion channel was observed. Now, with the same step density as in the previous case, the diffusion is enhanced by a factor of ~10 over the entire temperature range as compared to the terrace diffusion. At 0.3 ML CO coverage, this new channel is characterized by a simple Arrhenius behavior with E@sub D@=3.2 kcal/mol and D@sub o@=5x10@super -7@ cm@super 2@/sec. At 0.5 ML CO coverage, the diffusion is dominated by this new channel only at low temperatures but still by along step edge diffusion at high temperatures. Discussion on how the new channel is formed will be presented.

5:00pm SS1-ThA10 Potassium Surface Diffusion by Optical Techniques, *W. Zhao*, *M. Asscher*, The Hebrew University, Israel

Coverage grating-optical second-harmonic diffraction method has been used to measure the diffusion of pure potassium and coadsorbed with CO on Re (001) surface in the potassium coverage range of 0.6-1 ML. The activation energy (E@sub d@) and the preexponential factor (D@sub 0@) for diffusion in both show a clear compensation effect. For the pure potassium case, E@sub d@ and D@sub 0@ change quadratically with the coverage, having a minimum in the potassium coverage of 0.75 ML. The activation energies for diffusion are determined to be 5.0±0.2, 3.9±0.7, 3.6±0.2, and 5.0±1.0 kcal/mol, the preexponentials are 5.6x10@super -3±0.3@, 3.5x10@super -4±1.1@, 5.8x10@super -4±0.3@, and 3.7x10@super -1±1.9@ cm@super 2@/s corresponding to potassium coverages of 0.93, 0.84, 0.73, and 0.59, respectively. The results are discussed in terms of electrostatic dipole-dipole repulsive interactions among neighboring adsorbates. In the coadsorption case, it is found that CO hinders potassium surface diffusion significantly, with the effective activation energy for 0.8 ML K rising to 15 kcal/mol for CO average coverage of 0.06 ML. The attractive interaction and complex formation (observed by TPD) of CO-K are proposed as the main reasons for the increasing E@sub d@.

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