

# Wednesday Morning, October 22, 2008

## Surface Science

Room: 209 - Session SS2+NC-WeM

## Functional Metal Oxides and Quantum Metal Structures

Moderator: J.E. Reutt-Robey, University of Maryland, College Park

8:00am **SS2+NC-WeM1 Can Ferroelectric Polarization be Used to Manipulate Metal-Oxide Interactions?**, *Y. Yun, N. Pilet, U.D. Schwarz, E.I. Altman*, Yale University

Ferroelectric polarization creates high energy surfaces that are expected to reduce their surface energy by reconstructing or adsorbing compensating charges. Because opposite charges must be screened on opposite surfaces, different surface atomic structures and reactivities are anticipated. Since the polarization can be changed by applying an electric field, this suggests switchable surface chemical properties. We previously found that this effect can be exploited to alter how strongly polar molecules adsorb on  $\text{LiNbO}_3(0001)$  surfaces (Y. Yun and E.I. Altman, *J. Am. Chem. Soc.* 129 (2007) 15684). To determine if ferroelectric polarization can alter the catalytic properties of supported metals, the interaction of Pd with  $\text{LiNbO}_3(0001)$  was characterized using electron diffraction, photoelectron spectroscopy (XPS and UPS), ion scattering spectroscopy (ISS), atomic force microscopy, and CO temperature programmed desorption (TPD). Positively poled  $\text{LiNbO}_3(0001)$  surfaces behave like many other oxides. The Pd atoms aggregate into nanoparticles, with the smallest nanoparticles exhibiting XPS peak shifts that can be associated with a size effect. CO adsorption on these nanoparticles is largely unaffected by the size of the nanoparticles, the  $\text{LiNbO}_3$  support, and annealing. In contrast, preliminary results suggest that Pd behaves very differently on negatively poled  $\text{LiNbO}_3$ . In this case, the Pd photoemission peak shifts persist to higher Pd coverages and annealing causes the Pd peak intensity to decrease; annealing has no effect on Pd on positively poled  $\text{LiNbO}_3(0001)$ . Further, initial findings suggest that modest heating to just 600 K severely attenuates the ability of the Pd to adsorb CO.

8:20am **SS2+NC-WeM2 Temperature Dependence of Intrinsic Nucleation in Ferroelectrics**, *P. Maksymovych, S. Jesse*, Oak Ridge National Laboratory, *M. Huijben, R. Ramesh*, University of California, Berkeley, *A. Morozovska*, National Academy of Science of Ukraine, *S. Choudhury, L.-Q. Chen*, Pennsylvania State University, *A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Nucleation of domains is central to understanding and applying ferroelectric materials. In bulk ferroelectrics, the number of ferroelectric nuclei grows rapidly with temperature, verifying the involvement of thermal fluctuations, which are widely interpreted as a result of defect, modified local barriers. In homogeneous, low defect thin films, a local voltage source can produce intrinsic switching domain without the influence of defects. We have examined the temperature dependence of intrinsic domain nucleation for the first time using Piezoresponse Force spectroscopy of model oxide materials,  $\text{BiFeO}_3$  and  $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$  from 34 to 300 K. Measurements were performed in ultra high vacuum, which allowed cryogenic cooling but also precluded the presence of water known to significantly affect ferroelectric phase stability. The key finding is that the temperature dependence of ferroelectric switching initiated by a scanning probe tip is small and amounts to only a 20 percent increase in the nucleation voltage upon cooling of the films to the lowest temperature. These results are in stark contrast to previous reports for ferroelectric switching in the capacitor geometry where the coercive field increases by at least a factor of five over a similar temperature range. To complement the experimental data, a theoretical analysis was carried out based on two models, the rigid ferroelectric model and phase-field simulations. The temperature dependence predicted by the phase-field modeling is small and in good agreement with the experiments, while the rigid ferroelectric model overestimates it considerably. We conclude that the intrinsic ferroelectric switching induced by scanning probe experiments involves minimal contribution from thermal fluctuations. PM was supported as a Eugene P. Wigner Fellow at ORNL. Research was performed at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, and supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

8:40am **SS2+NC-WeM3 Catalysis of M-YSZ(100) Model Anodes for Solid Oxide Fuel Cells**, *R.G. Green, J.B. Giorgi*, University of Ottawa, Canada

Solid oxide fuel cells (SOFC's) convert chemical energy directly into electrical energy through a reaction involving the oxidation of fuels, such as hydrogen or natural gas. The oxidation reaction occurs at the anode which is typically composed of a nickel-yttria-stabilized-zirconia (Ni-YSZ) cermet. This composition provides the active triple phase boundary where gas (fuel), the active catalyst (metal) and the oxide ion provider (YSZ) meet. We will discuss a model system of this complex catalyst which has been studied under ultrahigh vacuum. To create this model, we deposit an active transition metal (Pd, Ni, Co) in the form of nano-particles onto single crystal YSZ (100). The defective YSZ surface offers a range of meta-stable nanostructures that can interact with the metal component. Additionally, the surface shows high reactivity toward carbon at high temperature. These properties add difficulty and complexity to the model systems. Results of catalytic activity toward methane as a function of metal composition and particle size will be discussed. The catalysts have been studied in-situ using photoelectron spectroscopy, scanning probe microscopy, as well as thermal desorption spectroscopy and reaction techniques.

9:00am **SS2+NC-WeM4 Structure of Au and Ag Clusters on  $\text{Al}_2\text{O}_3/\text{FeAl}(110)$** , *M.C. Patterson, O. Kizilkaya, R.L. Kurtz, P.T. Sprunger*, Louisiana State University

We present ultraviolet photoemission and STM studies of Ag and Au clusters deposited on both clean and oxidized  $\text{FeAl}(110)$ . Preliminary DFT calculations indicate that deposition of Ag or Au results in the formation of bilayer islands with  $\text{Ag}(110)$  or  $\text{Au}(110)$ -like structure, due to the almost perfect match between the adsorbate and substrate lattice constants. This is concordant with studies of Ag growth on the similar intermetallic alloy  $\text{NiAl}(110)$ .<sup>1</sup> High coverage levels of either adsorbate do not wet the  $\text{FeAl}$  surface, which can be seen by the presence of distinctive  $\text{FeAl}(110)$  valence band, Al 2p core level, and Fe 3p core level features at all levels of coverage. Angle dependent photoemission shows no dispersion in valence band features as a function of emission angle, and confirms that adsorbate, Fe, and Al are all present in the surface region. Additionally, some evidence of Al-Au alloying is observed in the Al 2p core level and Au 5p features in the  $\text{Au}/\text{FeAl}(110)$  system.

<sup>1</sup>B. Unal, F. Qin, Y. Han, D. Liu, D. Jing, A. R. Layson, C. J. Jenks, J. W. Evans, and P. A. Thiel, *Phys. Rev. B* 76, 195410 (2007).

9:20am **SS2+NC-WeM5 The Effect of Water and Surface Order on Reactivity**, *R.G. Quiller, L. Benz, T.A. Baker, M.E. Colling, C.M. Friend*, Harvard University

Understanding the effect of hydrating or hydroxylating a surface is an important aspect of interfacial chemistry. Intermolecular interactions including hydrogen bonding between water, hydroxyl groups, and oxide species play a crucial role in determining products and reaction rates in a range of heterogeneous reactions. Using surface science techniques such as temperature-programmed reaction and infrared reflection absorption spectroscopy, we studied the effects of such interactions on a number of catalytically and environmentally relevant systems on both Au and  $\text{TiO}_2$  single crystal surfaces. We found that in addition to changes induced by water-related interactions, defects and surface ordering also played an important role in surface reactivity. Our results, therefore, emphasize the role of surface preparation and water coverage. These results help determine the role of intermolecular interactions on gas-oxide reactions and have implications in heterogeneous catalysis and environmental chemistry.

9:40am **SS2+NC-WeM6 Engineering Thin Film Superconductivity Toward Single Atomic Layer: A Scanning Tunneling Microscopy/Spectroscopy Study**, *S.Y. Qin, J.D. Kim, A.A. Khajetoorians, C.K. Shih*, University of Texas at Austin

Ultra-thin Pb films on semiconductor substrates have exhibited many intriguing phenomena manifested by the quantum confinement of electronic states. Quantum stability has been a topic of interest for many years. Recently, it was shown that quantum confinements also play an interesting role on superconductivity. Oscillations of superconductivity gap and Tc as a function of film thickness have been observed in  $\text{Pb}/\text{Si}(111)$  and  $\text{Pb}/\text{Ge}(111)$  systems. Moreover, it is found that the superconductivity remains very robust even for films as thin as 5 ML. An interesting question arises as to what extent the robustness of superconductivity remains in even thinner regime. By using a different surface template, namely  $\text{Pb}/\text{Si}(111)$  root 3 surface, we have grown uniform Pb films down to 2 ML. The film shows preferred thicknesses of 2ML and 4ML, presumably a manifestation of the quantum stability. While superconducting gap remains robust down

to 4ML and shows BCS-like temperature dependence, superconductivity of 2ML Pb film exhibit several interesting features. First of all, the superconducting transition temperature is significantly lower. Moreover, we find that even with nearly perfect 2ML films, the magnitude of superconducting gap is strongly suppressed by a minute concentration of hole defects. On the contrary, the gap is not affected by distribution of small excess nano-islands.

10:40am **SS2+NC-WeM9 Effect of Quantum Well States on the Formation of MnCu c(2x2) Surface Alloy.** *W. Kim*, Korea Research Institute of Standards and Science, *I. Kim*, Chonnam National University, Republic of Korea, *C. Min*, Seoul National University, Republic of Korea, *H.-D. Kim*, Pohang Accelerator Laboratory, Republic of Korea, *C. Hwang*, Korea Research Institute of Standards and Science

The formation of quantum well states in metallic thin films under a certain boundary condition cause the sharp change in the intensity of electron density of states(DOS) at Fermi level of the thin films as the film thickness varies. This thickness dependence of DOS at Fermi level is the origin of quantum size effects found in many physical properties of the metallic thin films. In this study, we carried out the experiments to examine the effect of the quantum well states in the Cu/fcc Co(001) system on the formation of a surface alloy. It is well known that deposition of a half monolayer Mn on the Cu(001) leads to the formation of a very stable single layer MnCu c(2x2) surface alloy, and the origin of this process has been attributed to the magnetic energy of enhanced surface magnetic moment of Mn atom.<sup>1</sup> As the first step of the experiment, we examined the evolution of the Mn core level photoemission spectra with increasing Mn thicknesses, comparing the low energy electron diffraction(LEED) pattern for each Mn thickness. From the obtained spectra, we found out that there exist the features which are closely related to the surface alloy formation. Based on this spectroscopic evidence of surface alloying, we investigated the effect of quantum well states on the formation MnCu surface alloying. We deposited half monolayer Mn atoms on the wedge shaped Cu layers formed on the fcc Co(001) surface, and measured Mn core level photoemission spectra for the different Cu thicknesses. The observed spectra show overall correlation with the oscillating behavior of DOS at Fermi level as the thickness of Cu layers changed. Judging from the changes of Mn core level spectra, we could conclude that the lower electron density of states at Fermi level enhanced the formation of MnCu ordered surface alloy. This conclusion was also confirmed by the direct observation of the intensity of the half order spots of c(2x2) LEED pattern of MnCu surface alloy formed on the Cu/fcc Co(001) system with selected thicknesses of Cu layer. The results of our study strongly support the previous interpretation of the formation of stabilized MnCu surface alloy.

<sup>1</sup>. M. Wuttig et al., Phys. Rev. Lett. 70, 3619 (1993).

11:00am **SS2+NC-WeM10 Adsorption of the Thiol Molecule (SCH<sub>3</sub>)<sub>2</sub> on a Metallic Quantum Well System.** *L. Tskipuri*, *R.A. Bartynski*, Rutgers University

We have studied the bonding of the thiol molecule dimethyldisulfide (SCH<sub>3</sub>)<sub>2</sub> on ultrathin Cu and Co films that exhibit metallic quantum well (MQW) states using inverse photoemission (IPE), reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). This thiol is similar to more complex organic molecule that exhibits the self-assembled properties on metal surfaces. After a room temperature exposure of the Cu surface to the thiol molecule at a dose of ~ 2.5 L, a c(2 x 2) low energy electron diffraction (LEED) pattern confirmed that the adsorbate forms an ordered overlayer. A large sulfur signal is observed in Auger electron spectroscopy (AES) and the C-H stretch mode was observed in IR with a frequency of 2915 cm<sup>-1</sup> confirming molecular adsorption. Changes in the IPE spectrum upon adsorption are dominated by suppression of the substrate-related features, although some weak adsorbate-induced peaks are also observed. Both experimental and theoretical evidence indicates that electronic orbitals involved in molecule-surface bonding are in the same energy range as the MQW states of the substrate and the possible influence of MQW states on molecular adsorption and self-assembly of the thiol molecule will be discussed.

11:20am **SS2+NC-WeM11 Adsorbate Dynamics under Nanoscale Confinement.** *Z. Cheng*, *G. Pawin*, *D. Sun*, *M. Luo*, *D. Kim*, *Y. Zhu*, *L. Bartels*, University of California at Riverside

The diffusion of isolated adsorbates at extended low-index metal surfaces has been studied by scanning tunneling microscopy at many places, yet the behavior of isolated molecules may significantly differ from that of molecules at higher coverages and in confined structures such as nanometer-size metal clusters. We investigate the behavior of coverages of CO molecules confined to 4nm pores formed on Cu(111). While high-coverages form ordered patterns, in which vacancy diffusion and the behavior of dislocation lines can be studied, intermediate coverages aggregate to disordered islands or disperse completely across a pore, thus

resembling a 2D liquid and gas, respectively. Isolated molecules show different diffusive behavior at the perimeters of the pore and at their center, revealing the importance of substrate confinement for the molecular behavior.

11:40am **SS2+NC-WeM12 Charge Carrier Separation and Transport at Organic Semiconductor Interfaces.** *X.-Y. Zhu*, University of Minnesota **INVITED**

Charge carrier generation and transport are central to the operation of all organic electronic and optoelectronic devices, such as organic light-emitting diodes (OLEDs), field effect transistors (OFETs), and photovoltaic cells (OPVs). A fundamental distinction from their inorganic counter parts is the localized nature of charge carriers and electronic excitations in organic semiconductors. Localization is a fundamental character resulting from the narrowness of the electronic band, the flexibility of the organic molecule, the deformability of the van der Waals bonded lattice, and the low dielectric constants of organic solids. This is in addition to the prevalence of structural and chemical defects that form the bulk of charge carrier traps in organic semiconductors. We study the exciton dissociation and charge carrier localization problem in organic semiconductors using femtosecond time-resolved two-photon photoemission (TR-2PPE) spectroscopy to follow the formation and decay of excitons and small polarons in organic semiconductors. These experiments are beginning to answer the following critical questions: How do charge carriers separate at organic heterojunctions in an OPV? How does an electron localize to form a small polaron?

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