

## O 56: Oxide Surfaces I

Time: Wednesday 16:00–19:00

Location: H45

O 56.1 Wed 16:00 H45  
**scanning tunneling microscopy study of single-crystalline Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>** — ●BERNHARD STÖGER<sup>1</sup>, ZHIMING WANG<sup>1</sup>, MARCEL HIECKEL<sup>1</sup>, FLORIAN MITTENDORFER<sup>1</sup>, RAIMUND PODLOUCKY<sup>2</sup>, JOSEF REDINGER<sup>1</sup>, DAVID FOBES<sup>3</sup>, ZHIQIANG MAO<sup>3</sup>, MICHAEL SCHMID<sup>1</sup>, and ULRIKE DIEBOLD<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, Vienna University of Technology, Vienna, Austria — <sup>2</sup>Institute for Physical Chemistry, University of Vienna, Austria — <sup>3</sup>Department of Physics and Engineering Physics, Tulane University, New Orleans, LA, USA

Investigating surface defects such as oxygen vacancies and the adsorption of relevant molecules helps gaining more insight into the physics behind solid oxide fuel cells and catalytic processes.

High-quality Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> (SRO) single crystals were grown using the floating zone technique. The SRO samples were cleaved at 100 K under UHV conditions and subsequently investigated by STM at 78 K and 6 K. To determine which species are imaged in STM, doped SRO samples were investigated and STM simulations were performed. Furthermore, we have characterized the defects that are present at the as-cleaved surfaces, and how reactive they are if exposed to CO, O<sub>2</sub> and CO<sub>2</sub>.

CO adsorbs on the perfect surface at the position of the apical oxygen atom. The adsorbed CO can be easily manipulated by the STM tip. At +1 V a reaction takes place which changes the appearance of the adsorbed CO drastically. At +2.7 V the CO molecules start to diffuse on the surface and to desorb. This work was supported by the Austrian Science Fund (FWF project F45).

O 56.2 Wed 16:15 H45  
**Reversible transitions between surface reconstructions on SrTiO<sub>3</sub>** — ●STEFAN GERHOLD, ZHIMING WANG, XIANFENG HAO, MICHAEL SCHMID, and ULRIKE DIEBOLD — Institute of Applied Physics, TU Wien, Austria

SrTiO<sub>3</sub> as an archetypical perovskite oxide has attracted intense interest in diverse fields ranging from fundamental solid-state physics and chemistry, materials science to electronics applications. In all these applications, the surface properties are of vital importance. We study the evolution of surface reconstructions on the SrTiO<sub>3</sub>(110) and (001) surface using STM, LEED, XPS and ISS. Atomically well-defined SrTiO<sub>3</sub>(110) surfaces can be obtained by Ar<sup>+</sup> sputtering and annealing. Mono-phased reconstructions are obtained, and can be transformed into each other reversibly by depositing Sr or Ti followed by annealing. The most commonly-observed SrTiO<sub>3</sub>(110) (4 × 1) reconstruction consists of a layer of TiO<sub>4</sub> tetrahedra, which forms a network of six- and ten-membered rings by corner-sharing oxygen atoms. The mirror symmetry in the six-membered rings is broken along the [1-10] direction, therefore two degenerate anti-parallel (4 × 1) domains are formed. Two types of vacancies are present at domain boundaries. These can be tuned by adjusting the oxygen pressure during annealing; depending on the type of domain boundary different band bending is observed. At the SrTiO<sub>3</sub>(001) surface a reversible change between c(4 × 2), (2 × 2), (1 × 1), and c(2 × 2) reconstructions can also be achieved by evaporating Sr or Ti followed by annealing. This work was supported by the Austrian Science Fund (project F45).

O 56.3 Wed 16:30 H45  
**Reversible transformation between α-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>** — ●FRANCESCA GENUZIO, ALESSANDRO SALA, THOMAS SCHMIDT, and HANS-JOACHIM FREUND — Fritz-Haber-Institut, Abt. CP, 14195 Berlin

The characterization of the properties of iron oxide thin films and their surfaces is a promising research field, considering the variety of applications those materials are interesting for. The peculiarity of this class of oxides is to assume different properties according to their crystal structure, defined both by stoichiometry and preparation. In thin films, in particular, the influence of the substrate on the quality of the supported oxide-surface and on its thermodynamics is still not clear; moreover the phase diagram of these systems can differentiate significantly from that calculated for bulk materials. We present a combined LEEM and LEED study focused on the systematic characterization of the conditions to reversibly transform α-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> thin films on Pt(111) and on Ag(111). Experiments were carried out

with the SMART spectro-microscope, an aberration-corrected energy-filtered LEEM-PEEM system which allows the observation in real time and in situ of the surface with high acquisition rate. A complete characterization of oxidation and reduction of mixed-phase films, as well as the substrate role in such reactions, is discussed.

O 56.4 Wed 16:45 H45  
**Growth of ultrathin samaria films on Pt(111) studied by LEED and STM** — ●J.H. JHANG<sup>1</sup>, A. SCHAEFER<sup>1</sup>, W. CARTAS<sup>2</sup>, J.F. WEAVER<sup>2</sup>, and M. BÄUMER<sup>1</sup> — <sup>1</sup>Institute for Applied and Physical Chemistry, University of Bremen, Germany — <sup>2</sup>Department of Chemical Engineering, University of Florida, USA

Samaria has been considered as a highly selective catalyst for oxidative coupling of methane (OCM). It also exhibits catalytic activity for dehydration reactions, e.g. the decomposition of 2-propanol. Heterocatalytic reactions take place on the surface of catalysts, thus the selectivity and activity of oxide catalysts strongly depend on surface defects, surface structures, and also oxygen storage and release capabilities. While other rare earth oxides like ceria have been studied intensively, detailed surface science studies on samaria are still lacking. In this contribution we report an investigation of ultrathin samaria films grown on a Pt(111) substrate. Samaria films were prepared by physical vapor deposition (PVD) of Sm metal in O<sub>2</sub> (p = 5 × 10<sup>-7</sup> mbar) at 600 K substrate temperature, then post-annealed in O<sub>2</sub> at 1000 K in order to obtain well-ordered samaria structures. The well-ordered structures have been characterized via low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Both LEED and STM results reveal a lattice parameter of the samaria films close to the (111) surface orientation of C-type Sm<sub>2</sub>O<sub>3</sub>. Annealing treatments in UHV caused significant topographic changes to the films, accompanied by the formation of a cubic phase in (001) orientation, most likely SmO, due to partial reduction.

O 56.5 Wed 17:00 H45  
**Dynamic behavior of anti-phase boundaries in the layer-by-layer growth of Fe<sub>3</sub>O<sub>4</sub>(111)/Pt(111) thin films** — ALESSANDRO SALA, HELDER MARCHETTO, ●THOMAS SCHMIDT, and HANS-JOACHIM FREUND — Fritz-Haber-Institut, Abt. CP, 14195 Berlin

The transition-metal oxide Fe<sub>3</sub>O<sub>4</sub> (magnetite) has a wide range of applications in heterogeneous catalysis and magnetism. The kind of preparation influences the film properties; in particular, anti-phase boundaries, i.e. dislocations and rotational domain boundaries, play an active role for the anomalous film resistivity and magnetic susceptibility, and could be a considerable factor in the determination of surface electronic properties. A new preparation recipe has been applied to study in-situ and in-real-time the layer-by-layer growth of a complete Fe<sub>3</sub>O<sub>4</sub>(111) film on Pt(111) with the SMART, the aberration-corrected energy-filtered LEEM/PEEM installed at BESSY II in Berlin. In addition to the usual atomic steps, the oxide surface shows new line defects, which can be interpreted as line dislocations. Furthermore, dark field imaging of the Fe<sub>3</sub>O<sub>4</sub> surface visualize domains rotated by 180° against each other. The formation of the dislocations and the rotations domains and their behavior during growth and annealing are discussed.

O 56.6 Wed 17:15 H45  
**A first-principles view of the Cabrera-Mott Model of Metal Oxidation** — ●ANDERS HELLMAN, JAKUB BARAN, and HENRIK GRÖNBECK — Chalmers, Applied Physics, Göteborg, Sweden

Oxidation of metals is an every-day phenomenon, which can be an unwanted process, e.g., automotive corrosion. However, under controlled conditions oxidation is of enormous practical importance, both in industry and science. The work of Cabrera and Mott (CM) in the mid-twenty century still remains the main theoretical model for growth of thin oxides on metals [1]. Recently, Zhou et al. [2] have experimentally shown that the limiting thickness of the aluminum oxide on Al(111) can be tuned by the oxygen pressure. Our first-principles calculations [3] support many of the key assumptions of the CM model. For instance, based on our results we estimated the limiting thickness of Al<sub>2</sub>O<sub>3</sub> on Al(111) to around 16 Å, which agrees well with the experimental data. Furthermore, the charge transfer to adsorbed oxygen molecules generates a Mott potential which value also agrees well with experimental

estimates. However, the underlying reason for observing a limiting thickness of the protective oxide is not the diminishing effect of the Mott potential. Instead we will provide another underlying reason for the limiting thickness based on our first-principles calculations.

References 1.\*Cabrera, N. and N.F. Mott, Reports on Progress in Physics 12 163 (1948). 2.\*Cai, N., et al., Phys. Rev. Lett. 107 035502 (2011). 3.\*Baran, J., Grönbeck, H., Hellman, A., submitted

O 56.7 Wed 17:30 H45

**Adsorption of Fe on Fe<sub>3</sub>O<sub>4</sub>(111) surfaces** — TOMASZ PABISIAK and ●ADAM KIEJNA — University of Wrocław, Institute of Experimental Physics, Poland

Iron oxides are abundant and important in many geochemical and environmental processes, and technological applications. The chemical reactivity of the oxide surface can be significantly modified by deposition of various species that leads to catalytic activity of such complex. We applied the spin-polarized density functional theory (DFT) and the DFT+*U* method, accounting for the effect of strong on-site Coulomb correlations, to study the submonolayer adsorption of Fe atoms on magnetite (111) surfaces. Adsorption on two stable terminations has been studied: one terminated with iron and the other with oxygen. We have found that the presence of Fe adatom induces large changes in the geometry of magnetite surface. Fe binds strongly to magnetite and the bonding to the O-terminated surface is distinctly stronger than that to the Fe-termination. Structural, electronic and magnetic properties of magnetite surface covered with iron and noble metals [1] are compared and discussed. Similarly as for clean magnetite surface, upon Fe adsorption DFT and DFT+*U* provide qualitatively similar surface geometries but they differ substantially in the prediction of the surface energetics.

[1] A. Kiejna, T. Ossowski, T. Pabisiak, Physical Review B 85 (2012) 125414.

O 56.8 Wed 17:45 H45

**CO Induced Adatom Sintering in a Model Catalyst: Pd/Fe<sub>3</sub>O<sub>4</sub>** — ●ZBYNEK NOVOTNY<sup>1</sup>, GARETH S. PARKINSON<sup>1</sup>, GIACOMO ARGENTERO<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, JIRI PAVELEC<sup>1</sup>, RUKAN KOSAK<sup>2</sup>, PETER BLAHA<sup>2</sup>, and ULRIKE DIEBOLD<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, Vienna University of Technology, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria — <sup>2</sup>Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, 1060 Vienna

The coarsening of catalytically-active metal clusters is often accelerated by the presence of gases through the formation of mobile intermediates. We use scanning tunneling microscopy (STM) to follow the CO induced coalescence of Pd adatoms supported on the Fe<sub>3</sub>O<sub>4</sub>(001) surface at room temperature. Pd-carbonyl species, formed via the so-called 'skyhook' effect, are responsible for Pd mobility in the system. Using time-lapse STM, key steps of cluster nucleation and growth are observed in an atom-by-atom fashion.

This material is based upon work supported as part of the Centre for Atomic-Level Catalyst Design, an Energy Frontier Research Centre funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number #DE-SC0001058.

O 56.9 Wed 18:00 H45

**Water adsorption on ultra-thin ZrO<sub>2</sub>/Pt<sub>3</sub>Zr** — ●JOONG IL JAKE CHOI, HAO LI, CHRISTIAN WEILACH, ULRIKE DIEBOLD, and MICHAEL SCHMID — Technische Universität Wien, Wien, Austria

Despite its importance in many areas of industry such as catalysis, fuel cell technology and microelectronics, the surface properties of ZrO<sub>2</sub> are yet not well understood. We have prepared ultra-thin ZrO<sub>2</sub> films by oxidation of a Pt<sub>3</sub>Zr(0001) crystal [1] and studied adsorption and desorption of water on this surface by STM, XPS and AES. Water on ZrO<sub>2</sub>/Pt<sub>3</sub>Zr(0001) appears as a bright species on STM. Adsorption strongly depends on the structure of the substrate below the oxide; the lowest coverage is found in areas with unreconstructed Pt(111) below the oxide. Depending on the predominant substrate structures, we find a saturation coverage at room temperature between 0.14 and ≈ 0.25 ML with respect to the oxide lattice. The water species are adsorbed on equivalent sites of the oxide lattice, often also in equivalent sites with respect to the alloy substrate, thus influenced by the superstructure lattice (moiré). XPS suggests that the species observed by STM are the hydroxyl group. We have also created stable oxygen vacancies by electron irradiation of the ZrO<sub>2</sub> film and studied the adsorption of H<sub>2</sub>O on this surface with defects.

[1] M. Antlanger et. al., Phys. Rev. B 86, 035451 (2012)

O 56.10 Wed 18:15 H45

**Adsorbed water structures on alkaline earth metal oxide (001) surfaces at realistic conditions: A first-principles study** — ●XUNHUA ZHAO, ERIC HUYNH, SERGEY V. LEVCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem 14195, Germany

Understanding the interaction between water and oxide surfaces is of fundamental importance for basic and engineering sciences. Recently, one-dimensional structures have been observed on CaO(001) in the presence of H<sub>2</sub>O [1]. Such structures have not been reported so far for MgO and SrO. We performed a free-energy-based *ab initio* genetic algorithm and atomistic thermodynamics analysis to find stable structures of water adsorbed on MgO(001), CaO(001) and SrO(001). The structures were searched without stoichiometric constraints. Density-functional theory with semilocal (PBE) and hybrid (HSE06) exchange-correlation functionals with a first-principles dispersion interaction correction was employed. Our results confirm the presence of a range of H<sub>2</sub>O chemical potentials around the experimental conditions (*T* = 300 K, *p*<sub>H<sub>2</sub>O</sub> = 10<sup>-9</sup> atm) where one-dimensional adsorbed water structures are preferred on CaO(001). Trends in the range of stability and conditions for one-dimensional versus monolayer structures on MgO(001), CaO(001), and SrO(001) will be discussed and related to differences in the electronic structure of the oxides. The accuracy of the functionals is analyzed based on the "exact-exchange plus correlation in the random-phase approximation" approach.—[1] X. Shao, N. Niluis, M. Sterrer, Y. Fujimori, and H.-J. Freund, to be published.

O 56.11 Wed 18:30 H45

**DFT calculations of surface properties of Li<sub>2</sub>FeSiO<sub>4</sub>** — ●NICOLAS HÖRMANN<sup>1,2</sup> and AXEL GROSS<sup>1,2</sup> — <sup>1</sup>Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Albert-Einstein-Allee 11, 89069 Ulm — <sup>2</sup>Universität Ulm, Institut für Theoretische Chemie, Albert-Einstein-Allee 11, 89069 Ulm

Li<sub>2</sub>FeSiO<sub>4</sub> is a promising new electrode material for Lithium ion batteries, due to the abundance, low cost and safety of the elemental components and the high theoretical energy densities of up to 300 mAh/g [1]. Though rarely studied, surface properties can be decisive for electrode performance in Li ion batteries [2].

Electronic structure calculations based on density functional theory (DFT) have been performed for different surface terminations of Li<sub>2</sub>FeSiO<sub>4</sub> to determine the influence of surface properties on relevant electrode parameters. In particular, surface energies of stable surfaces and thus equilibrium crystallite morphologies are determined for different chemical environments, surface compositions and crystal structures. Furthermore, models are presented that allow the estimation of surface energies from bulk properties prior to time consuming *ab-initio* calculations. The applicability and range of validity of the models is analysed and discussed.

[1] M. Saiful Islam et al. , *J. Mater. Chem.*, **2011**, *21*, 9811.

[2] Kyu-Sung Park et al., *Chem. Mater.*, **2012**, *24* (16), pp 3212–3218.

O 56.12 Wed 18:45 H45

**Ab initio study of low-coordinated sites on MgO(100) using hybrid functionals** — ●PHILIPP AUBURGER<sup>1</sup>, MANUEL KOLB<sup>1,2</sup>, and MICHEL BOCKSTEDTE<sup>1</sup> — <sup>1</sup>Theoretische Festkörperphysik, FAU Erlangen-Nürnberg, Erlangen, Germany — <sup>2</sup>Leiden Institute of Chemistry, Leiden University, Leiden, Netherlands

Low-coordinated surface sites, such as surface oxygen vacancies and step edges are reactive centers at the MgO(100) surface. To unravel their role in chemical reactions and as optical recombination centers, it is pivotal to understand their electronic states. Density functional theory together with the (semi-)local exchange-correlation functionals, however, underestimate the band gap of metal oxides by a large margin. Hybrid functionals like the HSE06, are known<sup>1</sup> to improve the description of metal oxides considerably. Here we investigate surface color centers on the MgO(100) surface including the step edges, oxygen vacancy on the surface and at step edges, as well as kink sites using the DFT-HSE06 approach and a slab model. This enables a proper description of defect and dispersing shallow step edge states. For both states we find large corrections to values obtained with standard functionals. In addition, the calculations reveal a negative electron affinity in agreement with GW calculations.<sup>2</sup> We compare our results with recent STS-experiments on color centers at MgO-films.<sup>3</sup>

[1] G. Pacchioni, *J. Chem. Phys.* 128, 182505 (2008).

[2] M. Rohlfing, et al, *Phys. Rev. Lett.* 91, 2568021 (2003).

[3] M. Sterrer et al, *J Phys. Chem.B* 110, 46-49 (2006).