# **Tuesday Afternoon, November 5, 2002**

## Surface Science Room: C-112 - Session SS3-TuA

### Metal/Oxide Surfaces

Moderator: C.A. Ventrice, Jr., University of New Orleans

#### 2:00pm SS3-TuA1 High Quality Nanoscale Interfaces between Metals and Metal/Oxides: Co on Fully Hydroxylated Sapphire, S.A. Chambers, T. Droubay, Pacific Northwest National Laboratory, **D.R. Jennison**, T.R. Mattsson, Sandia National Laboratories

We present experimental and theoretical results that show Co metal deposited on fully hydroxylated alpha-Al2O3(0001) at room temperature produces a chemical reaction that leads to laminar growth of the metal film. A fraction of the initial metal dose is oxidized, and a concomitant amount of hydroxyl is reduced, resulting in hydrogen being released. The resulting Co cations are within the top layer of the oxide. These bind ionically to the substrate, but are also bound to neighboring metal atoms. Stronger interfacial binding results and near layer-by-layer metal growth is achieved, hot reactions are responsible and many other metals and oxides should display this phenomenon. All work was supported by the US Dept. of Energy.

#### 2:20pm SS3-TuA2 The Interaction and Reactivity of Hydrocarbons on Hydroxylated gAl<sub>2</sub>O<sub>3</sub>/NiAl(100), K.A. Layman, J.C. Hemminger, University of California, Irvine

γ-Al<sub>2</sub>O<sub>3</sub> is an important industrial catalyst and catalyst support. The surface OH groups on bulk y-Al<sub>2</sub>O<sub>3</sub> influence the Brönsted acidity and metal dispersion on these catalysts. However, the detailed understanding of A l<sub>2</sub>O<sub>3</sub> surfaces has been limited because of the complexity of the surface hydroxyl groups. We are able to grow highly-ordered and well-defined thin films of hydroxylated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which model bulk  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by exposing the NiAl(100) substrate to 100 L H<sub>2</sub>O at 1000 K. Unlike bulk γ-Al<sub>2</sub>O<sub>3</sub>, these films exhibit a single OH stretch at 3711 cm<sup>-1</sup> (FWHM approximately 100 cm<sup>-1</sup>). This frequency is indicative of non-interacting OH groups bonded to 2 or 3 Al atoms. We have used HREELS to study the interaction and reactivity of hydrocarbons, such as acetonitrile, pyrazine, 2,6-dimethylpyridine, and ammonia, on our thin films of hydroxylated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> following adsorption at 140 K. These molecules interact with surface OH groups, forming acid-base complexes. Complex formation causes the OH bond strength to decrease and the OH stretch to shift to lower frequency. We have observed that the magnitude of the OH shift depends on both the basicity and adsorption orientation of these hydrocarbons. Correlation of the OH frequency shift with the gas basicity of the adsorbate allows us to assign a pK<sub>a</sub> to the surface OH groups. The hydrocarbons can also interact with the surface Al<sup>3+</sup> cations. In the case of ammonia, this interaction leads to disruption of an N-H bond and the formation of surface NH<sub>2</sub> and OH species.

#### 2:40pm SS3-TuA3 Calculations of the Free Energy and Structure of Alpha-Alumina (0001), *M. Finnis*, *A. Marmier*, Queens University, UK INVITED

We report a study of the excess free energy of this surface using two different shell models (S1 and S2) and an ab initio (AI) model in which the total energy was obtained from self-consistent pseudopotential calculations using the local density approximation. We apply the quasi-harmonic approximation to estimate the phonon contribution to the free energy. The surface energies with S1 and S2 bracket the AI result. They also show that only two k-points are needed to sample the phonons in the Brillouin zone with good accuracy. A six layer slab is thick enough for obtaining all contributions to the surface free energy, which converges faster with slab thickness than the mean square amplitudes of atomic vibration, and in fact the latter diverges for a finite slab. Anharmonicity is insufficient to account for the discrepancy beween calculated and experimental surface relaxations. A stoichiometric AI-terminated surface is predicted to be stable over all but very low (close to decomposition of the oxide) and very high (> 1 atmosphere) oxygen partial pressures, in agreement with experiment.

# 3:20pm **SS3-TuA5 Effect of Annealing on the Crystallization of Ultrathin Al<sub>2</sub>O<sub>3</sub> Film on NiAl(110),** *T.T. Lay***,** *M. Yoshitake***, National Institute for Materials Science, Japan**

 $Al_2O_3$  is a wide band gap insulator and it is reported that clear band gap exits in 0.5nm-thick well-ordered  $Al_2O_3$  grown on NiAl(110).<sup>1</sup> It has high potential of application in metal-insulator-metal(M-I-M) electron emitter which needs wide gap insulator. Oxygen dose rate, oxidation temperature

and annealing are important parameters for well-ordered film. In our previous work, good crystalinity of  $Al_2O_3$  layer was obtained by optimizing the dose rate and oxidation temperature.<sup>2,3</sup> In the present work, change in crystalinity and surface composition due to annealing time is analyzed. NiAl(110) single crystal was put inside the UHV system and 1200L oxygen was introduced under pressure 5 x  $10^{-7}$  torr at 670K. After oxidation the specimen was annealed at 1070K. The oxide layer was amorphous before annealing and crystalline Al<sub>2</sub>O<sub>3</sub> appeared after annealing. Crystal structure and surface composition were measured by LEED and XPS every hour during annealing. Intensity ratio of Al<sub>2</sub>O<sub>3</sub> and NiAl spots was measured from LEED patterns. The intensity ratio is directly related to crystalinity and it increases linearly with annealing time. After 6 hours annealing, the ratio became saturated and there was less change by further annealing. The surface composition of O, Al and Ni changed only at the early stage of annealing and were almost constant one hour later. It is likely that the amount of oxygen contributed to well-ordered crystalline oxide is almost decided at oxidation. Annealing at 1070K for certain period of time is important for epitaxial growth of well-ordered oxide layer.

<sup>1</sup> R.M. Jaeger, H.Kuhlenbech, H.J.Freund, M.Wuttig, W. Hoffmann, R. Franchy and H. Ibach, Surf. Sci., 259,235(1991),

 $^2\,$  M. Yoshitake, B. Mebarki and Thi Thi Lay, Surf.Sci. Lett., in press.,

<sup>3</sup> Thi Thi Lay, M. Yoshitake and B. Mebarki, J.Vac. Sci. Technol., submitted.

3:40pm **SS3-TuA6 Ab-Initio Calculations of Pristine and Doped ZrO<sub>2</sub> Tilt Grain Boundaries**, *Z. Mao*, Northwestern University, *E.C. Dickey*, The Pennsylvania State University, *S.B. Sinnott*, University of Florida

The structure of the cubic-ZrO<sub>2</sub> symmetrical tilt sigma 5 (310)/[001] grain boundary is examined using density functional theory within the local density and pseudopotential approximations. Several pristine stoichiometric grain boundary structures are investigated and compared to Z-contrast scanning transmission electron microscopy and electron energy loss spectroscopy results. The lowest-energy grain boundary structure is found to agree well with the experimental data. When Y<sup>3+</sup> is substituted for Zr<sup>4+</sup> at various sites in the lowest-energy grain boundary structure, the calculations indicate that Y<sup>3+</sup> segregation to the grain boundary is energetically preferred to bulk doping, in agreement with experimental results.

4:00pm **SS3-TuA7 Role of the Stress in the Epitaxy of Silver on the Basal Planes of Zinc Oxide**, *J. Jupille*, Groupe de Physique des Solides, France, *S. Djanarthany*, Laboratoire des Geosciences, France, *D. Abriou*, Laboratoire CNRS/Saint-Gobain, France, *N. Jedrecy*, Laboratoire Mineralogie-Cristallographie, France, *R. Lazzari*, *G. Renaud*, CEA-Grenoble, France

In general late transition metals and noble metals poorly wet oxide surface oxides. However, rather high values of the critical coverage (onset of the formation of the second atomic layer [Campbell, Surf. Sci. Rep. (1997)]) have been observed for platinum, copper and silver. The present paper reports on two different  $(0001)_{ZnO}//(111)_{Ag}$  epitaxies for silver on the oxygen- and zinc-rich basal planes of zinc oxide. The [20-20]<sub>ZnO</sub> //[220]<sub>Ag</sub> orientation relation (OR I), corresponding to a misfit of + 2.75 %, is obtained on surfaces which are only prepared by annealing under oxygen. The  $[11\text{-}20]_{ZnO} // [220]_{Ag}$  orientation relation (OR II, rotated by 30° with respect to OR I) is observed after an ion bombardment of the surfaces. It corresponds to a misfit of 11 %. The two epitaxies show both a perfect reproducibility and a good thermal stability. Low energy electron diffraction, transmission electron microscopy and X-ray diffraction (XRD) measurements demonstrate that (i) the ion bombardment strongly increases the size of the surface domains (narrowing of diffraction spots and rods) and that (ii) OR II, which corresponds to within 0.11 % to a 9Ag/8ZnO lattice coincidence, does not show any stress even at the onset of the film growth. It is concluded that the OR II is favoured by large ZnO domains while the OR I, which shows a better fit on short range, appears on surfaces of poor crystalline quality.

#### 4:20pm SS3-TuA8 Vanadium Oxide Nanostructures on Rh(111): Novel Oxide Phases at the Interface<sup>1</sup>, J. Schoiswohl, S. Surnev, S. Eck, M.G. Ramsey, F.P. Netzer, Karl-Franzens University Graz, Austria

Ultrathin layers of materials develop novel physical and chemical properties due to confinement and interfacial proximity effects, which are not shared by their respective bulk phases. Here we report a study of thin vanadium oxide layers on Rh(111) surfaces using STM, STS, LEED, and XPS with synchrotron radiation. We have fabricated vanadium oxide nanostructures on Rh(111) by reactive evaporation of vanadium metal in an oxygen atmosphere onto the heated substrate surface and have characterised the atomic structures of the V-oxide with STM (STS) and LEED; the oxidation state of the oxide layers have been followed by XPS. We find a complex phase diagram of oxide structures as a function of oxide coverage and temperature, and observe a range of well-ordered two-dimensional oxide phases with novel structural properties. At submonolayer coverages higher oxidation states (>4<sup>+</sup>) prevail [( $\sqrt{7}x\sqrt{7}$ ) and/or ( $\sqrt{13}x\sqrt{13}$ ) structures], whereas the oxidation state converges to 3<sup>+</sup> and a bulk-type V<sub>2</sub>O<sub>3</sub> phase forms for thicker layers (> 2-3 ML). The monolayer phase is distinguished by a Moiré-type STM structure, resulting from the lattice mismatch between the ordered oxide overlayer and the substrate. Reduced oxide phases are obtained after vacuum annealing treatments, displaying a fascinating structureal complexity, with e.g. (5x5), (5x3 $\sqrt{3}$ ), (9x9) and other structures. <sup>1</sup>Supported by the Austrian Science Foundation.

#### 4:40pm SS3-TuA9 Room Temperature Growth and Thermal Sintering of Ag and Pd on Flat Ultra-thin SiO<sub>2</sub> and MoO<sub>2</sub> Films, *A.K. Santra*, *B.K. Min, D.W. Goodman*, Texas A&M University

The initial growth morphology of Ag and Pd particles has been investigated on epitaxial ultra-thin MoO2(100) and SiO2 films using STM. The room temperature growth of Ag and Pd particles is invariant with respect to the thickness of the SiO2 film, however, with increasing surface temperature the Pd particles undergo a 3DA" 2D transition on a 0.5nm thick SiO2 film and increase in particle size on films with a thickness >0.8nm. In contrast, Ag particles on a MoO2(100) substrate show striking differences with respect to the particle size distribution as a function of the oxide film thickness at room temperature. These results indicate that the initial growth and thermal sintering of metal particles depend critically on the strength of the metal-support interaction. The preparation procedure for these flat ultrathin films on Mo(112) will be discussed relative to the LEED and highly resolved STM data. Furthermore, STS data indicate that a minimum thickness (3 - 4 Si-atomic equivalent layers) is necessary to obtain a bulklike band-gap for SiO2 ultra-thin films, in excellent agreement with results recently reported by Muller and co-workers [Nature 399 (1999) 758] for Si/SiO2/Si gate-oxide samples.

5:00pm **SS3-TuA10 Structure and Properties of SnOx Wetting Layers and Crystallites on Pt(111)**, *J. Kim*, University of Southern California, *M. Batzill*, Tulane University, *D. Beck*, University of California-Los Angeles, *B.E. Koel*, University of Southern California

Tin-oxide films were grown on Pt(111) substrates by oxidation of Sn/Pt surface alloys using NO<sub>2</sub> exposures or by deposition of Sn in an NO<sub>2</sub> ambient gas. Based on the wide variety of structures of tin-oxide films that we have reported previously [Phys. Rev. B 64, 245402/1 (2001)], we now report detailed characterization of the vibrational and electronic properties of each structure using XPS, UPS, ELS, and HREELS. XPS confirmed the existence of three Sn states that have been labeled previously as metallic, "quasimetallic," and oxidic Sn. We conclude that the "quasimetallic" state results from oxidized Sn that is still alloyed within the Pt surface layer. UPS identified a SnO<sub>2</sub> stoichiometry for multilayer tin-oxide films. HREELS was used to identify characteristic vibrational modes for the different monolayer films. SnO<sub>2</sub> crystallites, although only a few monolayers high and tens of nanometers in width, remarkably exhibit bulk-like vibrational and electronic properties.

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