Thursday Afternoon, November 12, 2009

Surface Science
Room: M - Session SS1-ThA

Nucleation and Growth - Metals
Moderator: G.F. Verbeck, University of North Texas

2:20pm SS1-ThA2 Influence of Quantum Well States on the Formation of Surface Au/Pb Alloy in Pb/Si(111) Quantum Thin Films, *J.D. Kim, S.Y. Qin, A. Khajetoorians,* The University of Texas, Austin, *W.G. Zhu, Z.Y. Zhang,* Oak Ridge National Laboratory*, C.K. Shih*, The University of Texas, Austin

The thickness dependence of Au/Pb alloy formation on thin Pb quantum films is studied using *in-situ* low temperature STM/S. Sub-monolayer Au is deposited onto thin Pb films on Si(111) substrates. When Au deposition is carried out at low temperature (~100K), it is found that nano-islands with moire patterns form on top of Pb mesas. With annealing, these moire islands are transformed into three different types of Au/Pb surface alloys. Each type of alloy shows its unique electronic properties and can be clearly identified by STS. Interestingly, the formation of these alloys is directly related to quantum well states (QWS) of underlying Pb films. For thinner thicknesses of underlying Pb layers (below 12ML), it is also observed that the alloy formation probability has strong thickness preference.

2:40pm SS1-ThA3 Far-From-Equilibrium Film Growth on Alloy Surfaces: Ni and Al on NiAl(110), *Y. Han, D. Jing, B. Unal, P.A. Thiel, J.W. Evans*, Iowa State University

We have analyzed the deposition of Ni and Al on NiAl(110) surfaces by STM and by KMC simulation of multi-site atomistic lattice-gas modeling incorporating DFT energetics. The goal is to elucidate far-from-equilibrium growth of metal films on alloy surfaces, including self-growth of alloys. Deposition of Ni produces reversible formation of monolayer islands which have some preference for diagonal steps at 300K and which are distorted-hexagons at 400K. Deposition of Al at 300K produces irreversible formation of irregular monolayer islands perhaps favoring steps in the [-110] direction. These features are recovered by the modeling, which elucidates the distinct nature of terrace diffusion of Ni versus Al on NiAl(110), the details of island nucleation, and the complexity of edge diffusion which controls island growth shapes. Additional studies of sequential co-deposition reveal "history-dependent" structures far from perfect equilibrium alloy ordering. Depositing Al first then Ni creates monolayer islands with a core of Al surrounded by a ring of Ni (although intermixing may occur at the interface). In contrast, depositing Ni first then Al creates monolayer Ni islands with significant second layer population by Al (reflecting stronger binding of Al on top of the Ni islands versus on NiAl(110) according to DFT).

3:00pm SS1-ThA4 Growth Instabilities on Cu Vicinals: Metallic Impurities, *R. Sathiyanarayanan,* University of Maryland, College Park*, A. Bhadj Hamouda,* University of Monastir, Tunisia*, A. Pimpinelli,* Univ. B–Pascal Clermont-2, France & Science Attaché, French Embassy, Houston*, T. Einstein*, University of Maryland, College Park

Spontaneous pattern formation through kinetically controlled epitaxial growth provides a viable route for nanostructuring of surfaces. Ernst and co-workers found that during growth, Cu(100) undergoes a mounding instability, and its vicinal surfaces develop a meandering instability.[2] More specifically, (i) the meandering wavelength (λ_m) scales with deposition rate (F) as $\lambda_m \sim F^\gamma$, with $\gamma \approx 0.19$, (ii) both close-packed <110> and open <100> steps undergo meandering instability and (iii) above 10ML deposition, small pyramids appear near the steps. No previously-known instability mechanism, (esp. Bales-Zangwill, kink Ehrlich-Schwoebel effect, or unrestricted step-edge diffusion) could account for all of the experimental observations.

Using kinetic Monte Carlo simulations, A. Ben-Hammouda *et al.* showed that impurities codeposited on the surface could reproduce the λ_m–F scaling behavior and the formation of small pyramids.[3] Further, they found that only those impurity atoms (i) whose bond to Cu adatom is about 1.6 times the strength of the Cu-Cu bond and (ii) whose diffusion barrier is about 1.6 times the barrier of Cu adatom could cause the observed instabilities. Due to their stronger bonds with Cu adatoms, impurity atoms hinder Cu adatom diffusion, thereby shortening the diffusion length and making λ_m less sensitive to deposition rate (F). Also, impurity atoms act as nucleation centers for the formation of small pyramids.

By computing the binding energies and diffusion barriers for certain candidate impurity atoms, we could eliminate several species as possible sources of the observed instabilities. Using density-functional theory

(DFT)-based Vienna *Ab-initio* Simulation Package (VASP), we computed the adsorption energies and diffusion barriers for many candidate impurity atoms. Our calculations show that common impurities such as oxygen, sulfur, and carbon actually repel Cu adatoms. The bonds formed by elements that alloy with Cu, e.g. Zn, Ag and Sn, are too weak to cause the observed instabilities; also, these atoms have smaller diffusion barriers than Cu. Our results indicate that either Fe or Mn atoms are causing the observed instabilities.[4] We discuss the results of our calculations and the possible role of impurities in nanostructuring of surfaces.

[2]N. Néel *et al.*, J. Phys.: Condensed Matter **15** (2003) S3227.

[3]A. Ben-Hammouda *et al.*, Phys. Rev. B **77** (2008) 245430.

[4]R. Sathiyanarayanan *et al.*, in preparation.

3:40pm SS1-ThA6 Epitaxial Thin Films and Multilayers: Growth Mode, Microstructure and Physical Property Correlations, *R.A. Lukaszew*, College of William and Mary   **INVITED**

The nucleation and growth mode of thin films determines their microstructure and also many of their physical properties, as for example the magnetic anisotropy in the case of epitaxial magnetic thin films. It is also possible to make artificial multilayers via deposition of subsequent layers of different materials and the microstructure and morphology of the intervening layers and interfaces determines many of the final structure properties.

Artificial metallic superlattices are multilayered thin films prepared by alternately depositing two or more elements epitaxially using ultra-high vacuum deposition or sputtering techniques. The concept of the superlattice was originally developed by physicists Leo Esaki and Raphael Tsu, who were both working at the IBM T. J. Watson Research Center in the 1960s.

Since then a wide spectrum of elements and compounds have been found suitable for deposition into multilayers and superlattice structures. The range of properties displayed by the resulting structures is greatly dependent upon the properties of both individual lattices as well as the interaction between them. For example, multilayers composed of magnetic and non-magnetic materials behave differently than the bulk materials and demonstrate a multiplicity of couplings between the magnetic layers. These couplings can be manipulated by choosing different layer materials and modifying their thicknesses. In fact the Giant Magneto Resistance (GMR) effect was found through such combinations and its discovery led to a Nobel Price in Physics.

In this talk I will present our studies on nucleation and growth of metallic and magnetic layers and the correlation observed between their microstructure and some of their unique physical properties.

4:20pm SS1-ThA8 Nucleation and Growth of Ceria-supported Pt-Au Bimetallic Nanoparticles, *Y. Zhou, J. Zhou*, University of Wyoming

Ceria-supported metal particles have been under intensive study for their potential applications in fuel cells owing to the peculiar redox properties and oxygen storage capacity of ceria as well as the synergistic effect between the metal and ceria. Of particular interest are bimetallic systems because they can also exhibit unusual chemical and catalytic properties compared to the individual metals due to the synergistic effect between the two metals. To elucidate the nature of their chemistry in fuel cell applications, it is of significance to gain a fundamental understanding of their nucleation and growth processes on ceria supports. Here we report our recent study of bimetallic Pt-Au deposited on fully oxidized $CeO_2(111)$ and reduced $CeO_x(111)$ thin films using scanning tunneling microscopy and x-ray photoelectron spectroscopy. Ceria thin films with controlled degrees of cerium reduction were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Pt and Au were vapor-deposited onto ceria thin films. Our study demonstrates that the growth and sintering behavior of Pt-Au bimetallic particles is dependent on the Ce oxidation states, metal compositions, as well as the metal deposition sequence. The growth of Pt-Au on well-ordered $CeO_x(111)$ thin films was compared to that of pure Pt and pure Au as well as to that of bimetallic Pt-Au supported on nanocrytalline ceria surfaces. The research is sponsored by the start-up fund at University of Wyoming and the Wyoming NASA Space grant.

4:40pm SS1-ThA9 Growth of Iridium on Ge(111) Studied by STM and LEEM, *C. Mullet, S. Chiang, J. Morad, A. Durand*, University of California, Davis

Iridium on germanium is a system which is useful for understanding the interaction of 5d metals with semiconductors, with potential applications to electronic contacts. We have used both scanning tunneling microscopy

(STM) and low energy electron microscopy (LEEM) to characterize the submonolayer growth of iridium onto Ge(111) as a function of coverage, deposition temperature, and annealing temperature. Ir deposited onto the Ge(111) c(2x8) surface forms a ($\sqrt{3}$x$\sqrt{3}$)R30º phase with the island size dependent upon substrate temperature during deposition. Deposition at a sample temperature of 670 C yields large micron-sized regions of continuous ($\sqrt{3}$x$\sqrt{3}$)R30º coverage, as seen by LEEM. Deposition at 400 C produces Ir islands of three different sizes, all of which are too small to be resolved in LEEM but can be easily observed in room temperature STM images: large islands of roughly 10 to 20 nm diameter, consisting of multiple layers; medium-sized islands of roughly 4 nm in diameter, and small islands about 1 nm in diameter. The medium sized islands show a preference for growing at the bottom edges of steps. The small islands show a nearly uniform distribution on the sample surface, with the interesting exception of preferentially ordering in arrays of lines connecting medium-sized islands. Heating the sample over 640 C yields islands of large enough size to be resolved with LEEM, with the island size dependent upon annealing temperature. Ostwald ripening was observed in LEEM movies. When these large islands form during sample heating, they appear to 'avoid' areas of high step density near surface defects. At 840 C, desorption begins from these types of regions.

5:00pm SS1-ThA10 Adatom- and Addimer-Mediated Exchange Diffusion of Embedded Ge Atoms in the Ge/Si(001) Surface Alloy, *E. Bussmann, **B.S. Swartzentruber***, Sandia National Laboratories
Using low-bias empty-state STM images, we can resolve the location of embedded Ge atoms in the Ge/Si(001) surface alloy. We directly observe the diffusion of these embedded atoms at elevated temperatures (>100°C). That the diffusion of the embedded Ge atoms occurs in time bursts, is spatially correlated, and results in long displacements implies that the process is defect mediated. The responsible defects are adsorbed monomers and dimers. We have identified two exchange-diffusion pathways for the movement of the embedded Ge atoms, both of which are consistent with previous first-principles calculations [1, 2]. Adsorbed monomers of Si or Ge can readily place exchange with surface atoms as they anisotropically diffuse along the substrate dimer rows. These monomer exchange events are strongly correlated with common trap sites for monomers, such as, the ends of dimer rows of islands. Less frequent events are associated with adsorbed dimers that can exchange one of their atoms with a surface atom. That is, an adsorbed Si-Si dimer can exchange one of its Si atoms with an embedded Ge atom to become a Si-Ge dimer, which can subsequently re-exchange the Ge atom into the surface at a different location. Because the barrier for exchange in both of these pathways is only slightly higher than that for diffusion, Ge deposition on Si(001) leads to intermixing and surface-alloy formation at any temperature where diffusion is active. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE, and was performed at the Center for Integrated Nanotechnologies, a U.S. DOE-BES user facility.

[1] Lu *et al*., Surf. Sci. Lett., **506**, L282 (2002).

[2] Zipoli *et al*., APL, 92, **191908** (2008).

5:20pm SS1-ThA11 Substrate Effect on the Morphological Transition of Planar Magic Ag Nanoclusters, *Y.P. Chiu, B.C. Huang, C.Y. Shen*, National Sun Yat-sen University, Taiwan
Two-dimensional (2D) magic Ag nanoclusters have been demonstrated experimentally[1]. Experimental observations show that a template that originates from the electronic effect of quantum Pb islands grown on an Si(111) substrate can be used to develop Ag nanoclusters in planar feature with unusual size distributions, called a two-dimensional magic Ag nanocluster. Theoretically, the transition of Ag clusters from planar to 3D structures begins with Ag clusters of seven atoms without consideration of the substrate support [2]. However, utilizing the symmetry and size of the periodic pattern on the Pb islands, distinguishable planar hexagonal Ag clusters can be grown even for Ag clusters of 127 atoms [3]. How the substrate has influence on the morphological transition of Ag clusters from planar to 3D is of our interest and motivates the present work. To elucidate the effect of the substrate on the growth behavior of Ag clusters, highly oriented pyrolytic graphite (HOPG) is adopted as a template in the work. STM is used to characterize and analyze the growth behavior of Ag nanoclusters on HOPG. The process of the transition of Ag nanoclusters from planar to 3D and the onset of the formation of three-dimensional Ag clusters are also elucidated. A thorough analysis of the energetic optimization of Ag clusters not only yields information on the growth of Ag clusters on HOPG, but also elucidates how the substrate influences the formation of magic Ag clusters.
References

[1] Y.P. Chiu, L.W. Huang, C.M. Wei, C.S. Chang, and T.T. Tsong, Phys. Rev. Lett. **97,** 165504 (2006).

[2] Eva M. Fernández, José M. Soler, Ignacio L. Garzón, and Luis C. Balbás, Phys. Rev. B **70**, 165403 (2004).

[3] Y.P. Chiu, C.M. Wei, and C.S. Chang, Phys. Rev. B Vol. **78,** 115402 (2008).

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