

## O 40 Oxides and insulators

Time: Thursday 15:00–18:00

Room: WIL A317

O 40.1 Thu 15:00 WIL A317

**Thin oxide films: analysis of finite-size effects** — ●CHRISTOPH FREYSOLDT, PATRICK RINKE, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin

Oxide surfaces have attracted considerable interest over the last years. In order to employ surface science tools, oxides are often grown epitaxially on metals. Recent findings for SiO<sub>2</sub> on Mo(112) indicate that well-ordered films are only 2-3 atomic layers thick – less than previously thought [1,2]. But is the surface of the films characteristic for the surface of a bulk oxide? Not only the structure may differ from any known bulk structure, but also the metal might alter the electronic structure. Also, sizeable quantum effects are expected at these dimensions. We present DFT simulations for oxide films of various thicknesses for  $\alpha$ -quartz SiO<sub>2</sub>,  $\alpha$ -alumina Al<sub>2</sub>O<sub>3</sub> and cubic hafnia HfO<sub>2</sub>. In order to separate the thickness from the substrate dependence, free-standing films are considered. We find that the electronic structure at the DFT level becomes bulk-like for very few atomic layers. The case of silica is discussed in detail. The film structure on Mo(112) corresponds to the most stable quartz(0001) surface. The electronic structure is essentially bulk-like and independent of the film thickness. The presence of the substrate does not alter these findings. For the electronic response of the thin film, however, the quasiparticle picture predicts a thickness-dependent band gap due to the dielectric discontinuity at the interface. Likewise, the chemistry and stability of defects is expected to be influenced by the substrate.

[1] L. Giordano *et al.*, Surf. Sci. 584, 225 (2005).

[2] J. Weissenrieder *et al.*, Phys. Rev. Lett. 95, 076103 (2005).

O 40.2 Thu 15:15 WIL A317

**A Combined DFT/LEED-Approach for Complex Oxide Surface Structure Determination: Fe<sub>3</sub>O<sub>4</sub>(001)** — ●R. PENTCHEVA<sup>1</sup>, J. RUNDGREN<sup>2</sup>, S. FRANK<sup>1</sup>, D. SCHRUPP<sup>3</sup>, M. SCHEFFLER<sup>4</sup>, and W. MORITZ<sup>1</sup> — <sup>1</sup>Section Crystallography, University of Munich — <sup>2</sup>Physics Dept., Royal Institute of Technology, Stockholm — <sup>3</sup>Dept. of Physics, University of Augsburg — <sup>4</sup>Fritz-Haber-Institut der MPG, Berlin

The structural determination of complex oxide surfaces is a challenge for quantitative analysis techniques such as XRD or LEED. Density functional theory (DFT) total energy calculations provide a mean to compare the stability of different configurations. Still, for complex structures, when many atoms relax (e.g. 50-100 degrees of freedom) the energy landscape may be rather flat and/or corrugated. In this paper we show that a multi-technique approach (employing DFT→LEED→DFT) is indeed most useful: In the framework of *ab initio thermodynamics* we compiled a surface phase diagram of Fe<sub>3</sub>O<sub>4</sub>(001) for a variety of surface terminations. The novel (so far ignored) Jahn-Teller distorted, oxygen-rich surface structure predicted from the DFT-calculations [1] is confirmed by a LEED I/V (and XRD) analysis. Only the here put forward combined DFT-LEED-DFT approach where the atomic positions obtained from DFT were used as input for the LEED structural refinement and vice versa enables us to achieve a *quantitative* agreement between the different methods. Furthermore, we explored the influence of phase shifts obtained from the DFT-electron density for magnetite bulk and surface as opposed to conventional phase shifts.

[1] R. Pentcheva, et al., Phys. Rev. Lett. 94,126101 (2005).

O 40.3 Thu 15:30 WIL A317

**Frequency Modulated Atomic Force Microscopy and Scanning Tunneling Microscopy of the Ultrathin Aluminum Oxide Film on NiAl(110)** — ●MARKUS HEYDE, GEORG SIMON, HANS-PETER RUST, and HANS-JOACHIM FREUND — Fritz-Haber-Institute of the Max-Planck-Society, Faradayweg 4-6, D-14195 Berlin, Germany

Metal oxides are of great technological importance because they are involved in a variety of applications, such as microelectronics or heterogeneous catalysis. The characterization of their properties on the atomic scale is therefore of special interest. The thin aluminum oxide film grown on NiAl(110) serves as an often used model system in catalysis [1]. We have started a detailed analysis by low temperature (5 Kelvin) ultra-high vacuum frequency modulated atomic force microscopy (FM-AFM) and scanning tunneling microscopy (STM) [2] of the thin aluminum oxide film grown on NiAl(110). A model of the structure of this film has been recently published by Kresse et al. [3]. Here we compare our combined FM-AFM and STM measurements with the model of the thin aluminum

oxide film.

[1] M. Bäumer and H.-J. Freund, Progress in Surface Science 61, 127 (1999).

[2] M. Heyde, M. Kulawik, H.-P. Rust, H.-J. Freund, Rev. Sci. Instrum. 75, 2446 (2004).

[3] G. Kresse et al., Science 308, 1440 (2005).

O 40.4 Thu 15:45 WIL A317

**Ordered alumina film on NiAl(110): Structure of the antiphase domain boundaries and of metallic clusters** — ●EVELYN NAPETSCHNIG<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, GEORG KRESSE<sup>2</sup>, LUKAS KÖHLER<sup>2</sup>, MAXIM SHISHKIN<sup>2</sup>, and PETER VARGA<sup>1</sup> — <sup>1</sup>Institut f. Allgemeine Physik, Vienna University of Technology, Austria — <sup>2</sup>Institut fuer Materialphysik, University of Vienna, Austria

Transition metal clusters on alumina support are one of the most frequently used model systems for investigations of heterogeneous catalysis. When NiAl(110) is oxidized at elevated temperatures an alumina film of uniform thickness and structure [1,2] with a network of domain boundaries is formed. The domain boundaries act as nucleation centers for metal clusters. We could determine the structure of the antiphase domain boundary by combining STM images and density-functional theory calculations [3]. Our measurements of the morphology of Co, Pd and bimetallic Co-Pd clusters on the alumina film show that for Pd and Co non-crystalline clusters with a steep slope and a round top are thermodynamically favourable. For the bimetallic Pd-Co clusters we proof that Pd is covering pre-deposited Co clusters like a shell whereas for deposition in the reverse order Pd is segregating to the cluster\*s surface and intermixes with the added Co.

[1] M. Bäumer and H.J. Freund, Prog. Surf. Sci. 61 (1999) 127

[2] G. Kresse M.Schmid, E.Napetschnig, M.Shishkin, L.Köhler and P.Varga, Science 308 (2005) 1440

[3] M. Schmid, G. Kresse, M. Shishkin, E.Napetschnig, M. Kulawik, N. Nilius, H.J. Freund and P. Varga, to be published

O 40.5 Thu 16:00 WIL A317

**Structural investigation of the ultra-thin gallium oxide grown on the CoGa(100) surface** — ●ALINA VLAD<sup>1</sup>, ANDREAS STIERLE<sup>1</sup>, REINHARD STREITEL<sup>1</sup>, GEORG KRESSE<sup>2</sup>, MARTIJN MARSMAN<sup>2</sup>, and HELMUT DOSCH<sup>1</sup> — <sup>1</sup>Max-Planck Institut für Metallforschung, Heisenbergstraße 1, 70569 Stuttgart — <sup>2</sup>Institut für Materialphysik und Centre for Computational Materials Science, Universität Wien, A-1090 Wien, Austria

Understanding the oxidation of metallic alloy surfaces is not only of fundamental interest, but is also a important for industrial applications in sectors like heterogeneous catalysis, microelectronics, high-density data storage technologies. Beside having the desired properties, one of the requirements for practical applications is that the oxide layer should be reproducible in thickness and composition. Also, a detailed knowledge of the structural aspects is often important. The formation of a well-ordered ultra thin surface gallium oxide was previously observed when exposing the CoGa(100) surface at 450°C and an oxygen pressure of  $5 \cdot 10^{-7}$  mbar. The aim of this study was to determine the structure of the oxide film by means of Surface X-ray Diffraction (SXRD) and DFT calculations. The set of experimental data (surface rods and CTR's) were measured at the ID32 beamline at ESRF, Grenoble. A trilayer O-Ga-O model for the surface oxide is proposed. The overall stoichiometry of the film does not correspond to that of the stable bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> but it is Ga<sub>2</sub>O.

O 40.6 Thu 16:15 WIL A317

**Composition, structure, and catalytic activity of sulfated c-ZrO<sub>2</sub>(111) films on Pt(111)** — ●STEFAN FÖRSTER<sup>1</sup>, KLAUS MEINEL<sup>1</sup>, ALEXANDER HOFMANN<sup>2</sup>, RALF KULLA<sup>1</sup>, KARL-MICHAEL SCHINDLER<sup>1</sup>, HENNING NEDDERMEYER<sup>1</sup>, JOACHIM SAUER<sup>2</sup>, and WOLF WIDDRA<sup>1</sup> — <sup>1</sup>Martin-Luther-Universität Halle-Wittenberg, FB Physik, D-06099 Halle, Germany — <sup>2</sup>Humboldt-Universität zu Berlin, Institut für Chemie, D-10099 Berlin, Germany

Sulfated zirconia catalysts are very active in the low-temperature isomerization of n-alkanes. Single crystalline sulphated c-ZrO<sub>2</sub>(111) films of the cubic (c) type have been prepared as a model catalyst by reactive deposition of Zr onto Pt(111) in an O<sub>2</sub> atmosphere and subsequent expo-

sition to a  $\text{SO}_3$  atmosphere. Structure and composition of the film surface have been examined by scanning tunneling microscopy, low-energy electron diffraction (LEED), Auger electron spectroscopy, and density functional theory (DFT) calculations. The clean  $c\text{-ZrO}_2(111)$  films display a  $(2 \times 2)$  surface structure. During  $\text{SO}_3$  exposure, a clear  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure develops. At about 700 K, the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure disappears and the bright LEED pattern of the clean  $\text{ZrO}_2$  films reappears. The energies of plausible  $c\text{-ZrO}_2(111)/\text{SO}_3$  structures have been examined by DFT. The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure found in the experiments turned out to be the most stable one for temperatures below 700 K. During reaction with n-butane, the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  sulfation structure is stable and its chemical activity is indicated by the formation of surface carbon.

O 40.7 Thu 16:30 WIL A317

**Formation and splitting of paired hydroxyl groups on reduced  $\text{TiO}_2(110)$**  — ●STEFAN WENDT, JESPER MATTHIASEN, RENALD SCHAUB, EBBE K. VESTERGAARD, ERIK LAEGSGAARD, FLEMMING BESENBACHER, and BJØRK HAMMER — Interdisciplinary Nanoscience Center (iNANO)

A combination of high-resolution scanning tunneling microscopy and density functional theory is utilized in order to study the interaction of water with the reduced  $\text{TiO}_2(110)-(1 \times 1)$  surfaces. As the direct product of water dissociation at oxygen vacancies, paired hydroxyl groups are formed. The pairs are immobile and stable at the surface unless they interact with adsorbed water molecules. As a result of these interactions, one proton per paired hydroxyl group is net transferred to the next oxygen row, thereby forming single hydroxyl groups. Furthermore, we find that hydroxyl groups on the bridging oxygen rows facilitate water diffusion in the  $[1\bar{1}0]$  direction.

O 40.8 Thu 16:45 WIL A317

**Photon emission from MgO thin films on Mo(100)** — ●HADJ-MOHAMED BENIA<sup>1</sup>, STEFANIA BENEDETTI<sup>2</sup>, NIKLAS NILIUS<sup>1</sup>, and HANS-JOACHIM FREUND<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — <sup>2</sup>Università di Modena e Reggio Emilia, Dipartimento di Fisica and INFN-CNR National Research Center on nanoStructures and bioSystem at Surface (S3), Via G. Campi 213/a, 41100 Modena, Italy

MgO is a prototype material which exhibits color centers (oxygen vacancies). Such centers dominate the optical properties as well as the catalytic behavior of the MgO surface. The aim of our experiment is to locally characterize the optical properties of surface color centers by employing STM in combination with photon emission spectroscopy (PSTM). For this purpose, we have grown MgO films on Mo(100) with varying thicknesses ranging from 2-10 monolayers. Depending on the MgO deposition temperature we have found different morphological and structural properties of the film by LEED and STM. The optical spectra are dominated by two emission peaks located at around 300 and 400 nm with intensities depending on preparation procedure and film thickness. We tentatively attribute these peaks to excitonic and defect-mediated recombination processes within the oxide film.

O 40.9 Thu 17:00 WIL A317

**LASER DESORPTION OF METAL ATOMS BY SITE-SPECIFIC EXCITATION OF METAL OXIDE SURFACES** — ●MATTHIAS HENYK<sup>1</sup>, KENNETH M. BECK<sup>1</sup>, CHONGMIN WANG<sup>1</sup>, PAOLO E. TREVISANUTTO<sup>2</sup>, PETER V. SUSHKO<sup>2</sup>, ALEXANDER L. SHLUGER<sup>2</sup>, and WAYNE P. HESS<sup>1</sup> — <sup>1</sup>Pacific Northwest National Laboratory, EMSL, P.O. Box 999, Richland, WA 99352, USA — <sup>2</sup>Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Mg-atom emission is studied at MgO by using laser light tuned to excite specific surface sites at energies well below the excitation threshold of the bulk material. We find that at 4.66 eV laser excitation MgO nanocrystalline films and nanocube samples desorb neutral Mg-atoms with multi-modal distributions of kinetic energy (0.11, 0.18, 0.25 eV). Time-resolved desorption measurements reveal two distinct decay components (1.2, 100 ps) in addition to the typically observed coherence feature (80 fs, FWHM). These results are consistent with Mg-atom desorption driven by multiple electronic transitions, including an ultra-fast correlated 2-electron-transfer as well as the rapid decay of Mg+ surface states. Our ab initio calculations suggest an electron plus exciton mechanism, involving both excitation and trapping of electrons and surface excitons at 3-coordinated Mg surface sites. The proposed mechanism

exemplifies a scheme of atomic scale modification of a metal oxide surface and can be useful for the further understanding of photo-induced desorption of more complex metal oxide materials.

O 40.10 Thu 17:15 WIL A317

**Thin Manganese Oxide Films on Ag(001)** — ●MICHAEL HUTH<sup>1</sup>, KARL-MICHAEL SCHINDLER<sup>1</sup>, CHRISTIAN HAGENDORF<sup>1</sup>, JIAN WANG<sup>1</sup>, RICHARD BÖRNER<sup>1</sup>, STEPHAN GROSSER<sup>1</sup>, STEFFEN SACHERT<sup>1</sup>, WOLF WIDDRA<sup>1</sup>, FRANCESCO ALLEGRETTI<sup>2</sup>, MARTIN POLCIK<sup>2</sup>, DAVID SAYAGO<sup>2</sup>, and EMILY KRÖGER<sup>2</sup> — <sup>1</sup>Martin-Luther-Universität Halle-Wittenberg, FB Physik, D-06120 Halle — <sup>2</sup>Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin

Thin films of MnO (4 ML) were grown on a Ag(001) substrate by reactive evaporation of Mn in an  $\text{O}_2$  atmosphere and investigated with XPS and NEXAFS spectroscopy at the UE56/2 BESSY beamline. The identity of the MnO film was assessed using the exchange splitting (6.2 eV) of the Mn 3s photoemission line which is highest for stoichiometric MnO. After annealing such a film to 720 K the exchange splitting is reduced to 5.6 eV pointing to a composition of  $\text{MnO}_{1-x}$ . NEXAFS spectra of the O K-edge in normal and grazing incidence are very similar for MnO due to its cubic structure, but for  $\text{MnO}_{1-x}$  they show a strong dependence on the angle of incidence and nearly twice as many resonances. O 1s photoelectron diffraction (PED) curves were recorded in energy scan mode for both films. The intensity modulations of the MnO film are much stronger than the ones of the  $\text{MnO}_{1-x}$  films. We attribute this again to the lower symmetry of the  $\text{MnO}_{1-x}$  films. Finally, the intensity ratio of the two exchange split Mn 3s photoemission lines varies for kinetic energies which indicate the presence of a local magnetic ordering above the Neel temperature.

O 40.11 Thu 17:30 WIL A317

**Local differential conductance of thin CoO films on Ag(001) at low temperatures** — ●STEPHAN GROSSER, CHRISTIAN HAGENDORF, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, FB Physik, D-06120 Halle(Saale)

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) have been applied to study simultaneously the local electronic and geometric structure of thin CoO films on Ag(001). CoO has been grown by reactive deposition of Co in an  $\text{O}_2$  atmosphere. Growth at 480 K substrate temperature leads to precursor or unordered phases and subsequent annealing to ordered CoO(001) films.  $dI/dV$  spectra for structurally well-characterized different precursor phases, CoO bilayer and layers up to 5 ML show distinct differences. The region of the unoccupied states up to 5 eV is dominated by the local density of states within the oxide film. Especially for 2 ML islands and thicker films, a strong and well-resolved unoccupied Co d-state at about 2.3 eV is found. For higher bias voltages between 5 and 10 V the spectra exhibit strong field emission resonances which are characteristically modified by the different oxide structures as compared to the bare metal substrate. Topographic and simultaneous measured spectroscopic maps reveal details of the lateral electronically homogeneity and defect distribution down to atomic resolution. The results will be compared with spectra for Ag(001) and first results of NiO on Ag(001).

O 40.12 Thu 17:45 WIL A317

**In-situ investigation of the Nb(110)/oxygen interface** — ●MELISSA DELHEUSY<sup>1,2</sup>, ANDREAS STIERLE<sup>1</sup>, CLAIRE ANTOINE<sup>2</sup>, and HELMUT DOSCH<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, Germany — <sup>2</sup>Commissariat à l'énergie atomique, Dapnia/SACM- Centre d'étude Saclay F-91191 Gif-sur-Yvette

Interstitial oxygen impurities are known to affect strongly the physical properties of Nb. This is of first importance for numerous superconducting high technology applications and in particular, for the future improvement of radio-frequency (RF) accelerating cavities. In-situ surface sensitive x-ray studies during oxidation and mild thermal treatments (RT-300°C, UHV) of Nb(110) have been performed. Different aspects of the interaction oxygen/Nb were investigated in the first 50-100 nm below the surface, corresponding to the penetration length of a RF field in Nb. The oxide layer has been characterised by x-ray reflectivity; the depth-distribution of interstitial oxygen was studied with a nm-resolution by depth-resolved grazing incidence x-ray diffuse scattering; finally, the structure of the Nb/oxide interface was investigated by crystal trunca-

tion rods measurements. The experiments were realised at the Max-Planck-Institute surface diffraction beamline at the synchrotron source ANKA, and reveal an ordering of the interstitial oxygen atoms below the metal/oxide interface at 300°C parallel to the dissolution of the oxide layer.