## Monday Afternoon, October 2, 2000

### Surface Science Room 210 - Session SS3-MoA

#### Surface Diffusion and Wetting

Moderator: E.D. Williams, University of Maryland

#### 2:00pm SS3-MoA1 Theory of Surface Electromigration on Heterogeneous Metal Surfaces, *P.J. Rous*, University of Birmingham, U.K., UK

We report a calculation of the magnitude and direction of the wind force for the self-electromigration of adatoms on heterogeneous metal surfaces. Using layer-KKR and jellium methods we have computed the wind valence of adatoms interacting with adatom islands and voids on the low Miller index surfaces of several simple and noble metals. In the vicinity of an island, we find that the magnitude and direction of the electromigration driving force is significantly different from the force felt by an isolated adatom on a large terrace. Therefore, the usual assumption that driving force in surface electromigration is uniform and isotropic is shown to be inaccurate. Using the results of these calculations as input to kinetic Monte-Carlo simulations, we explore how this inhomogeneity of the wind force is manifest in the driven surface diffusion of adatom islands on a current-carrying metallic substrate.

#### 2:20pm SS3-MoA2 Direct Measurement of Long Jumps of Pd on Cu(001) using Atom-Tracking STM, B.S. Swartzentruber, Sandia National Laboratories; M.L. Grant, J.B. Hannon, Carnegie Mellon University

When Pd atoms are deposited onto a Cu(001) crystal surface, they readily place exchange with the surface Cu atoms, forming a 2-d surface alloy phase. At low coverage, Pd atoms are distributed randomly in the surface layer. At coverages approaching 0.5 ML, an ordered (2x2) alloy phase forms. The kinetic processes by which the incorporated Pd atoms form ordered structures are currently poorly understood. Using atom-tracking STM, a technique in which the probe tip is locked onto the diffusing species using lateral, XY, feedback, we have directly measured the diffusion of the Pd atoms as a function of temperature. The position of individual Pd atoms is recorded as a function of time with millisecond time resolution, thus recording the diffusion path of the incorporated atom. From these data, the relative binding energies of the sites visited by the atom, as well as the local diffusion barriers, are determined. We find that a large percentage (~25%) of the diffusion events involve displacements that are greater than a single lattice spacing - so-called long jumps. The distribution of jump lengths is well described by a process in which a Pd atom is thermally activated to a metastable binding-energy state, perhaps to a site on the surface, where it can perform several unit-length hops before it comes to rest in another stable binding site. Measuring the details of this atomistic process allows us to better understand the formation, growth, and mass transport kinetics of binary surface alloy structures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US-DOE under contract DE-AC04- 94AL85000.

# 2:40pm SS3-MoA3 Bronze Formation through the Motion of Tin Islands on Cu(111), A.K. Schmid, N.C. Bartelt, R.Q. Hwang, Sandia National Laboratories

When Sn atoms are deposited on top of a Cu (111) surface at room temperature, they exchange into the surface to form a surface bronze alloy. One might have expected that this process would be rather simple, the understanding of which would be largely complete when one understood how a single Sn atom exchanged with a single Cu atom. We find, however, that the alloying occurs by an entirely unanticipated cooperative process that is considerably more intriguing than this. Using a combination of atomic resolution scanning tunneling microscopy (STM) and low-energy electron microscopy (LEEM) we find that shortly after Sn deposition large, 100,000 atom 2-D Sn islands coalesce on the Cu surface. These islands proceed to run across the surface. As they move, Sn atoms within the islands randomly exchange with Cu atoms in the surface. The exchanged Cu atoms are ejected from the Sn islands in the form of ordered 2-D bronze crystals. Sn islands consistently move away from their trail towards unalloyed regions of the Cu surface. We are able to trace the motion of the Sn islands to a simple atomic fact: Sn atoms on top of the Cu surface are strongly repelled by Sn atoms already incorporated into the Cu. The islands thus lower the free energy of the surface by moving. We find that island velocity is independent of size, consistent with a model in which the mobility of the Sn islands is determined by diffusion through the interior of the islands.

3:00pm SS3-MoA4 Low Energy Electron Microscope Investigations of Pb Film Growth on Cu Surfaces, G.L. Kellogg, R. Plass, Sandia National Laboratories INVITED

To develop a more fundamental understanding of the microscopic processes that control the dynamics of liquid-metal wetting and spreading, we are using low energy electron microscopy (LEEM) to investigate the properties of Pb overlayers on Cu surfaces. The experiments probe a wide range of surface processes -- from the dynamic properties of submonolayer films to the growth, ripening and melting of three-dimensional islands. Measurements of changes in morphology during surface alloying and dealloying provide new insights into the nature of submonolayer Pb structures on Cu(100). By combining different imaging modes of the LEEM, we have discovered an interesting correlation between the shape of threedimensional Pb islands and the domain structure of the Pb/Cu(100) overlayer upon which they grow. Direct observations of Ostwald ripening combined with modeling studies indicate that mass transfer between three-dimensional islands is inhibited at domain boundaries of the submonolayer structure. The implication of these and other results as they relate to liquid-metal flow processes will be discussed. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. DOE under Contract DE-AC04-94AL85000.

#### 3:40pm SS3-MoA6 Comparison of Behavior of Wetting-related Adsorption Transitions in the Ga-Pb, Ga-Tl, Ga-Pb-Tl Systems, *H. Shim, P. Wynblatt,* Carnegie Mellon University; *D. Chatain,* CRMC2-CNRS, France

In this presentation, we summarize investigations of prewetting behavior in three Ga-rich liquid alloy systems, Ga-Pb, Ga-Tl and Ga-Pb-Tl. The adsorption of Pb and/or Tl at the surfaces of these alloys was determined by Auger electron spectroscopy, as a function of temperature and composition. Most of the surface composition measurements reported were performed below the freezing points of the alloys (~300 K) where the alloys exist in a supercooled liquid state. However, measurements cannot be conducted below about 240 K, where the alloys undergo nonequilibrium freezing (presumably by homogeneous nucleation). Extrapolation to lower temperatures of the results obtained in the metastable liquid state (between 300 and 240 K) indicates the existence of possible prewetting critical points at about 240 K for Ga-Pb alloys, and at about 150 K for Ga-Tl alloys. The motivation for studying Ga-Pb-Tl ternary alloys was that small additions of TI might raise the prewetting critical point of Ga-Pb to temperatures above 240 K, and lead to more definitive observations of prewetting behavior. However, although ternary TI additions do lead to increased Pb adsorption, as expected, the temperature of a possible prewetting critical point is lowered even further to about 215 К.

#### 4:00pm SS3-MoA7 Shape Relaxation of Crystals via Layer-by-Layer Pealing Observed in Real Time, K. Thürmer, J.E. Reutt-Robey, E.D. Williams, University of Maryland

How does a small faceted crystal adjust its shape to a changing temperature and is it possible to reach its equilibrium shape? A positive answer to the latter question would allow an elegant experimental determination of absolute values of surface and step free energies.@footnote 1@ Small defect-free crystals near equilibrium experience an energy barrier for both growth and removal of atomic layers on a facet. Under growth conditions the 2D nucleation barrier gives rise to shape oscillations.@footnote 2@ Recently Mullins et al.@footnote 3@ concluded that for crystals larger than a few nm the magnitude of this barrier prevents surface free energy driven reshaping. We studied  $\mu m$  sized Lead crystals with an variable temperature STM under UHV-conditions. By tracking several crystals during a temperature increase from 110°C up to 205°C we confirmed Mullins suggestion that these crystallites are immobilized in their initial shapes. To investigate how a crystal establishes its shape we guenched the sample to temperatures between 65 and 110°C. STM observations of the (111) top facet starting shortly after the quench reveal a scenario of facet growth, where all layers smaller than a critical size peal off one-by-one. Uwaha@footnote 4@ treated the kinetics of such a collapse of step loops applying a constant critical size. Our experiments indicate a modification of the critical radius by a slow redistribution of atoms over the curved region of the crystal. @FootnoteText@ Work supported by NSF-MRSEC @footnote 1@ H.P. Bonzel et al, to be published @footnote 2@ J. Tersoff et al, Phys Rev. Lett. 70, 1143 (1993) @footnote 3@ W.W. Mullins et al, J. Am. Ceram. Soc., 83, 214 (2000) @footnote 4@ M. Uwaha, J. Phys. Soc. Jap., 57, 1681 (1988).

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4:20pm SS3-MoA8 LEEM Study of Mass Transport on Si(111), H. Hibino, C.-W. Hu, Arizona State University; T. Ogino, NTT Basic Research Laboratories, Japan; I.S.T. Tsong, Arizona State University

How does the surface morphology change during annealing, growth, and/or sublimation? In order to ask the question, we need understanding of the process of the mass transport. In this paper, we investigate two aspects of mass transport on Si(111) using LEEM. One aspect is the decay of 2-dimensional islands or holes near the phase transition between 1x1 and 7x7. The evolution of the island or hole provides the information about the rate-limiting process. The radii of the islands and holes show power-law dependences on time. The measured exponents are close to 1/3 rather than 1/2. This means that the decay is governed by the diffusion of atoms on the terraces rather than the attachment and detachment of atoms at the steps. We also measure the decay rate as a function of the temperature, and clarify that the decay rate changes steeply at the phase transition between 1x1 and 7x7. The decay rate is faster on 1x1 than on 7x7. The other aspect is the shape changes of the islands and holes during the 1x1-to-7x7 phase transition. The atom density in 1x1 is higher than that in 7x7. This difference in the atom density causes the steps to advance during the 1x1-to-7x7 phase transition. Comparing the changes of the islands and holes, the island tends to capture more atoms than the hole. More atoms are incorporated into the step from the lower terrace than the upper terrace. The 7x7 reconstruction nucleates at the upper step edges. Therefore, this result as well as the faster decay rates of islands and holes on 1x1 than on 7x7 suggest that the mass transport is faster on 1x1 than on 7x7.

# 4:40pm SS3-MoA9 First-Principles Study of Vacancy Ionization Effects on Surface Diffusion, H.Y.H. Chan, E.G. Seebauer, University of Illinois, Urbana-Champaign

While the effects of charged point defects on diffusion in bulk semiconductors have been studied extensively for many years, such phenomena have received almost no attention in connection with diffusion on surfaces. Recent studies in our laboratory using second harmonic microscopy (SHM) on Si have strongly suggested that charged vacancies can significantly affect observed activation energies and prefactors in a manner analogous to that observed for bulk diffusion. Furthermore, these studies have revealed significant non-thermal effects of photon illumination that also appear to be mediated by charged vacancies. Unfortunately, a more quantitative and complete description of these various phenomena requires a knowledge of the energy levels of the various surface vacancy charge states. Until now these energy levels have remained unknown on Si. We report herein the results of densityfunctional-theory based quantum calculations that fill this gap. Totalenergy calculations using a plane-wave/pseudopotential approach within the local-density approximation were used to determine the charge-state dependent formation energies of vacancies as a function of Fermi level. The computed electronic structure, lattice reconstruction, and their effects on surface diffusion are discussed.

## 5:00pm **SS3-MoA10 Surface Supercooling and Stability of Si(111)-"1x1" High Temperature Phase**, *C.-W. Hu*, Arizona State University; *H. Hibino, T. Ogino*, NTT Basic Research Laboratories, Japan; *I.S.T. Tsong*, Arizona State University

Si(111) high temperature phase transition is one of the most studied surface processes. It is well known that high temperature "1x1" phase converts into the most stable (7x7) surface reconstruction at about 830°C by the first order phase transition. However, the high temperature "1x1" phase can be locked down to 10~20°C below the phase transition temperature. This supercooling behavior is in situ observed by low energy electron microscopy within  $\mu$ m-sized two-dimensional depressions on Si(111) surface. The phenomenon can be readily explained as the lack of the nucleus of (7x7) reconstruction in depressions because the step edges of upper terrace take the roles of nucleation centers for stable (7x7) reconstruction. The supercooling temperatures are observed strongly depending on the sizes of depressions and the cooling rates of Si substrate. A normal depression with (7x7) reconstruction on it is formed by fast cooling through phase transition temperature. In this way, the filling-up rates can be measured respectively for supercooling depressions and normal depressions. The preliminary experimental results exhibit the downward movement of Si adatoms from (7x7) upper terrace and the stepedge attachment within depressions are responsible for the stability of Si(111)-"1x1" supercooling phase.

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