

## Surface Science

Room: 201 A - Session SS+AS-TuM

## Synthesis, Structure and Characterization of Oxides

Moderator: Z. Dohnalek, Pacific Northwest National Laboratory

8:00am **SS+AS-TuM1 Low-Energy Electron Microscopy (LEEM) Studies of Langmuir-Blodgett (LB) Deposited Titania Films for Electrochemical Energy Storage**, C.K. Chan, L.B. Biedermann, Sandia National Laboratories, A.G. Dylla, The University of Texas at Austin, G.L. Kellogg, Sandia National Laboratories, K.J. Stevenson, The University of Texas at Austin

Nanostructured titania is a promising anode in Li-ion batteries because of its higher operating potential and minimal solid-electrolyte interphase formation. The TiO<sub>2</sub>(B) polymorph has an open crystal structure, and TiO<sub>2</sub>(B) nanosheets (NS) have higher surface areas to facilitate faster lithiation kinetics. Structure-dependent lithiation energetics and dynamics have been inferred from rate-dependent cyclic voltammetry, but the underlying mechanisms for this dependence have not been directly measured. We aim to apply low-energy electron microscopy (LEEM) to directly image real-time lithium nucleation and migration on the surfaces of TiO<sub>2</sub>(B)-NS, and to correlate these behaviors with fundamental chemical and electronic structure properties of the Li/TiO<sub>2</sub>(B)-NS system. These studies require well-ordered "molecularly flat" TiO<sub>2</sub>(B)-NS layers, but obtaining these ideal NS assemblies is challenging due to the tendency of nanomaterials to reduce free energy by minimizing surfaces. TiO<sub>2</sub>(B)-NS generally accomplish this by folding to form nanoclusters. We solved this problem by suspending TiO<sub>2</sub>(B)-NS in a spreading solvent, depositing the TiO<sub>2</sub>(B)-NS across a liquid subphase, and transferring them onto substrates by Langmuir-Blodgett (LB) technique. After investigating various spreading solvents and subphases, the best conformal films were obtained using TiO<sub>2</sub>(B)-NS suspended in TBAOH/water or TBAOH/methanol, and deposited on a water subphase. TiO<sub>2</sub>(B)-NS were capped by residual ethylene glycol (EG) from their synthesis procedure, and a surfactant like TBAOH was likely required to displace the EG and stabilize the unfolded TiO<sub>2</sub>(B) sheets. TiO<sub>2</sub>(B)-NS were deposited by LB technique onto multicrystalline Au substrates. Imaging of these thin conformal films were difficult with standard SEM and AFM techniques, but LEEM showed large areas of densely packed nanosheets with discrete intensity steps. Electron reflectivity spectra was used to identify distinct TiO<sub>2</sub>(B)-NS regions, where the discrete intensity steps corresponded to discrete increases in the TiO<sub>2</sub>(B)-NS layer thickness. Low-energy electron diffraction (LEED) patterns of TiO<sub>2</sub>(B)-NS deposited by TBAOH/water on water indicated rotational disorder in TiO<sub>2</sub>(B) sheets, with a 1.65 Å<sup>-1</sup> diffraction ring consistent only with the (01) spacing of anatase. We believe that TBAOH acts as a surfactant to displace the protective EG capping ligand surrounding the TiO<sub>2</sub>(B)-NS clusters, allowing the nanosheets to unfold. The resulting water ingress facilitates transformation of the metastable TiO<sub>2</sub>(B) phase to the thermodynamically stable anatase phase. Preliminary results of *in situ* surface lithiation of TiO<sub>2</sub>-NS will also be discussed.

8:40am **SS+AS-TuM3 Reactions on the Rutile TiO<sub>2</sub>(110) Surface Studied by High-resolution STM and TPD**, S. Wendt, Aarhus University, Denmark **INVITED**

In this talk, I will summarize surface science studies conducted at the iNANO center addressing a prototypical model oxide system – the rutile TiO<sub>2</sub>(110)-(1 × 1) surface. The identification of point defects on the terraces such as oxygen vacancies, hydroxyl groups, and near surface defect such as Ti interstitials will be discussed. Using high-resolution scanning tunnelling microscopy (STM) several examples for reaction of molecules with oxygen vacancies will be presented [1]. These reactions were directly imaged in so-called STM movies. Whereas the reactions on the terraces can be imaged directly, a combination of static STM results with temperature-programmed desorption (TPD) measurements was used to study the reactions at step edges, with the focus particularly on the <1-11> step edges [2,3]. Both, for the reaction on the terraces and at the step edges, water and ethanol were used as probe molecules [1-3]. Accompanying density functional theory (DFT) calculations support the assignments made in the STM studies. In addition, I will address the complex oxygen-TiO<sub>2</sub>(110) interaction [4]. Specifically, the role of bulk defects in the oxygen chemistry on reduced rutile TiO<sub>2</sub>(110) is highlighted. Finally, I will show that these surface science studies help to improve our understanding of TiO<sub>2</sub> as photocatalysts. Specifically, the photo-reaction of ethanol on differently prepared TiO<sub>2</sub>(110) surfaces will be compared.

[1] J. Ø. Hansen, P. Huo, U. Martinez, E. Lira, Y.Y. Wei, R. Streber, E. Lægsgaard, B. Hammer, S. Wendt, F. Besenbacher, Phys. Rev. Lett. **107**, 136102 (2011).

[2] U. Martinez, J. Ø. Hansen, E. Lira, H. H. Kristoffersen, P. Huo, R. Bechstein, E. Lægsgaard, F. Besenbacher, B. Hammer, S. Wendt, Phys. Rev. Lett. **109**, 155501 (2012).

[3] H. H. Kristoffersen, J. Ø. Hansen, U. Martinez, Y.Y. Wei, J. Mathiessen, R. Streber, R. Bechstein, E. Lægsgaard, F. Besenbacher, B. Hammer, S. Wendt, Phys. Rev. Lett. **101**, 146101 (2013).

[4] S. Wendt, P. T. Sprunger, E. Lira, G. K. H. Madsen, Z. Li, J. Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, F. Besenbacher, Science **320**, 1755 (2008).

9:20am **SS+AS-TuM5 Atomic Structures on BaTiO<sub>3</sub> (001): Reconstructions, Step Edges and Domain Boundaries**, E.H. Morales, D.A. Bonnell, J.M. Martinez, University of Pennsylvania, W.A. Al-Saidi, University of Pittsburgh, A.M. Rappe, University of Pennsylvania

BaTiO<sub>3</sub> is a ferroelectric material that finds applications in a range of traditional and emerging devices. Understanding the surface is prerequisite to controlling interactions during device processing, potential for surface mediated device properties and surface chemical reactions.

Here we present scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of atomically resolved reconstructions on BaTiO<sub>3</sub> (001) surfaces,  $\sqrt{5} \times \sqrt{5} R26.6^\circ$  and  $\sqrt{2} \times \sqrt{2}$ ,  $C(4 \times 4)$ , and  $\sqrt{13} \times \sqrt{13} R33.7^\circ$ . We experimentally show the coexistence of two reconstructions  $\sqrt{2} \times \sqrt{2}$  and  $C(4 \times 4)$  while DFT calculations indicate that  $C(4 \times 4)$  is a thermodynamically favorable phase, the  $\sqrt{2} \times \sqrt{2}$  persists due to a more kinetically favorable path of formation. The structures of the boundaries between the two reconstructions is determined. In the case of the  $\sqrt{5} \times \sqrt{5} R26.6^\circ$  surface a comparison of electronic structure determined by STS with theoretical calculations shows that the surface is Ti terminated. In this and other reconstructions Ti-ad atoms create filled and empty states that are imaged in STM. We will briefly discuss a complete BaTiO<sub>3</sub> (001) phase diagram and the influence to Ti adatoms in the choice of step edge direction in the case of the various surface reconstructions mentioned above.

9:40am **SS+AS-TuM6 Growth and Optical Properties of Cr- and V-Doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Epitaxial Thin Films**, S.E. Chamberlin, Y. Wang, T.C. Kaspar, M.E. Bowden, Pacific Northwest National Laboratory, A.W. Cohn, D.R. Gamelin, University of Washington, P.V. Sushko, University College London, S.A. Chambers, Pacific Northwest National Laboratory

There is widespread interest in discovering materials that can effectively harvest sunlight in the visible region of the solar spectrum in order to drive chemical processes on surfaces. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has received renewed interest recently as the active photoanode in photoelectrochemical water splitting to store solar energy as H<sub>2</sub> [1]. Hematite is very abundant, has a narrow bandgap of 2.1 eV, and is stable in aqueous and oxidizing environments. However, it has extremely poor electron and hole mobilities, which results in short hole diffusion lengths and ultrafast recombination of photogenerated e<sup>-</sup> - h<sup>+</sup> pairs. Additionally, it does not efficiently absorb photons in the 500-600 nm range where the solar spectrum is most intense. The utility of hematite could therefore be significantly increased by red shifting its band gap to harvest more of the solar spectrum.

Escolaite ( $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>) has a band gap of 3.3 eV, but alloying Cr and Fe to make  $\alpha$ -(Fe<sub>1-x</sub>Cr<sub>x</sub>)<sub>2</sub>O<sub>3</sub> solid solutions as epitaxial films has been found to result in a reduction in gap down to as low as ~1.7 eV at x = ~0.5 [2,3]. We examine the optical absorption in  $\alpha$ -(Fe<sub>1-x</sub>Cr<sub>x</sub>)<sub>2</sub>O<sub>3</sub> thin films grown by oxygen-plasma-assisted molecular beam epitaxy (OPA-MBE) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates and explain the observed excitations, and the nature of the band gap dependence on x, through first principles calculations. Photoconductivity (PC) measurements show that the onset of photocurrent decreases by nearly 0.5 eV when x is increased from 0 to ~0.4. However, for x > ~0.6, the films are not sufficiently conductive for PC to be measured.

Karelianate ( $\alpha$ -V<sub>2</sub>O<sub>3</sub>) is weakly metallic at room temperature, so  $\alpha$ -(Fe<sub>1-x</sub>V<sub>x</sub>)<sub>2</sub>O<sub>3</sub> films may overcome the conductivity challenges of the  $\alpha$ -(Fe<sub>1-x</sub>Cr<sub>x</sub>)<sub>2</sub>O<sub>3</sub> system. Substitutional V impurities have also recently been predicted to lower the band gap of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> further than that of Cr-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [4]. Heteroepitaxial thin films of  $\alpha$ -(Fe<sub>1-x</sub>V<sub>x</sub>)<sub>2</sub>O<sub>3</sub> were deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates by OPA-MBE. Film quality was monitored *in situ* by reflection high energy electron diffraction (RHEED). *In situ* x-ray photoemission spectroscopy (XPS) was utilized to characterize the charge states of the cations. Film crystallinity and lattice parameters were determined *ex situ* by high resolution x-ray diffraction (HRXRD). The

effects of the doping concentration on the conductivity and optical properties will be discussed.

- [1] K. Sivula *et al.*, *Chemoschem* **4**, 432 (2011).
- [2] H. Mashiko, *et al.*, *Appl. Phys. Lett.* **99**, 241904 (2011).
- [3] S.E. Chamberlin *et al.*, *J. Phys. Chem. Lett.*, submitted (2013).
- [4] Z.D. Pozun and G. Henkelman, *J. Chem. Phys.* **134**, 224706 (2011).

10:40am **SS+AS-TuM9 Growth of Oxide Nanowires on Vicinal Metal Surfaces: Atom Exchange Processes at Step Edges**, *L. Ma, A. Picone, M. Wagner, S. Surnev*, Karl-Franzens University, Austria, *G. Barcaro, A. Fortunelli*, CNR-IPCF, Italy, *F.P. Netzer*, Karl-Franzens University, Austria

Low-dimensional model systems are of fundamental importance to elucidate emergent phenomena in condensed matter physics and chemistry. Here we present 1-dimensional oxide-metal hybrid model systems, Co-oxide and Mn-oxide nanowires coupled to a Pd surface, which have been fabricated by the decoration of steps of a vicinal Pd(100) surface. We have studied the growth of Co-oxide and Mn-oxide nanostructures on a Pd(1 1 23) surface using LEED and STM, and have probed their electronic properties by STS in a low-T (5K) STM. At low oxide coverages and suitable kinetic conditions, the Pd step edges are decorated by oxide nanostripes, while the Pd(100)-like terraces are covered by a (2x2) layer of chemisorbed oxygen (as a result of the reactive metal oxide deposition procedure). However, there are significant structural differences between Co- and Mn-oxide nanowires: whereas Mn-oxide decorates the Pd steps by monoatomic MnO<sub>x</sub> lines in a pseudomorphic (1x1) arrangement, Co-oxide grows in form of 2-4 atom-wide CoO<sub>x</sub> nanostripes, with a strained hexagonal structure partially embedded into the outer terrace areas. In addition, rod-like structures attached to the CoO<sub>x</sub> step edges are periodically observed, which have been identified by STS as rows consisting of 4±1 Pd atoms that have been ejected from the Pd steps. This indicates that Co-Pd atom exchange at the step edges is a dominant feature during oxide step decoration and growth. The absence of such structures on the MnO<sub>x</sub> covered Pd(1 1 23) surface demonstrates that Mn-Pd atom exchange is much less pronounced, thus revealing a significant difference in growth behavior between MnO<sub>x</sub> and CoO<sub>x</sub> nanostructures and in their interactions with Pd surfaces.

Work supported by the ERC Advanced Grant SEPON.

11:00am **SS+AS-TuM10 Surface Structure of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>(0001) by X-ray Photoelectron Diffraction after Activated Oxygen Exposure**, *T.C. Kaspar, S.E. Chamberlin, S.A. Chambers*, Pacific Northwest National Laboratory

The detailed structure and electronic properties of the surfaces of the corundum-type oxides  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -V<sub>2</sub>O<sub>5</sub>,  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> continue to be of significant interest due to their importance in catalysis, photocatalysis, and environmental chemistry. The surface structure, and thus the properties of the surface, can be dramatically altered with different processing or treatment conditions. Recently, Henderson<sup>1</sup> has shown that the Cr-terminated  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>(0001) surface can be fully passivated by exposure to activated oxygen from an electron cyclotron resonance (ECR) plasma source, blocking both the dissociative and the molecular H<sub>2</sub>O adsorption channels. We use x-ray photoelectron spectroscopy (XPS) and x-ray photoelectron diffraction (XPD) to investigate the surface structure of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>(0001) epitaxial thin films before and after exposure to activated oxygen from an ECR plasma source. The films are deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates by oxygen-plasma-assisted molecular beam epitaxy. When cooled or annealed in vacuum, strong evidence for a Cr-Cr-O<sub>3</sub>-termination is obtained by comparing the Cr<sup>3+</sup> XPD angular scan to single scattering simulations. However, after plasma exposure, a high binding energy feature is observed in the Cr 2p XPS spectrum that possesses an ordered structure distinct from the underlying Cr<sup>3+</sup> of Cr<sub>2</sub>O<sub>3</sub>, which remains Cr-Cr-O<sub>3</sub>-like. Investigation of this new surface structure with simulations of various candidate structures tentatively rules out CrO<sub>2</sub>-like configurations. The high binding energy feature likely arises from a higher oxidation state of Cr, although a quantitative charge state assignment is not straightforward. One possibility is the oxidation of the surface layer of Cr to Cr<sup>6-δ</sup> with a double chromyl structure (O=Cr=O).

1. M. A. Henderson, *Surf. Sci.* **604**, 1502 (2010).

11:20am **SS+AS-TuM11 Preparation and Characterization of Rare Earth Oxide Thin Films on Metal and Silicon Substrates**, *A. Schaefer, J.-H. Jhang*, University of Bremen, Germany, *W. Cartas, S.R. Eperi*, University of Florida, *M.H. Zöllner, IHP*, Germany, *H. Wilkens*, University of Osnabrück, Germany, *T. Schroeder, IHP*, Germany, *J.F. Weaver*, University of Florida, *M. Bäumer*, University of Bremen, Germany

The rare earth oxides (REOs) have potentially versatile applications in heterogeneous catalysis. Catalysis of reactions like dehydrogenation and selective oxidation of organic compounds, methane conversion to syntheses gas or applications in three way catalysis may be mentioned as examples. The versatility of the REOs is based on the ease of valency changes of rare earth metals (change of f-electron configuration) as compared to, e.g., that of d-block elements. In particular, the possible dioxides in the REO series (ceria, praseodymia and terbia) are highly interesting materials for oxidation catalysis due to their ability to easily give off oxygen and switch to different oxidation states. As lattice oxygen participates directly in the molecule-surface reactions (cf. the Mars-van Krevelen mechanism), the selectivity of REO catalysts in oxidation chemistry depends strongly on their oxygen storage/release capabilities. The oxide of samarium for instance, which only forms the sesquioxide Sm<sub>2</sub>O<sub>3</sub>, seems to be the most effective REO catalyst for partial (selective) oxidation of methane.

In the recent years considerable progress has been made in the study of ceria thin films and oxide structures on a variety of transition metal substrates. Surface Science studies of REO films other than ceria are however fairly limited. In this context we will present two approaches to study other complex REOs like samaria, praseodymia and also terbia in ultra high vacuum (UHV). The presentation concerns a more classical approach for the preparation of samaria and terbia on a Pt(111) single crystal by reactive physical vapor deposition. Praseodymia thin films on the other hand were prepared on a Si(111) substrate by molecular beam epitaxy and new routes for adjusting the oxidation state of those films will be presented. By means of plasma treatment, e.g., we achieved to prepare even the dioxide of praseodymium (PrO<sub>2</sub>), a complex oxide which has not been available for UHV studies up to now. In combination with temperature-programmed desorption of oxygen a range of different oxidation states from PrO<sub>2</sub> to Pr<sub>2</sub>O<sub>3</sub> can be adjusted and made accessible for model studies. This concept has been expanded to ceria on Si(111) as well, making it possible to even stabilize the surface of the iota-phase (Ce<sub>7</sub>O<sub>12</sub>), which contains ordered oxygen vacancies, for UHV model studies.

While it is a common concept in microelectronics and adjacent fields to dope and mix

oxides to tune their properties this concept has not yet entered the world of surface

catalytic studies of thin films to a large extent. The talk will close with an outlook and first results on the mixture of REOs for UHV model studies.

11:40am **SS+AS-TuM12 Surface Core Level BE Shifts for MgO**, *C.J. Nelin*, Consultant, *F. Uhl, V. Staemmler*, Ruhr-Universität Bochum, Germany, *P.S. Bagus*, University of North Texas, *H. Kühlenbeck, M. Sterrer, H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We present theoretical and experimental results for the surface core-level shifts, SCLS, of MgO(100). Since MgO is an ideal ionic insulator, [1] one would expect shifts to higher binding energy, BE, for a surface Mg<sup>2+</sup> cation and shifts to lower BE for a surface anion; furthermore, the magnitudes of the shifts of opposite sign should be comparable. This expectation follows from the electrostatics of the different coordination of the bulk and surface atoms. However, we have found that while the Mg(2p) core-level shift is ~+1 eV, as expected, the O(1s) SCLS is almost zero. This unexpected difference between the cation and anion SCLS has been found for a large range of theoretical models for MgO, which include extended embedded cluster models and periodic calculations. The experiments, which also show the different SCLS, were carried out for MgO films on Mo supports. While the electron density of the bulk Mg and O ions and the surface Mg ions have the dominantly spherical shape expected for closed shell species, the distortion of the surface O anions from spherical symmetry is the effect that leads to the different chemical shifts. Thus the SCLS provide another manifestation of the polarizability of the O anions that is associated with the catalytic activity of thin oxide films; see, for example, Ref. [2]. However, in this case the polarization is of the electronic charge density rather than of the geometric structure of the oxide. We analyze the nature of the polarization of the surface O anions and show how this leads to the anomalously small SCLS for these anions. We also consider the broadening of the XPS lines and we relate the Full Width at Half Maximum of the core-levels to the final state geometric modification of bond distances between Mg and O. [3]

1. C. Sousa, T. Minerva, G. Pacchioni, P. S. Bagus, and F. Parmigiani, *J. Electron Spectrosc. Relat. Phenom.* **63**, 189 (1993).

2. H. J. Freund, *Chem. Eur. J.* **16**, 9384 (2010).

3. C. J. Nelin, P. S. Bagus, M. A. Brown, M. Sterrer, and H.-J. Freund,  
*Angew. Chem. Int. Ed.* **50**, 10174 (2011).

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Al-Saidi, W.A.: SS+AS-TuM5, 1

## — B —

Bagus, P.S.: SS+AS-TuM12, 2

Barcaro, G.: SS+AS-TuM9, 2

Bäumer, M.: SS+AS-TuM11, 2

Biedermann, L.B.: SS+AS-TuM1, 1

Bonnell, D.A.: SS+AS-TuM5, 1

Bowden, M.E.: SS+AS-TuM6, 1

## — C —

Cartas, W.: SS+AS-TuM11, 2

Chamberlin, S.E.: SS+AS-TuM10, 2; SS+AS-TuM6, 1

Chambers, S.A.: SS+AS-TuM10, 2; SS+AS-TuM6, 1

Chan, C.K.: SS+AS-TuM1, 1

Cohn, A.W.: SS+AS-TuM6, 1

## — D —

Dylla, A.G.: SS+AS-TuM1, 1

## — E —

Epuri, S.R.: SS+AS-TuM11, 2

## — F —

Fortunelli, A.: SS+AS-TuM9, 2

Freund, H.-J.: SS+AS-TuM12, 2

## — G —

Gamelin, D.R.: SS+AS-TuM6, 1

## — J —

Jhang, J.-H.: SS+AS-TuM11, 2

## — K —

Kaspar, T.C.: SS+AS-TuM10, 2; SS+AS-TuM6, 1

Kellogg, G.L.: SS+AS-TuM1, 1

Kuhlenbeck, H.: SS+AS-TuM12, 2

## — M —

Ma, L.: SS+AS-TuM9, 2

Martirez, J.M.: SS+AS-TuM5, 1

Morales, E.H.: SS+AS-TuM5, 1

## — N —

Nelin, C.J.: SS+AS-TuM12, 2

Netzer, F.P.: SS+AS-TuM9, 2

## — P —

Picone, A.: SS+AS-TuM9, 2

## — R —

Rappe, A.M.: SS+AS-TuM5, 1

## — S —

Schaefer, A.: SS+AS-TuM11, 2

Schroeder, T.: SS+AS-TuM11, 2

Staemmler, V.: SS+AS-TuM12, 2

Sterrer, M.: SS+AS-TuM12, 2

Stevenson, K.J.: SS+AS-TuM1, 1

Surnev, S.: SS+AS-TuM9, 2

Sushko, P.V.: SS+AS-TuM6, 1

## — U —

Uhl, F.: SS+AS-TuM12, 2

## — W —

Wagner, M.: SS+AS-TuM9, 2

Wang, Y.: SS+AS-TuM6, 1

Weaver, J.F.: SS+AS-TuM11, 2

Wendt, S.: SS+AS-TuM3, 1

Wilkens, H.: SS+AS-TuM11, 2

## — Z —

Zöllner, M.H.: SS+AS-TuM11, 2