

Surface Science

Room: 208 - Session SS+NC-MoM

Catalysis and Alloy Formation

Moderator: G.B. Fisher, Delphi Research Laboratories

8:20am **SS+NC-MoM1 Surface Structural Investigation of Ultra-Thin Films of Pd Deposited on Au(111)**, *P.A.P. Nascente*, Federal University of Sao Carlos, Brazil, *A. Pancotti, M.F. Carazzolle, A. de Siervo*, State University of Campinas, Brazil, *D.A. Tallarico*, Federal University of Sao Carlos, Brazil, *R. Landers, G.G. Kleiman*, State University of Campinas, Brazil

Bimetallic surfaces have attracted considerable interest due to their catalytic, electronic, electrochemical, and magnetic properties. The deposition of an ultra-thin metal film on a single crystal metal substrate can produce a bimetallic surface. The interfacial interactions between the two metals can lead to preferential surface orientation, surface relaxation, surface reconstruction, order/disordered effects, and surface alloying. In this work, ultra-thin films (1 and 3 monolayers) of Pd were deposited on the Au(111) surface and then characterized by X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and X-ray photoelectron diffraction (XPD). We have considered three models: Pd overlayers on the Au(111) substrate, Pd islands covering the Au(111) surface, and a random AuPd_{1-x} alloy. The reliability of the theoretical simulations as compared to the experimental XPD data was measured through the R-factor analysis. The comparison between experimental and theoretical XPD results indicated that, for the 1 ML film annealed at 450 C, Pd diffused into the Au bulk, causing alloy formation, and for the thicker film, the Pd islands were, at most, 3 ML thick.

8:40am **SS+NC-MoM2 Epitaxial Growth Ag Films on Al Surfaces: Strain Relief Mechanisms**, *R.J. Smith, N.R. Shivaparan, M.A. Teter, W. Priyantha, M. Kopczyk, M. Lerch, C. Pint*, Montana State University, *G. Bozzolo*, Ohio Aerospace Institute

We report the results of a characterization of 0-6 nm thick Ag films, deposited onto Al(001) and Al(110) surfaces at room temperature, using high energy ion backscattering and channeling, x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and BFS model calculations. For the Al(001) surface, measurements of the backscattered ion yields from Al and Ag atoms show that the Ag atoms occupy fcc lattice sites and shadow Al substrate atoms. However, the ion scattering yields and photopeak intensities do not follow layer-by-layer model growth curves. Together with the evolution of the Ag 3d core level binding energies and the valence band shape as a function of Ag coverage, these results support a model of Ag-Al interface alloy formation as a mechanism for strain relief in this system with ~1% lattice mismatch. For the Al(110) surface the observations are closer to those expected for layer-by-layer growth, but still show evidence of some Al diffusion into the well-ordered Ag overlayer.

9:00am **SS+NC-MoM3 Growth of Ag Islands on a Twofold Surface of a Decagonal Al-Cu-Co Quasicrystal**, *B. Unal*, Ames Laboratory and Iowa State University, *T. Duguet*, Ecole des Mines, France, *D. Jing*, Ames Laboratory and Iowa State University, *C.J. Jenks*, Ames Laboratory, *P.C. Canfield*, Iowa State University, *V. Fournee*, Ecole des Mines, France, *P.A. Thiel*, Ames Laboratory and Iowa State University

Quasicrystals are well ordered, but not periodic solid materials which have peculiar surface properties such as low friction and high oxidation resistance. Using a variable temperature scanning tunneling microscope (VT-STM), for the first time, we have studied the (0001) clean twofold surface of a decagonal Al-Cu-Co quasicrystal. Our STM studies have showed that annealing at ca.1000K causes the formation of two different surface phases one of which has a periodic structure while the other is aperiodic. At room temperature, we have also investigated the growth of Ag on these two different surface domains. In the aperiodic one, Ag prefers to segregate into highly anisotropic islands whose longer edges are parallel to the periodic axis (i.e. the tenfold axis). As the total coverage increases, Ag islands grow vertically while preserving their highly anisotropic shape. In the other (periodic) domain, we observe smoother, more conventional growth. These two different growth behaviors strongly indicate that the aperiodic nature of the surface has a strong effect on the growth kinetics.

9:20am **SS+NC-MoM4 Collective Migration of Cu Nanostructures on Ag(111)**, *A.W. Signor, H.H. Wu, D.R. Trinkle, J.H. Weaver*, University of Illinois at Urbana-Champaign

Experimental studies of island migration, an important process in crystal growth and nanostructure synthesis, have largely been limited to homoepitaxial systems. In these systems, either diffusion or evaporation and condensation of adatoms at the island edge gives rise to a Brownian-like motion of the center of mass with size-independent barriers, and diffusivities that smoothly decrease with size according to an inverse power-law relationship. The present work with Cu-Ag(111), a lattice-mismatched system, provides compelling evidence for a strain-driven collective mechanism involving nucleation and glide of misfit dislocations. With this mechanism, the entire structure is moved by one Burger's vector as a dislocation nucleates and glides through the island and the shape is retained as the structure moves from one site to another. Quantitative analysis of island trajectories in scanning tunneling microscopy movies at multiple temperatures yields activation barriers ranging from 0.14-0.39 eV with prefactors ranging from 10^5 - 10^{18} s⁻¹ for islands containing 5-30 atoms. Significantly, the barriers are very sensitive to island size and shape, and hence island diffusivities do not scale with size in the ways predicted for traditional atomistic mechanisms, greatly affecting the overall coarsening kinetics. Temperature-accelerated dynamics simulations corroborate experimental findings, showing that collective motion of sub-units within the island, due to strain effects, result in misfit dislocation nucleation and glide, with barriers that are very sensitive to size and shape.

9:40am **SS+NC-MoM5 Step Structure and Motion on an icosahedral AlPdMn Quasicrystal**, *Y. Sato*, Lawrence Berkeley National Laboratory, *B. Unal*, Iowa State University, *K.F. McCarty, N.C. Bartelt*, Sandia National Laboratories, *A.K. Schmid, T. Duden*, Lawrence Berkeley National Laboratory, *K. Pussi*, Lappeenranta University of Technology, Finland, *T.A. Lograsso, C.J. Jenks*, Ames Laboratory, *P.A. Thiel*, Iowa State University

We have used LEEM and STM to characterize step structure and motion on a well-ordered, aperiodic icosahedral-AlPdMn quasicrystal surface. Real-time imaging capability of LEEM allows us to understand how the room temperature quasicrystal surface develops following high temperature annealing up to 910K. The way steps move on this surface at high temperature is remarkable. Two types of steps move with different velocities and cross each other. What is more, the two steps form a chicken wire-like hexagonal and rhombohedral mesh structure, as the steady-state surface morphology. From the STM step height measurement, the two steps are identified to be L and (L+M) steps, with different step heights. (L(6.8Å) and M(4.2Å) steps are two steps known to occur on this surface.¹) When the surface is cooled, extensive mass flow from the surface into the bulk has large consequences upon the step motion dynamics and resultant step structure at room temperature. M steps hidden in the step crossings of chicken wire step-networks open up and extend, as it allows a new surface layer to be exposed, and thereby forming the brick-like step structure observed at room temperature, composed of L, M, and (L+M) steps. An obvious question is how one might understand the presence of periodic step arrays at the surface of quasicrystalline samples. One would expect the stacking of the two step heights to follow the Fibonacci sequence of the bulk quasiperiodic order.¹ By permitting localized regions of the surface where the topmost plane trades position with the near-surface plane directly underneath, we propose a construction scheme that allows a step network consistent with experimental observations. Specific planar defects observed in icosahedral AlPdMn could enable such mechanism.² We discuss possible ways for this "carpet" of surface layers to be connected with the underlying bulk aperiodicity.

¹ T.M. Schaub, D.E. Beurgler, and H.-J. Guntherodt, 1994 Phys.Rev.Lett. 73, 1255.

² M. Feuerbacher, M. Heggen, and K. Urban, 2004 Mat.Sci.and Eng. A 375-377, 84.

10:20am **SS+NC-MoM7 Reactivity Trends in CO Oxidation from UHV to Elevated Pressures: Never Mind the Gap**, *D.W. Goodman*, Texas A&M University **INVITED**

CO oxidation on Ru, Pd, Rh, and Pt surfaces has been investigated between 10⁻⁸ - 10 Torr and for a variety of temperatures and O₂/CO ratios. Polarization modulation reflectance absorption infrared spectroscopy (PM-RAIRS) was used to identify the CO coverage as a function of the reaction rate for a variety of conditions up to 10 Torr. For reaction pressures less than 10⁻⁶ Torr, X-ray photoelectron spectroscopy (XPS) was used to measure the surface coverages of CO and O_{ads}. A clear continuum with respect to reaction rates, surface composition, and overall mechanism is apparent over the entire pressure range investigated, i.e. there is no evidence of a pressure gap.

11:00am **SS+NC-MoM9 Structural Evolution of Platinum Catalyst in Different Pressure of CO: A Study of High Pressure STM and High Pressure XPS**, *F. Tao, Z. Liu, C.Y. Chung, D. Butcher, Y.W. Zhang, M. Grass, M. Salmeron, G.A. Somorjai*, Lawrence Berkeley National Laboratory

Bridging pressure gap of catalytic model studies is one of the most challenging issues to be addressed for elucidating mechanism of heterogeneous catalysis. A new high pressure STM was homebuilt for this purpose. CO adsorption and oxidation on a stepped platinum single crystal was selected as a model to study in a wide range of CO pressure from 10⁻⁹ to 1000 Torr as the adsorption and surface structure of CO on noble metals under a realistic catalytic condition is an important topic for pollution control. STM study revealed a significant pressure dependence of surface structure of CO adsorption. The clean platinum single crystal surface prepared in UHV progressively reconstruct by adsorbing CO at step sites and breaking the step edge at low pressure. At high pressure the surface reconstructs into clusters with a size of 1-3 nm. The dramatic structural evolution from low pressure to high pressure is reversible. The reversibility is confirmed with a synchrotron-based high pressure XPS. A model rationalizing the pressure dependence of CO adsorption on this catalyst is suggested.

11:20am **SS+NC-MoM10 From Near-surface to Surface CuPt Alloy: Cu Surface Segregation Induced by CO Adsorption**, *K. Andersson, F. Calle, J. Rossmeis, I. Chorkendorff*, Technical University of Denmark

Bimetallic alloys offer a way of tuning electronic structure and hence also surface catalytic properties. For example, a CuPt near-surface alloy¹ has recently been suggested as a promising catalyst for the water-gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$. Crucial to the catalytic performance of such alloys is the surface composition and structure under reaction conditions. Examples of segregation of one component to form a surface oxide in oxidizing environments are many. However, largely unexplored are the effects of molecular adsorbates. Using a combination of XPS, in-situ and ex-situ IR, LEED, ISS and TPD, we have studied reversible surface changes induced by elevated CO pressures and sample temperatures for surfaces with varying Cu concentrations (up to 3 ML) in the near-surface region of Pt(111). We show that at sample temperatures high enough to overcome Cu diffusion barriers (~470 K),² a CO pressure of 2 mbar is sufficient to induce segregation of Cu to the topmost surface layer, switching a CuPt near-surface alloy to a novel well-ordered CuPt surface alloy with very different properties. The thermodynamic driving force behind the surface changes is rationalized on the basis of the much greater bondstrength of CO to Pt surface atoms in the presence of Cu atoms in the topmost surface layer. This is observed experimentally as large, well-defined and high temperature CO desorption peaks (up to 580 K). The so-called "d-band model"³ explains our findings.

¹ J. Knudsen et al., *J. Am. Chem. Soc.* 129 (2007) 6485.

² N. Schumacher et al., *Surf. Sci.* 602 (2008) 702.

³ J. Greeley, J.K. Norskov, M. Mavrikakis, *Annu. Rev. Phys. Chem.* 53 (2002) 319, and references therein.

11:40am **SS+NC-MoM11 CO Adsorption on Ru(0001) and PtRu/Ru(0001) Near Surface Alloys Using Ambient Pressure Photoemission Spectroscopy**, *D.E. Starr*, Brookhaven National Laboratory, *H. Bluhm*, Lawrence Berkeley National Laboratory

Carbon supported PtRu alloy particles are currently used as the anode catalyst in proton exchange membrane fuel cells. Small amounts of CO, in the ppm concentration range, present in the H₂ fuel are known to poison the catalyst. The role of Ru is to increase the CO tolerance of the catalyst. Since both Pt and Ru are expensive metals, understanding the catalyst's susceptibility to CO poisoning and the function of Ru in reducing this susceptibility are important aspects for cost reduction of proton exchange membrane fuel cells. The increased CO tolerance of these catalysts has been attributed either to CO oxidation by adsorbed OH groups on Ru or by weaker adsorption of CO on the alloy surface than either of the pure metals leading to a decrease in the steady-state coverage of CO. Direct proof of the mechanism for the alloy's increased CO tolerance requires detailed knowledge of the surface composition under reaction conditions. As a first step towards gaining this knowledge, we have used the Ambient Pressure Photoemission Spectroscopy experiment at Beamline 11.0.2 of the Advanced Light Source to study the adsorption of CO onto Ru(0001) and PtRu near surface alloys on Ru(0001) at 300 K and pressures up to 0.5 torr. The results of this study show that at 300 K the coverage of CO on the Ru(0001) surface saturates at ~1x10⁻⁶ torr and remains constant up to 0.5 torr. At pressures greater than 10⁻² torr a second peak appears in the O1s spectra indicating the presence of a second CO species. Comparison of these results to those obtained with a PtRu surface alloy formed on the Ru(0001) surface will be presented.

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