Surface Science
Room 210B - Session SS1-WeM
Metal Oxides and Clusters I: Formation and Structure

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS1-WeM1 The Chemistry of Au Clusters Supported on Titania: Early Steps Towards Understanding the Mechanism of Propene Epoxidation***, G. Mills, S. Chretian, V. Shapovalov,* ***H. Metiu,*** University of California, Santa Barbara **INVITED**

We use density functional calculations to try to increase our understanding of the interactions of hydrogen, oxygen, propene, and propene oxide with gold clusters in gas phase, with titania, and with gold clusters supported on titania. Our goal is to clarify the mechanism of propene epoxidation. I will also report briefly on a collaboration with Martin Moskovits concerning the modification of catalytic activity of CO oxidation, by manipulating the electron density in tin oxide nanowires.

9:00am **SS1-WeM3 Surface and Subsurface Oxidation of Ni(100) and Ni(111) Studied by Medium Energy Ion Scattering***,* ***M.A. Muñoz-Márquez,*** University of Warwick, UK, United Kingdom*; R.E. Tanner, D.P. Woodruff,* University of Warwick, UK

Using medium energy ion scattering (MEIS) and specifically 100 keV H@super +@ incident ions, the oxidation of the Ni(100) and Ni(111) surfaces have been investigated at temperatures around 200-300°C and with oxygen exposures up to 6000 L. This treatment range corresponds to that typically used to produce well-defined NiO(100) surfaces on Ni(100) and involves significantly thicker oxide formation than has been investigated by conventional surface science techniques in the past. The potential of MEIS to probe the deeper subsurface is highly relevant in these studies, as oxide formation >100 Å is seen on Ni(111). While it is well-established that the earliest stages of oxidation occur at lower exposures on Ni(111) than Ni(100), attributed to site blocking in the different chemisorbed oxygen phases on the two surfaces, our results show that this greater reactivity of Ni(111) persists to rather deep oxidation. Throughout these oxide films the stoichiometry of NiO is retained. Through the use of 'double-alignment' scattering geometries and qualitative LEED, the crystallography of these oxide layers has been investigated. LEED shows that on Ni(111) two (of the possible three) orientational domains of NiO(100) form, attributed to a slight misorientation of the surface. In general, the average crystalline registry with the bulk is poor, although at intermediate exposures a surprising result is that the outermost layers appear better-ordered than the near sub-surface. This is attributed to the probable influence of thick islands of limited lateral extent which causes the more penetrating ions to pass through differently oriented oxide islands. On Ni(111) simulations using the VEGAS code confirm that the data are consistent with this rationale. On Ni(100), the apparent poor order can also be reproduced in simulations assuming the NiO(100) crystallites are tilted on the surface as previously proposed on the basis of SPA-LEED investigations.

9:20am **SS1-WeM4 Thermodynamics of Pd(111) Oxidation from 10@super -7@ to 25 Pa: An In-Situ Photoemission Study***,* ***D.F. Ogletree****, G. Ketteler, H. Liu, E.L.D. Hebenstreit, H. Bluhm, M. Salmeron,* Lawrence Berkeley National Laboratory

The oxidation of Pd(111) has been studied in equilibrium with oxygen gas between 10@super -7@ and 25 Pa over a temperature range of 300 to 925 K. The experiments were carried out in a newly commissioned, second-generation high pressure photoemission spectroscopy (HPPES) system operating at the Molecular Environmental Sciences synchrotron beamline@footnote 1@. After UHV sample cleaning, the Pd(111) crystal was transferred to a variable pressure experimental cell coupled to a differentially pumped electron spectrometer. High resolution photoemission spectra were recorded for the Pd 3d@sub 5/2@, O1s/Pd3p@sub 1/2@ and valence band regions at different combinations of oxygen pressure and sample temperature. Dynamic and reversible changes in surface oxidation were observed in response to changes in the thermodynamic environment of the palladium substrate. An analysis of the thermodynamics and kinetics of the palladium-oxygen system will be presented. @FootnoteText@ @footnote 1@ Beamline 11.0.2 at the LBNL Advanced Light Source, Berkeley, CA USA.

9:40am **SS1-WeM5 Oxidation of Pt(111) by Gas-Phase Oxygen Atoms***,* ***J.F. Weaver****, A.L. Gerrard, J.J. Chen,* University of Florida

The oxidation of Pt(111) by an atomic oxygen beam has been investigated as a function of surface temperature using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (ELS). For oxygen coverages below about 0.50 ML (where 1 ML = 1.5 x 10@super 15@cm@super -2@), the rate of atomic oxygen adsorption is found to be insensitive to surface temperature over the range from 150 to 450 K. After 0.5 ML of atomic oxygen is adsorbed, the oxidation rate decreases with decreasing temperature, and the oxygen coverage saturates at values that also decrease with decreasing temperature. At the highest temperature investigated (450 K), the oxygen coverage at saturation is about 2 ML, whereas only 0.25 ML can be generated by dissociatively adsorbing O@sub 2@ on Pt(111) in ultrahigh vacuum. The mechanism for Pt(111) oxidation involves the initial formation of a chemisorbed layer, within which the oxygen atoms experience significant repulsive interactions after the coverage is increased above 0.25 ML. Long-range order in the high-coverage adsorbed layer could not be observed with LEED. At each surface temperature investigated, islands of platinum oxide begin to form after the oxygen coverage exceeds about 0.5 ML. TPD and ELS data suggest that the oxide islands grow three-dimensionally at surface temperatures ranging from 150 to 450 K, and that their formation is accompanied by the regeneration of metallic regions on which additional oxygen adsorbs and subsequently incorporates into growing islands. The kinetics of the oxidation process and the reactivity of the surface oxygen phases will also be discussed.

10:00am **SS1-WeM6 Thermodynamically Controlled Self-Assembly of Oxide Nanostructures@footnote *@***,* ***F.P. Netzer****, J. Schoiswohl, M Sock,* University of Graz, Austria*; G. Kresse,* University of Vienna, Austria*; S. Surnev, M.G. Ramsey,* University of Graz, Austria

The fabrication of surface-supported nanoscale oxide materials in low dimensions via a chemically driven self-assembly process of novel oxide cluster molecules is reported. As opposed to usual molecular self-assembly, where the construction units are deposited directly from the gas phase, the oxide building blocks with a unique stoichiometry and structure form spontaneously on a Rh(111) metal surface. These can be organised into different two-dimensional oxide structures by careful adjustment of the chemical potential of oxygen µ@subO@, allowing the controlled design of oxide nanostructures on a metal surface. This is demonstrated by following, at the atomic level, the formation and aggregation of planar vanadium oxide V@sub6@O@sub12@ clusters. The planar V@sub6@O@sub12@ cluster molecules form under appropriate conditions of µ@subO@ and of the vanadium concentration at the Rh(111) surface. The structure and stability of these hexagonal V@sub6@O@sub12@ clusters have been elucidated by STM and density functional theory (DFT) calculations. The V@sub6@O@sub12@ structures do not exist in the gas phase and constitute a novel kind of cluster material, that is stabilised by the metal-cluster interface. The V-oxide clusters are mobile at elevated temperature and their surface diffusion has been studied in variable-temperature STM experiments: the diffusion parameters indicate diffusion of the entire clusters. The V@sub6@O@sub12@ units can be organised by self-assembly into different 2D oxide structures, depending on µ@subO@. The assembly process occurs via a reductive or oxidative condensation process, which involves strong chemical bonding interactions with partly covalent and ionic character. Nevertheless, the here reported aggregation is reversible, and by adjustment of µ@subO@ and the Rh surface temperature the V@sub6@O@sub12@ clusters can be regenerated from the oxide islands by 2D re-evaporation. @FootnoteText@ @footnote *@ Work supported by the Austrian Science Funds.

10:20am **SS1-WeM7 STM/AFM Study of WO@sub 3@ Cluster Growth on Highly-Oriented Pyrolitic Graphite***,* ***O. Bondarchuk,*** University of Texas at Austin*; Z. Dohnalek, B.D. Kay, J. Kim,* Pacific Northwest National Laboratory*; J.M. White,* University of Texas at Austin

With the ultimate goal of understanding the catalytically activity of WO@sub 3@ clusters supported on oxide surfaces, we have investigated WO@sub 3@ deposition on highly-oriented pyrolitic graphite (HOPG) using in-situ scanning probes. Our efforts were aimed at understanding how the WO@sub 3@ cluster size and morphology depend on deposited amount and substrate temperature. In this work we have studied tungsten oxide films grown on HOPG substrate at temperatures ranging from 300 to 650 K and having thickness from submonolayer up to ~1 µm. STM images of WO@sub 3@clusters formed from submonolayer WO@sub 3@ deposition at room temperature show fractal-like shape. This shape suggests that a diffusion-limited aggregation mechanism governs the growth. Scanning tunneling spectroscopy indicates that the WO@sub 3@ clusters are semiconducting in nature. Tip induced effect leading to complete removal of WO@sub 3@ clusters from HOPG are observed upon extended scanning. In contrast, non-contact AFM imaging does not does not perturb the WO@sub 3@clusters. Possible mechanisms of the tip induced removal of WO@sub 3@ on HOPG will be discussed. Deposition of a submonolayer amount of WO@sub 3@ at ~ 600 K leads to the formation of WO@sub 3@ needle like crystallites of relatively uniform width (~15-20 nm) and length (~100-300 nm). The crystallites are mostly attached to the steps indicating that steps are the preferred nucleation centers. The needle-like growth of WO@sub 3@ crystallites persists even for thicker deposits (~ 1 µm). Ex-situ X-ray diffraction (XRD) analysis performed on thick films suggests that the WO@sub 3@ crystals have cubic symmetry. @FootnoteText@ Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

10:40am **SS1-WeM8 Surface and Interface Analysis of MgxZn1-xO for Cubic, Hexagonal and Intermediate Phases by X-Ray Photoelectron and Rutherford Back Scattering Spectroscopies***, S. Hullavarad,* University of Maryland*; R. Vispute,* Bluewave Semiconductors, Inc.*; S. Dhar, T. Venkatesan, **I. Takeuchi**,* University of Maryland

MgZnO has attracted increased attention for its unique properties of existence in multiphases either in hexagonal for 0<Mg<0.35 or cubic for 0.35<Mg<1 in MgxZn1-xO. This material is of significant importance for various applications in flame sensors, UV index monitors and missile plume detection. The presence of Mg with a composition of 0-100% in ZnO lead to higher bandgaps ranging from 3.6eV to 7.8 eV of resulting MgZnO. This allows picking up desired Mg composition corresponding to suitable UV sensitive window and growing on lattice matched substrate. In this study we have picked up three Mg compositions representing hexagonal, cubic and intermediate regions. The samples are characterized by X-Ray Diffraction, Rutherford Back Scattering techniques for crystalline quality, and composition of the films. UV-Visible spectroscopy is used for analyzing the optical property of MgZnO films. In this work we emphasize the role of surface and interface in quality of material from crystal structure, grain boundary related defects and the cumulative effect on devices fabricated on such materials by surface sensitive study carried out using X-Ray Photoelectron and interface study by Rutherford Back Scattering spectroscopy.

11:00am **SS1-WeM9 Novel Stages of Growth of Metal Oxide Nanodots: Cu2O on SrTiO3(100)@footnote 1@***, **I. Lyubinetsky**, A.A. El-Azab, A.S. Lea, S.T. Thevuthasan, D.R. Baer,* Pacific Northwest National Laboratory

Although similar to semiconductor nanostructures in some ways, oxide nanodots have been observed in greater structural variations. Here we report on a significant difference in the growth process which exhibits novel stages. Self-assembled formation of the crystalline cuprous oxide (Cu2O) nanodots on the SrTiO3(100) substrate has been carried out using oxygen plasma assisted MBE and evaluated by XPS, AES, XRD and AFM. Selective formation of the nanodots of single Cu2O-phase occurs only in a very narrow growth parameter window, in comparison with the bulk phase diagram. Formation of Cu2O nanoclusters (with the size range of 10-50 nm) may be described as progressing through several stages. Unlike lattice-mismatched heteroepitaxy in the majority of semiconductor systems, initial stages of the growth of oxide nanodots proceed without formation of the wetting layer. Already at sub-monolayer coverages, small, truncated square Cu2O dots start to form. At next, novel stage a continued deposition leads to increase of the dot density, not the size, and results in reaching a critical dot density, upon which larger nanoclusters start to grow. Resulting morphology consists of large islands on top of the closed-packed layer of the small nanodots. Using a kinetic model of film morphology development, we show that the larger island formation can be caused by small dot coalescence, driven by fluctuation of island-island separation at increased dot density. Under different surface conditions of the SrTiO3(100) substrate (high temperature annealed, perfect TiO2-terminated surface vs. original mixed-terminated surface) significant differences in the uniformity of the nanodot distribution have been observed. @FootnoteText@ @footnote 1@ This work was jointly supported by the Department of Energy (DOE), Basic Energy Sciences Division and the Laboratory Directed Research and Development at PNNL, which is operated by Battelle for the DOE.

11:20am **SS1-WeM10 Surface Stability of Epitaxial SrRuO@sub 3@ Films***, **A.P. Baddorf**,* Oak Ridge National Laboratory*; J. Shin,* The University of Tennessee*; S.V. Kalinin,* Oak Ridge National Laboratory*; R.G. Moore,* The University of Tennessee*; H.N. Lee, H.M. Christen,* Oak Ridge National Laboratory*; E.W. Plummer,* The University of Tennessee

Strontium ruthenium oxide, SrRuO@sub 3@, may play an important role in oxide electronic devices because of its metallic nature and lattice constant compatible with many transition metal oxide perovskites. Use in device fabrication requires excellent surface and interface stability without reduction or loss of volatile oxides. Thin films of SrRuO@sub 3@ appear to be quite stable, retaining their crystalline nature, as observed with electron diffraction, even after exposure to atmosphere. Surprisingly, this stability disappears after annealing in vacuum to only 200@degree@C. We have studied the surface stability of epitaxial SrRuO@sub 3@ films using a combination of electron spectroscopies, diffraction, and scanning probe microscopy. Epitaxial SrRuO@sub 3@ thin films were grown by pulsed laser deposition using a stoichiometric target on (001) SrTiO@sub 3@ substrates. Atomic force microscopy images taken in air confirm the high quality of the films, showing uniformly spaced terraces with single steps on the film surface, which closely imitate those of the SrTiO@sub 3@ substrate. After reinsertion into vacuum, a (1x1) Low Energy Electron Diffraction (LEED) pattern has been observed at room temperature, revealing an excellent chemical stability in air. The LEED pattern disappears after a brief anneal in vacuum at 200@degree@C, indicating surface disordering. Films were annealed in high vacuum in steps of 100@degree@C up to 800@degree@C and studied after cooling by LEED, x-ray photoelectron spectroscopy, scanning tunneling microscopy and thermal desorption spectroscopy. Loss of SrO from the surface leads to surface pitting and then balling of metallic Ru at temperatures below 400@degree@C. Vibrational spectroscopy relates this monolayer decomposition to submonolayer concentrations of surface hydrocarbons. Stabilities are compared with in-situ films in a new chamber combining high pressure growth with surface characterization.

11:40am **SS1-WeM11 Effect of Polarization on Reactivity of BaTiO@sub 3@ (100)}***, **J. Garra**, B. Halevi, J. Vohs, D.A. Bonnell,* The University of Pennsylvania

Surface reactivity of ferroelectric compounds is an important component of a new approach to nano lithography, may be an interesting catalytic support, and is indicated in ferroelectric memory failure. In order to examine the relationship between atomic polarization and surface adsorption, reactions with single crystal BaTiO@sub 3@ (100) were characterized by temperature programmed desorption, x-ray photo emission spectroscopy, scanning surface potentiometry, and piezo response force microscopy. Similar to the case of other perovskite oxides, water does not adsorb at room temperature or above unless the surface contains a high density of defects. Adsorption of CO2 on BaTiO3 is more complex than on SrTiO@sub 3@. The domain orientation dependence of these reactions will be discussed in the context of proposed reaction mechanisms.

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