Surface Science
Room: C-110 - Session SS2-WeA

Structure and Chemistry at Metal Surfaces
Moderator: B.J. Hinch, Rutgers University

2:00pm **SS2-WeA1 Real Time Monitoring of the Structure and Morphology of Growing Nanoparticles by Grazing Incidence Small and Wide Angle X-ray Scattering, in situ, in UHV**, ***G. Renaud***, CEA-Grenoble, France **INVITED**

Islands of nanometer size grown on substrates display a set of fascinating properties, which are of interest for both basic and applied research. They include model catalysts made of supported metallic particles whose reactivity and selectivity can be adapted to given needs, single-domain magnetic particles which show original spin-dependent transport properties and coherently strained semiconductor aggregates, the so-called "quantum dots", which exhibit remarkable opto-electronic properties. A strong promise of novel device applications merges up provided that nanoparticles could be purposely tailored to specific uses. The properties of these particles depend to a great extent on their internal atomic structure, their strain, their shape, size, size distribution and ordering, which in turn rely on the growth mechanisms. In this context, a challenging issue is to control the growth of large collections of particles by monitoring the relevant parameters in situ and in real time. A unique technique to probe collections of very small objects is Grazing Incidence Small Angle X-ray Scattering (GISAXS). However, to date, due to technical limitations, GISAXS has never been used during growth. In this report, we demonstrate this possibility using two prototypical cases. The first is the growth of metals (Ag, Pd, Pt) on MgO(001) at different temperatures, which are models of Volmer-Weber 3D growth of metal on oxide surfaces, and is thoroughly studied to investigate the elementary processes of heterogeneous catalysis. The second is the growth of cobalt on the herringbone reconstructed Au(111) surface, which is a model of self-organized cluster growth. We show that a complete description of the islands can be obtained by supplementing GISAXS measurements by grazing incidence wide angle x-ray scattering measurements performed in situ during growth, at the same time.

2:40pm **SS2-WeA3 Structural Analysis of Quasicrystalline Al-Pd-Mn using Angle-Resolved Low Energy Ion Scattering**, ***C.J. Jenks***, *P.A. Thiel, A.R. Ross, T.A. Lograsso,* Iowa State University, Ames Laboratory, *J.A. Whaley, B. Bastasz,* Sandia National Laboratories

We have used angle-resolved low-energy ion scattering to examine the clean surface structure and composition under ultra-high vacuum conditions of a single grain of icosahedral $Al_{71}Pd_{20}Mn_9$ oriented with a five-fold axis perpendicular to the surface. Our results are consistent with the surface maintaining five-fold symmetry after sputtering followed by annealing at 800 K. We find that the topmost surface layer is > 85 atomic % aluminum. A predominant neighbor atom distance of 7.6 Â± 0.5 Å and a nearest neighbor distance of 3.0 Â± 0.1 Å is calculated from our results. Our results are consistent with previous low energy electron diffraction intensity versus voltage (LEED-IV) calculations, recently published scanning tunneling microscopy results and a bulk model of Al-Pd-Mn quasicrystals.

3:00pm **SS2-WeA4 Structural Studies of Ti/Pt(111) Surfaces**, ***S. Hsieh***, *T. Matsumoto, J. Kim, B.E. Koel*, University of Southern California

Alloys of platinum and a second metal component are of increasing interest for a number of applications. Structural studies have been carried out for bimetallic surfaces with Pt alloyed with many transition metals and main group metals. In this work, we have used He^+-ion scattering (He^+-ISS), X-ray photoelectron spectroscopy (XPS), and low energy diffraction (LEED) to determine the structure of ordered Ti/Pt(111) surface alloys formed by depositing ultrathin Ti films on Pt(111) and annealing to different temperatures up to 1100 K. The Ti film coverage was determined by He^+-ISS. No LEED pattern was observed at room temperature immediately after Ti deposition. At 800 K, Ti started to alloy with Pt and formed a (6x √43) structure in LEED that grew sharper as the temperature was increased to 1000 K. A weak (2 x 2) pattern was observed for Ti coverages larger than 1 monolayer, but this structure was less stable and disappeared at high temperature leaving only the (6x √43) pattern. XPS showed that the Ti core level spectra shifted by 2.0 eV upon alloying compared to that from a thick Ti film. Observation and further characterization of the new Ti/Pt(111)-(6x √43) surface structure should aid in understanding and tailoring chemical properties of practical catalysts.

3:20pm **SS2-WeA5 Thermal Stability of Thin Ti Films on Al Single Crystal Surfaces**[1], ***C.V. Ramana***, *R.J. Smith,* Montana State University, *B.S. Choi*, Jeonju University, Korea, *B.S. Park, A. Saleh*, Charles Evans & Associates, *D. Jeon*, Myongji University, Korea

Chemical roughness and alloy formation at metallic interfaces can significantly degrade the performance of multilayer thin film magnetic device structures. We have investigated the use of metal interlayers, one or two atoms thick, to stabilize the interface for ordered growth of metal films with minimal intermixing. Specifically, thin Ti interlayers have been used to stabilize the Fe-Al(100) interface, a system characterized by considerable interdiffusion at room temperature. The benefits of the interlayer concept are strongly coupled to the stability of the interlayer at elevated temperatures. In this investigation we have characterized the structure of thin Ti layers on Al single crystal surfaces as a function of temperature using Rutherford backscattering and channeling (RBS/c) and low-energy ion scattering (LEIS). The Ti layers are shown to be stable up to temperatures of about 400Â° C, at which point diffusion of Ti into the Al lattice occurs. LEIS measurements, combined with RBS show clearly that the Ti atoms move into the surface at these temperatures. Channeling measurements show that the Ti atoms sit on Al lattice sites as a substitutional impurity. The stability of the Ti film appears to increase with the packing density of the Al surface, being slightly more stable for the close-packed Al(111) surface, and diffusing into the more open Al(110) surface at a lower temperature.

[1] Work supported by NSF Grant DMR-0077534.

3:40pm **SS2-WeA6 Nucleation and Growth of Ag Films on a Quasicrystalline AlPdMn Surface**, *V. Fournée, T. Cai, A.R. Ross, T.A. Lograsso, J.W. Evans,* ***P.A. Thiel***, Iowa State University

Nucleation and growth of thin films of Ag on the 5-fold surface of an Al72Pd19.5Mn8.5 icosahedral quasicrystal is studied with STM. For low coverages, flux-independent island nucleation is observed, likely involving adatom capture at "traps". With increasing coverage, islands start growing vertically, but then spread, and ultimately form hexagonal nanocrystals. These have fcc symmetry and pyramid-like multilayer stacking along the <111> direction. The constituent hexagonal islands have five different orientations, rotated by 2p/5, thus remembering the symmetry of the substrate. These results are discussed in the context of strategies most likely to yield pseudomorphic growth.

4:00pm **SS2-WeA7 Helium Atom Scattering Studies of Si-Cu (001) and Sn-Cu (001) Surface Alloys**, ***L.V. Goncharova***, *D.V. Potapenko, B.J. Hinch*, Rutgers University, *X. Zhang, D.R. Strongin,* Temple University, *L. Wood*, Dow Corning Corporation

Copper acts catalytically in the commercial "Direct Synthesis" of dimethyldichlorosilane; the later being a key component in the manufacturing of silicone materials. While Cu-Si systems have been studied intensively, the roles of other components, such as Sn, Zn and Al, which act as promoters in the "Direct Synthesis", are not well understood. We report on the growth and dynamics of silicon and thin tin films on Cu (001), as studied with high-resolution helium atom scattering (HAS), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). We have shown that the incommensurate "5x3" structure is formed when silicon is deposited on Cu (001) via saturation exposure to silane at 420K.[1] With Sn deposition temperatures above 200K a series of ordered reconstructions are observed on Cu (001) in the submonolayer regime.[2] Coadsorption of tin and silicon on Cu (001) is of a key importance as it enables a new low temperature desorption mechanism of methylsilanes. The relationships between structures in coadsorbed tin and silicon on the Cu (001) surface, and yields of different methylsilane products will be presented.

[1] A.P.Graham, B.J. Hinch, G.P.Kochanski, E.M. McCash, and W. Allison, Phys.Rev.B 50 (1994) 15304.

[2] E.McLoughlin, A.A. Cafolla, E. AlShamaileh, C.J. Barnes, Surf.Sci. 482-485 (2001) 1431.

4:20pm **SS2-WeA8 Growth and O_2 Reactivity of the Cu/Si(5 5 12) System**, *P.H. Woodworth, J.C. Moore,* ***A.A. Baski***, Virginia Commonwealth University

Our group has extensively studied the growth behavior of Group IB metals such as Ag and Au on the row-like template provided by the clean Si(5 5 12) surface.[1] Here, this work is extended to the remaining IB metal of Cu. Our scanning tunneling microscopy studies show that Cu forms two distinct phases on Si(5 5 12): a lower temperature phase (< 600 °C) where Cu decorates the underlying (5 5 12) surface, and a higher temperature phase (> 600 °C) where it induces faceting to the nearby (113) plane. Similar to the Ag and Au systems, the lower temperature phase results in the formation of

Cu "nanowires" with a spacing equal to the 5.4 nm periodicity of the (5 5 12) surface. When the annealing temperature is increased, however, the (5 5 12) orientation is no longer stable to (113) faceting. At lower Cu coverages (< 0.5 ML), (113) planes appear to coexist with (5 5 12), but at higher coverages (> 0.5 ML) these planes form sawtooths with opposing (111) faces. The occurrence of (113) planes has also been seen for the higher temperature growth of Au on Si(5 5 12), indicating the inherent stability of this plane. We have also studied the O_2 reactivity of the Cu-induced (113)/(111) sawtooths at exposures of 50 to 200 Langmuirs and temperatures of 600 to 800 °C. As expected, an amorphous oxide appears to grow on the surface at lower temperatures (<650 °C), and etching occurs at higher temperatures (>650 °C). For the case of etching, the sawtooths are gradually removed to produce trapezoidal (113)/(111) islands. The density of these islands decreases with increasing temperature, providing a possible route for the controlled fabrication of such nanostructures on the surface.[1] A.A. Baski, K.M. Saoud, K.M. Jones, Appl. Surf. Sci. 182, 216 (2001).

4:40pm **SS2-WeA9 NIXSW Analysis of the Disorder Transition of Chlorine on Cu(111)**, ***A.G. Shard***, University of Sheffield, UK, *C. Ton-That,* University of Cambridge, UK, *P.A. Campbell*, University of Dundee, UK

Chlorine adsorbs on Cu(111) primarily in threefold hollow sites, with a slight preference for the 'fcc' site (above a third layer copper atom) as opposed to the 'hcp' site. We have monitored the relative population of the two sites at a variety of coverages and temperatures using Normal Incidence X-ray Standing Waves (NIXSW). Disordered surfaces at low coverages or high temperatures have approximately equal populations of the two hollow sites, providing a measure of confirmation for the small energy difference recently calculated between them.[1] Adsorption of chlorine to a Cu(111) crystal at 180K results in an ordered root 3 surface, with equal populations of 'fcc' and 'hcp' sites, implying the prolonged existence of metastable 'hcp' domains at this temperature. The room temperature root 3 structure has a large 'fcc' population, which decreases close to the disorder transition at 350K. These data are discussed and compared with Monte Carlo simulations.

[1] K. Doll and N. M. Harrison, Chem. Phys. Lett., 317, 282 (2000).

5:00pm **SS2-WeA10 Vibrations of Water Adsorbed on Ru(0001)[1]**, ***P.J. Feibelman***, Sandia National Laboratories

To see whether vibration spectroscopy confirms or contradicts the idea that the wetting layer of D_2O/Ru(0001) is half-dissociated,[2] vibration spectra have been computed from first principles for comparison to experiment. The calculations show that dissociation of the non-hydrogen-bonding O-D bonds of a heavy-water bilayer eliminates the highest-energy O-D stretch feature, and replaces it with a lower frequency mode. This behavior agrees with recent Sum Frequency Generation observations,[3] lending credence to the argument that a half dissociated D_2O layer is needed both to explain why water wets Ru(0001) at all, and to account for the inference drawn from Low Energy Electron Diffraction data, that the O atoms of $\sqrt{3}x\sqrt{3}$-D_2O/Ru(0001) are nearly coplanar. Beyond helping to clarify the nature of the wetting layer, the computed vibration spectra also permit an estimate of its zero-point energy relative to that of competing adsorption structures. Zero-point energy is found to favor half-dissociated adlayers because, of every four oxygen-hydrogen bonds in an intact-water-molecule structure, one is replaced by a softer metal-hydrogen bond in a half-dissociated arrangement. For $\sqrt{3}x\sqrt{3}$-D_2O/Ru(0001), this zero-point stabilization amounts to about 30 meV per D_2O. In the case of H_2O adsorption, it would be ~50 meV/ad-molecule.

[1] Work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. DOE.

[2] P. J. Feibelman, Science 295, 99(2002).

[3] D. N. Denzler, unpublished.

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