Surface Science
Room 200 - Session SS1-WeM

Growth and Alloying of Surfaces

Moderator: K.F. McCarty, Sandia National Laboratories

8:20am **SS1-WeM1 Surface Alloy Compositions with Temporal and Spatial Resolution**, *J.B. Hannon,* IBM Research Division; ***J. Sun,*** University of New Hampshire; *G.L. Kellogg,* Sandia National Laboratories; *K. Pohl,* University of New Hampshire

Controlling the composition of thin-film alloys is critical in a wide range of technologies. However, measuring alloy compositions at surfaces is difficult. Quantitative information on surface alloy compositions can be obtained from analysis of low-energy electron diffraction intensity versus energy spectra (LEED-IV). However, so far the structure and composition had to be assumed as spatially uniform. In this presentation we will describe low-electron energy microscopy (LEEM) studies on the formation of the well-known CuPd surface alloy phase grown on Cu(001). We will show how the presence of steps in the growth process makes the alloy layer inherently inhomogeneous. These variations in the CuPd alloy composition introduce strong measurable changes in the electron reflectivity in the regions around steps. By analyzing spatially resolved IV curves taken every 10 nm along a scan line normal to a step, we have determined the local surface alloy composition in the first 3 layers by using the average t-matrix approximation on a c(2x2) grid. In the process we are simultaneously optimizing both structural and non-structural parameters, while special emphasis is given to characterize the individual error bars of the method. We have investigated the composition on the terrace, far from steps, and the step-induced inhomogeneous structure caused by the step-flow growth. Depositing Pd at 500 K will cause an exponential increase of the Pd concentration with time and the formation of a c(2x2) Pd checkerboard structure in the 2nd Cu layer up to a 50% Pd concentration; far from the steps where the alloy is spatially uniform. However, during growth the steps flow over the 2nd layer Pd alloy, bury it and convert it to a 3rd layer alloy. This 3rd layer Pd is immobile and its concentration increases exponentially toward the step edge along the upper terrace, in agreement with the step-flow-growth model.

8:40am **SS1-WeM2 Formation and Vibrational Entropy-Driven Disordering of Mo(100) and W(100) Surface Alloys**, *K.L. Man, Y.J. Feng, C.T. Chan,* Hong Kong University of Science and Technology; ***M.S. Altman,*** Hong Kong University of Science and Technology, Hong Kong

Atoms that are deposited on a surface of a dissimilar material may either remain on the surface or they may become incorporated in a surface or bulk alloy. Although the T = 0 energetic differences between alloy and overlayer structures can now be understood from first principles in many systems, entropy differences should also be revealed in the formation and stability of alloy versus overlayer structures. However, the entropic contribution to the system free energy is much less well understood than the energetic. The formation and stability of Cu, Ag and Au-induced c(2x2) alloys at the Mo(100) and W(100) surfaces have been investigated with low energy electron microscopy and diffraction. The dependence of the c(2x2) diffraction intensity upon metal deposition flux reveals that alloy formation is governed by atomistic processes that are analogous to those that dictate overlayer island nucleation. A second-order order-disorder transition is also observed that converts the surface from ordered alloy to disordered overlayer structure. Combined with knowledge of energetics obtained from first principles calculations, a comparison of disordering temperatures for alloys of the different metal species and substrates provides information on the vibrational entropic contribution to the system free energy. Effective Debye temperatures for metal adatoms are determined that are substantially lower than bulk values, but exhibit the expected mass dependence. Knowledge of the vibrational properties of metal adatoms should also be relevant to other common surface phenomena such as diffusion and desorption.

9:00am **SS1-WeM3 Bulk/Surface Mass Exchange and the Special Role of Bulk Dislocations in the Growth of NiAl Alloy**, ***J.P. Pierce***, *K.F. McCarty, N.C. Bartelt,* Sandia National Laboratories

When aluminum atoms are deposited on the surface of an Al-depleted NiAl crystal at high temperatures (> 900 K), new layers of NiAl alloy grow on the surface. We directly observe the appearance of new alloy by watching atomic steps advance across the surface using low-energy electron microscopy (LEEM). This behavior means that while Al atoms are delivered to the surface by our evaporator, Ni atoms are supplied to the surface by the bulk of the crystal. The competition in the arrival rates of these species determines how the surface evolves. At low temperatures (< 750 K), Ni atoms are unable to diffuse to the surface fast enough to accommodate the incoming Al atoms, so the Al atoms form a film on top of the alloy. At intermediate temperatures (750 to 900 K), we find that dislocations play a special role in transporting mass between the surface and the bulk. Al deposition causes the composition (i.e., the relative concentration of Al and Ni) at the surface to reach a critical level at which the points where bulk dislocations terminate on the (110) surface begin to move linearly. The dislocations provide a channel for mass exchange between the surface and the bulk; as the dislocations move, new crystal is left in their wake. As predicted by the one-dimensional diffusion equation, we find that the duration of Al exposure required bring the surface to the critical composition for dislocation motion grows as the inverse square of the Al flux. This confirms that the behavior on the surface is indeed limited by the diffusion of atoms through the bulk. We use our observations to identify the point defects that allow the Ni and Al atoms to diffuse and use the one-dimensional diffusion model to determine how the depth profile of the relative concentration of Ni and Al atoms evolves with time as the crystal tries to equilibrate. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

9:20am **SS1-WeM4 Real-Time Microscopy of Phase Transitions on Pb/Ge(111)**, ***S. Chiang***, *Y. Sato,* University of California, Davis

Using low energy electron microscopy (LEEM), we have elucidated the phase diagram for the growth of Pb on Ge(111). The Pb layer can form two stable @sr@3x@sr@)R30° phases on the surface, less dense @alpha@ and denser @beta@ phases. As Pb is deposited on Ge, the Pb atoms substitute into the top layer, causing released Ge atoms to form into c(2x8) adatom islands, with the size and density of these Ge islands controllable by the substrate temperature. With 11.6 eV electrons at 300C, we see the growth of the white (1x1) phase with respect to the darker @alpha@ phase in a coexistence region. During the reversible @beta@ to (1x1) phase transition, we discovered a novel phase separation mechanism. Above the 1.33ML @beta@ saturation coverage, a sharp first order phase transition is observed near 295C. For Pb coverage just <1.33ML, the @beta@ to (1x1) phase transition is no longer sharp, with the @beta@ and (1x1) phases coexisting and the transformation occurring from 232C to 181C. Reducing coverage by ~0.01ML causes a dramatic change. When the transition starts, small domains of the new phase appear and disappear, due to fluctuations between the two phases. As the initial domains stabilize in the new phase, additional domains appear and fluctuate until the whole surface is completely transformed. By using statistical mechanics analysis,@footnote 1@ we attribute the fluctuating domains to thermal fluctuations of the density of Pb atoms within a domain. By comparing LEEM images of the @beta@ and (1x1) phases during the phase transition between [@alpha@+(1x1)] and (@alpha@+@beta@), the Pb coverage of the (1x1) phase at the eutectic point was determined to be ~1.29 ML. @FootnoteText@ @footnote 1@ N. Bartelt, Sandia National Laboratories, Livermore, CA.

9:40am **SS1-WeM5 Self-Organized Growth and Magnetism of Nanostructures at Surfaces**, ***H. Brune***, École Polytechnique Fédérale de Lausanne - EPFL, Switzerland **INVITED**

We will discuss the state-of-the-art of self-organized atomic beam growth at single crystal surfaces enabling one to create well ordered superlattices of metal islands with sizes going all the way down to the single atom limit. We will focus on mutual interactions between adsorbed atoms mediated by Friedel oscillations in the 2D electron gas of a surface state, and on static templates with a periodic modulation of the binding energy for the adsorbed species. The templates to be discussed are strain relief patterns in thin films of metals, semiconductors, oxides, and nitrides. We then show model systems suited to explore the ultimate density limit of magnetic information storage. These are Co islands self-assembled on Au(788). The temperature dependence of the zero-field susceptibility @chi@ shows that the homogeneity in the anisotropy K and in the moment M would permit sin-gle particle bits, and that mutual interactions between the monodomain particles are absent up to densities of at least 26 Tera particles/in@super 2@. We further show results on the anisotropy of bimetallic islands as a function of their composition.

10:20am **SS1-WeM7 Steering Induced Nanopatterning: Super Poisson Growth at Grazing Incidence**, ***H. Wormeester***, *F.L.W. Rabbering, B. Poelsema,* University of Twente, The Netherlands

Analysis of high-resolution LEED data of 40 ML Cu on Cu(001) deposited at various polar angles led to the conclusion that attractive forces between the surface and the incoming particles have a dramatic steering effect on the trajectory of the particle. Incoming particles are attracted towards protruding structures leading to increased roughness and the formation of 1D nanopatterns at grazing incidence deposition. Already in the submonolayer coverage range consequences of the steering effect is observed for grazing incidence deposition. The steering induced heterogeneous distribution of the incoming flux has been modeled by a combination of long range Van der Waals forces and EAM calculations. The resulting trajectories have been combined with kMC simulations taking into account a large variety of intra and inter layer diffusion processes. The simulations are in good accordance with diffraction measurements up to 40 ML at both normal and grazing incidence. The evolution of the 1D nanopattern at glancing incidence deposition in terms of the distance between the ripples, the anisotropy and the roughness has been studied. The roughness evolves from a layer-by-layer fashion in the initial phase towards a strongly roughened interface above 10 ML. At 30 ML the roughness turns out to be even larger than for a Possion distribution, i.e. super Poisson growth is observed. The steering effect thus implies the necessity of a very different view for understanding the morphology development in growth at oblique incidence.

10:40am **SS1-WeM8 Ostwald Ripening of Manganese Silicide Islands on Si(001)**, ***M.R. Krause***, *A. Stollenwerk, J. Reed, V.P. LaBella,* University at Albany SUNY

Theoretical considerations suggest that epitaxial MnSi thin films should order ferromagnetically on Si(001)@footnote 1@ and it has been demonstrated that Si can be made ferromagnetic well above room temperature by Mn ion implantation.@footnote 2@ These recent discoveries indicate that the Mn-Si system may have potential to be utilized as a spin injector in future spintronics devices. Therefore the deposition of Mn onto Si(001) in the submonolayer regime has been studied with scanning tunneling microscopy (STM) to gain insight into the bonding and energetics of Mn with Si. The as deposited Mn films at room temperature are unstructured. Upon annealing to 300-500°C no smooth films but clusters of Mn or Mn@sub x@Si@sub y@ form while between the clusters the Si(001)-(2x1) reconstruction becomes visible. With increasing annealing time the density of clusters per surface area decreases while the average size of the remaining clusters increases. The time dependence of the coarsening shows the typical characteristics of Ostwald Ripening (OR). The cluster density and average cluster size will be presented as a function of annealing time for different initial Mn coverages. The results will be discussed within the framework of the OR theory. @FootnoteText@ @footnote 1@H. Wu, et al. Phys. Rev. Lett. 92 237202 (2004). @footnote 2@M. Bolduc et al. Phys. Rev. B 71 033302 (2005).

11:00am **SS1-WeM9 Self-assembly of Aperiodic Nanostructures using Quasicrystal Surfaces as Templates**, ***R. McGrath***, The University of Liverpool, UK **INVITED**

Quasicrystals are metallic alloys which posess long-range order but not periodicity; hence they may display structural symmetries not observed in periodic materials. The surfaces of these materials offer opportunities for the fabrication of nanostructures and thin films which themselves have unusual symmetries and structures. In turn, measurements of such nanostructured systems may offer insights into the larger question of the relationship between physical properties and aperiodicity. Several such systems, ranging from individual atoms to nanoclusters to thin films, have been fabricated and are under investigation in our laboratory. The growth of Si on quasicrystal surfaces is one recent example. On the AlPdMn quasicrystal, at submonolayer coverages, individual Si atoms occupy a unique adsorption site; thus the Si atoms can be considered to be arranged in a two-dimensional quasiperiodic array. On decagonal AlNiCo, the Si atoms form 5-fold nanoclusters, again indicative of a preferred adsorption site. Another spectacular example is that of an ultrathin film grown by the deposition of copper atoms on the five-fold surface of the icosahedral Al@sub 70@Pd@sub 21@Mn@sub 9@ quasicrystal.@footnote 1@ STM images show that the in-plane structure comprises rows having separations of S=4.5Â±0.2 Ã. and L=7.3Â±0.3 Ã., whose ratio is the golden mean @tau@=1.618... within experimental error. The sequences of such row separations form segments of terms of the Fibonacci sequence, indicative of the formation of a pseudomorphic Cu film. Finally, we have recently demonstrated that pseudomorphic films can also be grown using magnetic elements such as Co, Fe and Ni. Atoms in a quasiperiodic pattern are predicted to form new types of frustrated structures; such films therefore offer the possibility of observing these novel magnetic effects. @FootnoteText@@footnote 1@J. Ledieu, J.T. Hoeft, D.E. Reid, J.A. Smerdon, R.D. Diehl, T.A. Lograsso, A.R. Ross and R. McGrath, Phys. Rev. Lett. 92 (2004) 135507.

11:40am **SS1-WeM11 Coexistence of Periodic and Quasiperiodic Order in a Two-Fold Al-Ni-Co Decagonal Quasicrystal Surface**, *J.Y. Park, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory; *R.A. Ribeiro, P.C. Canfield, C.J. Jenks,* ***P.A. Thiel***, Iowa State University

The atomic structure of the two-fold surface of a decagonal Al-Ni-Co quasicrystal has been investigated using scanning tunneling microscopy (STM). In the bulk the decagonal quasicrystal is composed of quasiperiodic planes that are periodically arranged. Atomically resolved scanning tunneling microscopy images of the 2-fold (10000) plane reveal the presence of atomic rows along the 10-fold direction with an internal periodicity of 0.4 nm. The spacing between the parallel rows is aperiodic, with distances following a Fibonacci sequence and exhibiting inflation symmetry. The bias polarity dependence of the STM images reveals three electronically-different types of atomic rows. A bulk model for Al-Ni-Co shows excellent agreement with these STM observations, and indicates that Al sites have a higher tunneling probability than transition meta sites. These data are compared with previous results for both the 10-fold and 2-fold surfaces.

Author Index

Bold page numbers indicate presenter