

# Wednesday Morning, October 20, 2010

## Surface Science

Room: Picuris - Session SS1-WeM

## Oxide Surface Structure

Moderator: C.H.F. Peden, Pacific Northwest National Laboratory

8:00am **SS1-WeM1 How Valuable Is Information from *Ab Initio* Phase Diagrams Beyond the Thermodynamically Allowed Region - the Puzzling (1 × 1)-H Structure on Polar ZnO(0001)-Zn**, *M. Valtiner, M. Todorova, J. Neugebauer*, Max-Planck-Institut fuer Eisenforschung, Germany

The (1 × 1) hydrogen reconstruction observed on Zn-terminated polar ZnO(0001) surfaces [1] is a prominent surface structure, which has so far defied any explanation attempts: none of the surface reconstructions observed in *ab initio* based equilibrium surface phase diagrams is consistent with the experimental observations [2]. Extending these equilibrium phase diagrams into the region of non-equilibrium conditions for the hydrogen chemical potential we show the occurrence of a new and so far not reported surface structure. The new structure consists of a (1 × 1) H covered triangular shaped reconstructions. It is stabilised and obeys electron counting, due to a simultaneous protonation of step-edge oxygen and surface terminating Zn atoms. It will be shown that the experimental conditions justify the consideration of hydrogen chemical potential outside the stability range of the H<sub>2</sub> molecule [3].

[1] T. Becker et al., Surf. Sci. 486, L502 (2001).

[2] M. Valtiner et al., Phys. Rev. Lett. 103, 065502 (2009).

[3] M. Valtiner et al., submitted (2010).

8:20am **SS1-WeM2 Hydroxylation of the MgO(001) Surface and its Effect on Metal Nucleation**, *M. Brown, E. Carrasco, M. Sterrer, H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The water-oxide interaction is of great importance in a number of technologically relevant fields, among them heterogeneous catalysis. Several studies report on the promoting effect of water in catalytic reactions, the participation of surface hydroxyls in reaction mechanisms, and the influence of hydroxylation on the binding of metals to oxide surfaces. Achieving a fundamental atomic scale understanding of water-oxide interaction at environmentally and catalytically relevant conditions (e.g. ambient pressure) represents, therefore, a challenge for surface science studies related to heterogeneous catalysis. Here, we present a detailed study of water interaction with the surface of thin MgO films in a wide pressure range and the effect of surface hydroxylation on metal nucleation.

Adsorption of water on the surface of MgO(001) thin films of different thickness (2-20 ML) has been studied extensively from UHV to mbar pressure conditions using IRAS, XPS and TDS. Hydroxylation studies at room temperature were carried out in a high pressure cell up to water pressures of 1 mbar. The hydroxylation behavior of thick MgO films obtained from analysis of the O1s photoemission signal is comparable to MgO(001) single crystal studies showing a threshold pressure of 10<sup>-3</sup> mbar H<sub>2</sub>O for hydroxylation. With decreasing MgO film thickness the threshold pressure gradually shifts to lower H<sub>2</sub>O pressures. In the limit of 2 ML MgO it is three orders of magnitude lower than for thick MgO films. Corresponding IR spectra confirm the enhanced reactivity of thin MgO films at high pressure conditions. The influence of surface hydroxylation on nucleation and sintering of gold nanoparticles was studied by comparison of Au deposition and thermal sintering on ideally terminated MgO(001) and hydroxylated MgO thin films, respectively. A combination of different spectroscopic techniques (TDS, XPS, IRAS) allows to establish a correlation between the degree of surface hydroxylation and the stability of gold atoms and clusters. Hydroxyl groups destabilize gold atoms on the MgO surface at 90 K; however, they enhance the stability of small gold clusters towards sintering at higher temperatures.

8:40am **SS1-WeM3 First, Find the Atoms: Mapping Epitaxial Nanostructures with Direct X-ray Methods**, *R. Clarke*, University of Michigan, Ann Arbor **INVITED**

9:20am **SS1-WeM5 W-oxide Clusters on Cu(110) Surfaces: Electronic Structure and Selforganisation**, *M. Wagner, A. Gumbsch, S. Surnev*, Karl-Franzens University Graz, Austria, *Z. Dohnalek*, Pacific Northwest National Laboratory, *A. Fortunelli*, CNR Pisa, Italy, *F.P. Netzer*, Karl-Franzens University Graz, Austria

Oxide clusters with well-defined size and stoichiometry supported on metal surfaces are interesting nanoscale objects with attractive features for both fundamental research and technological applications. It has been shown recently that (WO<sub>3</sub>)<sub>3</sub> cluster molecules, formed by vacuum sublimation of WO<sub>3</sub> powder, can be deposited as monodisperse clusters on TiO<sub>2</sub> (110) surfaces [1]. In the present work, we investigate the interaction and electronic properties of (WO<sub>3</sub>)<sub>3</sub> species at the single molecule level with Cu(110) and reconstructed Cu(110)-O surfaces using low-temperature (5K) scanning tunneling microscopy (STM) and spectroscopy (STS). In order to decouple the (WO<sub>3</sub>)<sub>3</sub> cluster states from the metal substrate states, the clusters have been deposited also on a NaCl buffer layer (grown on Cu(110)). The comparison of the STM (STS) fingerprints of the (WO<sub>3</sub>)<sub>3</sub> clusters on the NaCl and the Cu surfaces, together with respective DFT calculations, allows us to gauge the cluster-Cu interaction and to determine the hybridisation of the cluster orbitals with metal states. At low temperature (<20K) the (WO<sub>3</sub>)<sub>3</sub> clusters are stable as individual units on the Cu(-O) surfaces, but at elevated temperature (room temperature and above) the clusters react with Cu substrate atoms. They selforganise via condensation and, depending on the coverage, form 1-D W-oxide line structures (nanowires) or arrange into ordered 2-D W-oxide nanolayer phases with well-defined atomic structures. These 2-D structures are investigated experimentally with STM and LEED and theoretically by DFT calculations.

Supported by the ERC Advanced Grant SEPON

[1] O. Bondarchuk, X. Huang, J. Kim, B.D. Kay, L.-S. Wang, J.M. White, Z. Dohnalek, Angew. Chem. Int. Ed. 45 (2006) 4786

9:40am **SS1-WeM6 Growth and Properties of Iron Oxides on YSZ(001)**, *I. Ermanoski, G.L. Kellogg*, Sandia National Laboratories

We have used low energy electron microscopy (LEEM) to study in real time the growth of iron oxides on the (001) surface of yttria-stabilized zirconia - YSZ(001). The Fe<sub>x</sub>-YSZ system is currently used as a working material for solar thermochemical splitting of H<sub>2</sub>O and CO<sub>2</sub> [1], but little fundamental information is available concerning the structure and composition of the mixed oxides and their surfaces. Upon Fe deposition in ~10<sup>-6</sup> Torr of O<sub>2</sub> background pressure, iron oxides grow on the surface. Observation of low energy electron diffraction (LEED) patterns during growth shows the development of 3 distinct patterns with 12-fold symmetry, and one pattern with 4-fold symmetry. Dark field LEEM imaging shows a complicated domain structure where each of the 12-fold patterns corresponds to 2 or 4 rotationally equivalent domains. Some of the domains overlap laterally, pointing to a layered arrangement of different oxide structures. We use LEEM I-V and LEED to determine the oxide composition (hematite, magnetite, wüstite) and surface structure, both of which depend on the layer thickness, substrate temperature, and background oxygen pressure.

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC0494AL85000. Funding for this work was provided through Sandia's LDRD Office.

[1] Diver, R.B., Miller, J.E., Allendorf, M.D., Siegel, N.P., Hogan, R.E., "Solar thermochemical water-splitting ferrite-cycle heat engines", Journal of Solar Energy Engineering, 130 (2008) 041001

10:40am **SS1-WeM9 Growth and Characterization of Ordered Tungsten Trioxide Films on Pt(111)**, *Z. Li, Z. Zhang, Y.K. Kim, S. Smith*, Pacific Northwest National Laboratory, *F.P. Netzer*, Karl-Franzens University Graz, Austria, *R.J. Rousseau, B.D. Kay, Z. Dohnalek*, Pacific Northwest National Laboratory

Catalysts based on WO<sub>3</sub> have been found to be active in a number of reactions including isomerization of alkanes and alkenes, partial oxidation of alcohols, selective reduction of nitric oxide, and metathesis of alkenes. In the present study we explore the growth of novel ordered WO<sub>3</sub> thin films on Pt(111) via direct sublimation of monodispersed (WO<sub>3</sub>)<sub>3</sub> clusters. The prepared films are characterized using x-ray photoelectron spectroscopy

(XPS), temperature-programmed desorption (TPD), low energy electron diffraction (LEED), reflection-adsorption infrared spectroscopy (RAIRS), and scanning tunneling microscopy (STM). The factors that affect the  $\text{WO}_x$  structure such as  $\text{WO}_3$  exposure and substrate temperature were explored. At submonolayer coverages, the as-deposited  $(\text{WO}_3)_3$  clusters are partially reduced leading to chainlike tungsten oxide structures with W in (6+) and (5+) oxidation states. Higher substrate temperatures ( $< 800$  K) lead to further reduction of deposited  $(\text{WO}_3)_3$ . At higher coverages, an ordered  $(3 \times 3)$  structure composed of  $(\text{WO}_3)_3$  trimers is observed upon 700 K deposition. The experimental findings are complemented by DFT calculations that provide further insight into the observed  $\text{WO}_3$  structures.

This research was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

11:00am **SS1-WeM10 Towards a Reliable Characterisation of Oxide Layers on Pure Aluminium using High Energy Resolution FE-AES**, *I. Vandendael, T. Hauffman, Y. Van Ingelgem, A. Hubin, H. Tarryn*, Vrije Universiteit Brussel, Belgium

$\text{Al}_2\text{O}_3$  on metallic aluminium is a widely used material of high technological importance. For the local chemical characterisation of these substrates FE-AES bears potential thanks to its high lateral resolution. In this study, the O KLL and Al KLL Auger electron spectral lines are recorded with a high energy resolution from pure aluminium, thin  $\text{Al}_2\text{O}_3$  and thick  $\text{Al}_2\text{O}_3$  layers on metallic aluminium. The behaviour of these aluminium oxide layers under electron beam irradiation is investigated.

It is demonstrated that, thanks to the high energy resolution used, it is possible to discriminate between the metallic and oxidised aluminium on the basis of the  $\text{Al}_0$   $\text{KL}_{2,3}\text{L}_{2,3}$  and  $\text{Al}^{3+}$   $\text{KL}_{2,3}\text{L}_{2,3}$  Auger electron peaks recorded within one and the same spectrum. Oxygen electron-stimulated desorption is observed for both aluminium oxides. Effective cross-sections for this oxygen desorption are estimated for the thin and thick oxide layers. It is shown that when an  $\text{Al}_2\text{O}_3$  layer is irradiated with an electron beam surface charging occurs. These phenomena remain limited thanks to the presence of the underlying metallic aluminium substrate. The electron beam-induced effects are compensated by setting the angle of incidence of the primary electron beam to  $15^\circ$ . Finally, it is shown that inhomogeneities at the surface of the analysed oxides result in significant chemical shifts of the O KLL and Al KLL Auger electron transitions. It is investigated whether these inhomogeneities can be linked with lateral differences in hydroxyl fraction at the surface.

# Authors Index

**Bold page numbers indicate the presenter**

**— B —**

Brown, M.: SS1-WeM2, **1**

**— C —**

Carrasco, E.: SS1-WeM2, **1**

Clarke, R.: SS1-WeM3, **1**

**— D —**

Dohnalek, Z.: SS1-WeM5, **1**

Dohnálek, Z.: SS1-WeM9, **1**

**— E —**

Ermanoski, I.: SS1-WeM6, **1**

**— F —**

Fortunelli, A.: SS1-WeM5, **1**

Freund, H.-J.: SS1-WeM2, **1**

**— G —**

Gumbsch, A.: SS1-WeM5, **1**

**— H —**

Hauffman, T.: SS1-WeM10, **2**

Hubin, A.: SS1-WeM10, **2**

**— K —**

Kay, B.D.: SS1-WeM9, **1**

Kellogg, G.L.: SS1-WeM6, **1**

Kim, Y.K.: SS1-WeM9, **1**

**— L —**

Li, Z.: SS1-WeM9, **1**

**— N —**

Netzer, F.P.: SS1-WeM5, **1**; SS1-WeM9, **1**

Neugebauer, J.: SS1-WeM1, **1**

**— R —**

Rousseau, R.J.: SS1-WeM9, **1**

**— S —**

Smith, S.: SS1-WeM9, **1**

Sterrer, M.: SS1-WeM2, **1**

Surnev, S.: SS1-WeM5, **1**

**— T —**

Terryn, H.: SS1-WeM10, **2**

Todorova, M.: SS1-WeM1, **1**

**— V —**

Valtiner, M.: SS1-WeM1, **1**

Van Ingelgem, Y.: SS1-WeM10, **2**

Vandendael, I.: SS1-WeM10, **2**

**— W —**

Wagner, M.: SS1-WeM5, **1**

**— Z —**

Zhang, Z.: SS1-WeM9, **1**