

DS 29: Oxide and insulator surface: Structure, epitaxy and growth (joint session with O)

Time: Wednesday 15:00–18:15

Location: MA 042

DS 29.1 Wed 15:00 MA 042

Surface phonons of BaTiO₃(001) and BaTiO₃ ultrathin films on Pt(001) and Au(001) — ●FLORIAN SCHUMANN¹, KLAUS MEINEL¹, ANDREAS TRÜTZSCHLER¹, and WOLF WIDDRA^{1,2} —
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Phonons and their softening are key elements for the understanding of the long-range coupling in ferroelectric and multiferroic materials, which causes, e.g., the paraelectric to ferroelectric phase transition. In thin films, these ferroelectric properties are often controlled by strain from the underlying substrate or heterostructures. Here we study the surface phonons of BaTiO₃(001) ultrathin films in comparison with a BaTiO₃ single-crystal with high-resolution electron energy loss spectroscopy (HREELS). For all BaTiO₃ structures, three well-developed phonon peaks at about 210, 460, and 670 cm⁻¹ dominate the HREELS spectra. Calculations of the energy loss spectra within a semi-classical approach identify the three phonons as the A(TO) surface phonon-polaritons (Fuchs-Kliewer modes) of BaTiO₃(001). In comparison to the single crystal, the surface phonons of the thin films on Pt(001) and on Au(001) are shifted due to the lattice misfit of +2% and -2%, respectively. Furthermore, the surface phonons show a thickness dependent red shift in the thin films. Calculations identify this shift as phonon-polariton coupling to the metallic substrate.

DS 29.2 Wed 15:15 MA 042

Preparation of Bi₂Se₃(0001) surface studied by scanning tunneling microscopy — ●VASILII SEVRIUK, ALBERTO CAVALLIN, SAFIA OUAZI, DIRK SANDER, and JÜRGEN KIRSCHNER — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

Despite the fact that the Bi₂Se₃(0001) surface is relatively inert [1], carbon is a common surface contaminant. It is detected by Auger electron spectroscopy (AES) and in scanning tunneling microscopy (STM) it appears as protrusions. Here we report the preparation of Bi₂Se₃(0001) by Ar sputtering and annealing and by in vacuo cleavage. We find by STM that sputtering and annealing cycles lead to surface and sub-surface defects, which can be ascribed to Se vacancies [2] and Bi interstitials [3]. After several cycles of sputtering and annealing, a periodic spatial modulation on the length scale of 10–15 nm is observed in STM constant current maps, which we ascribe to a dislocation network [4]. Samples prepared by cleavage do not show this spatial modulation.

[1] V. A. Golyashov, K. A. Kokh, S. V. Makarenko, K. N. Romanyuk, I. P. Prosvirin et al. *J. Appl. Phys.* 112, 113702 (2012).

[2] Y. S. Hor, A. Richardella, P. Roushan, Y. Xia, J. G. Checkelsky, A. Yazdani, M. Z. Hasan, N. P. Ong and R. J. Cava. *Phys. Rev. B* 79, 195208 (2009).

[3] S. Urazhdin, D. Bilc, S. H. Tessmer, S. D. Mahanti, Theodora Kyratsi, and M. G. Kanatzidis, *Phys. Rev. B* 66, 161306(R) (2002).

[4] M. Schmid, A. Biedermann, H. Stadler, and P. Varga. *Phys. Rev. Lett.* 69, 925 (1992).

DS 29.3 Wed 15:30 MA 042

Growth of cuprous oxide on Au(111) and Mo(001) - Role of the support — ●HANNA FEDDERWITZ, BORIS GROSS, HENDRIK STRÄTER, and NIKLAS NILIUS — Carl-von-Ossietzky Universität Oldenburg, Carl-von-Ossietzky-Str. 9 - 11, 26129 Oldenburg

Physical vapor deposition of Cu in an oxygen ambience is used to prepare Cu₂O films on two single crystalline supports of different reactivity and lattice symmetry. While on Au(111), the oxide grows in a layer by layer fashion and develops atomically flat films, formation of nanoparticles is observed on a Mo(001) surface. The size and shape of the crystallites can be controlled by varying the temperature and O₂ partial pressure during oxide growth. Insight into the atomic configuration of the Cu₂O facets is obtained from low-temperature STM measurements. Whereas Au-supported films expose the ideal (111) termination of cuprous oxide, modified only by a network of dislocation lines, a variety of low-index planes is discernable for deposits on the Mo support. The underlying growth mechanism is analyzed with the Wulff theory for nanoparticles in thermodynamic equilibrium. We discuss consequences of the different growth schemes on the two supports for possible applications of our cuprous-oxide samples in photocatalysis and photovoltaics.

DS 29.4 Wed 15:45 MA 042

Atomic structure and electronic properties of Cu₂O(111) films — ●BORIS GROSS, HANNA FEDDERWITZ, HENDRIK STRÄTER, and NIKLAS NILIUS — Carl-von-Ossietzky Universität Oldenburg, Carl-von-Ossietzky Str. 9-11, 26129 ,Oldenburg

Atomically flat films of cuprous oxides were prepared by Cu deposition in oxygen onto an Au(111) surface, and analyzed by XPS, electron diffraction and STM. Depending on the preparation conditions, different surface reconstructions are obtained. Whereas the low-temperature structures have no analogy to respective bulk phases and are governed by interactions with the metal support, the high-temperature films have a similar atomic configuration as bulk-cut Cu₂O(111). STM conductance spectroscopy reveals the pronounced 2.0 eV band gap of the oxide, in addition to an unoccupied surface state that occurs in the high-temperature phase. Field-emission resonances that govern the high-energy part of the STM spectra are used to monitor local variations in the work function of the system. Given their high crystallographic quality, our Cu₂O films provide an ideal starting point to explore the defect landscape and optical properties for this reference material for photo-catalysis and photovoltaics.

DS 29.5 Wed 16:00 MA 042

Growth of ultrathin Silica films on Ru(0001) — ●HAGEN W. KLEMM, GINA PESCHEL, EWA MADEJ, ALEXANDER FUHRICH, MARTIN TIMM, THOMAS SCHMIDT, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

The SiO₂ bilayer on Ru(0001) offers magnificent possibilities for understanding the transition from crystalline to vitreous phase[1], tuning of electronic structure, doping and catalysis[2]. In the thickness range of one to three monolayers we studied the growth of ultrathin Silica films by LEEM, LEED, XPS and XPEEM. We found that the oxidation temperature plays a crucial role for the quality of the resulting film, varying from incomplete oxidation to dewetting of the film. A special focus of our investigation was the transition from crystalline to vitreous phase, as could be clearly seen in LEED. The influence of holes in the film and the morphology of the substrate will be discussed.

[1] Lichtenstein, L. et. al., *Angew. Chem. Int. Ed.* 51, 404 (2012)

[2] Shaikhutdinov, S. et. al., *Chem. Phys. Chem.* 14, 71 (2013)

DS 29.6 Wed 16:15 MA 042

Ultrathin Iron-Silicate films on Ru(0001) — ●GINA PESCHEL, HAGEN KLEMM, THOMAS SCHMIDT, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

Iron silicate can be seen as a model system for zeolites [1], which are important for catalysis and widely used in industry as desiccant, detergent or as molecular sieves. Of special interest is the relation between the specific structure and reactivity. In our case we studied the growth only of a one to two atomic layer thin film on a Ru(0001) support by LEEM, LEED, XPS and XPEEM measurements.

We found the formation of structural domains. The size of these domains increase with temperature and Fe/Si ratio. Furthermore, XPEEM measurements indicate that the domains contain iron and Silica, while in between the domains only Silica is found. The Si2p level shows a chemical shift between Silica bound to FeO and Silica on Ru(0001)only. Beside the (2x2) spots, typical for silica, LEED shows additional spots rotated by 30 ° and a Moiré structure. The unit cell of the new structure is about three percent larger than for ultra-thin silica films.

[1] R. Wlodarczyk, J. Sauer, X. Yu, J. Boscoboinik, B. Yang, S. Shaikhutdinov, H.-J. Freund, *J. Am. Chem. Soc.* 135 (2013), 19222-19228

DS 29.7 Wed 16:30 MA 042

First-Principles Embedded Cluster Calculations of Surface Defects at TiO₂(110) — ●DANIEL BERGER, HARALD OBERHOFER, and KARSTEN REUTER — Technische Universität München

Bulk and surface defects critically determine many of the properties and functions that make TiO₂ such an interesting and widely studied material. Given this importance, it is both surprising and disconcerting to see how little is actually known especially about the surface defects of TiO₂. For surface oxygen vacancies not even their thermodynamically favored charge state is unambiguously clear. We contribute

to this context with first-principles embedded cluster calculations [1] of the rutile $\text{TiO}_2(110)$ surface. Our approach allows for a numerically particularly efficient application of hybrid density-functional theory inside the quantum mechanic (QM) cluster region. In the extended molecular mechanic (MM) embedding region specifically optimized interatomic potentials provide a quantitative account of the strong TiO_2 polarization response. We discuss the advantages of this QM/MM approach against more common periodic supercell calculations especially for charged O vacancies. Over a wide range of electrochemical potentials and oxygen partial pressures our calculations show the +2 state to be thermodynamically favored, which can be rationalized by the huge dielectric constant of TiO_2 .

[1] D. Berger *et al.*, J. Chem. Phys. **141**, 024105 (2014).

DS 29.8 Wed 16:45 MA 042

Ordered Indium and Iron Adatoms on the Reduced $\text{In}_2\text{O}_3(111)$ Surface — ●MARGARETA WAGNER¹, PETER LACKNER¹, STEFFEN SEILER², BERND MEYER², LYNN A. BOATNER³, MICHAEL SCHMID¹, and ULRIKE DIEBOLD¹ — ¹Institut für Angewandte Physik, Technische Universität Wien, Wiedner Hauptstrasse 8-10/134, 1040 Wien, Österreich — ²Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center Friedrich-Alexander-Universität Erlangen-Nürnberg, Nögelsbachstrasse 25, 91052 Erlangen, Deutschland — ³Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Indium oxide is one of the most important TCOs and commonly used as a contact material in many devices. Recently, In_2O_3 single crystals, prerequisite for fundamental surface studies, have become available.

The $\text{In}_2\text{O}_3(111)$ surface can be transformed from a bulk-terminated surface to one that is covered by single indium adatoms. The transformation and the intermediate stages were followed with Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT). DFT supports the formation of a stable array made of indium adatoms, which is favored over vacancy formation at the given oxygen chemical potential during reduction. The formation of an ordered adatom array is different from any known response of an oxide surface to chemical reduction. Also iron atoms deposited on the oxidized surface arrange as single adatoms in the same (1x1) superstructure. The adatom-covered and oxidized $\text{In}_2\text{O}_3(111)$ surfaces are expected to exhibit very different chemical and electronic properties.

DS 29.9 Wed 17:00 MA 042

Infra-red and Raman frequencies of Co_3O_4 – an *ab initio* study — ANDRII TITOV¹, ●DOMINIK LEGUT^{2,3}, and LUCIE OBALOVA³ — ¹Nanotechnology Centre — ²IT4Innovations Centre — ³Inst. Env. Techn., VSB–TU Ostrava, Ostrava, Czech Republic

Among well known catalyst for N_2O decomposition belongs Co_3O_4 . Since this reaction has oxidation-reduction mechanism, the electronic properties of Co_3O_4 represent important feature. We have calculated electronic structure and lattice dynamics, i.e. atomic vibrations using first-principles calculations. We determined Raman and infra-red frequencies of the phonon modes. Our results were calculated using single electron framework within the density functional theory. For the electronic exchange correlation the general gradient approximation as parametrized by Perdew–Burke–Ernzerhof [1] was used. To obtain the correct description of the insulating behaviour the Hubbard U technique was used. The anti-ferromagnetic ordering and spin-orbit interaction were also considered. Lattice vibrations were calculated using Phonopy package [2]. The dependences of the band gap, infra-red and Raman frequencies on the Coulomb interaction (Hubbard U) were revealed and compared with experimental data measured at the VSB-TU Ostrava. The work was supported by the Grant Agency of the Czech Republic, project reg. No. 14-13750S.

References:

1. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
2. A. Togo, F. Oba, I. Tanaka, Phys. Rev. B **78**, 134106 (2008).

DS 29.10 Wed 17:15 MA 042

Surface energy, structure and stability of crystalline corundum surfaces — ●LILIT AMIRKHANYAN, TORSTEN WEISSBACH, and JENS KORTUS — Institute of Theoretical Physics, TU Bergakademie Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany

Using first-principles density function theory as implemented in Quantum-ESPRESSO we examined the surface energy of the stable $\alpha\text{-Al}_2\text{O}_3$ corundum phase. Corundum is very important for applications due to its outstanding hardness, high melting point, high thermal

conductivity and low dielectric constant.

The [001], [100], [110], [112], [114], [113] and [223] crystal planes of $\alpha\text{-Al}_2\text{O}_3$ were studied. The surfaces have been modeled using slabs with periodic boundary conditions. We investigated the impact of different termination and the effect of relaxation on surface properties. Further, we discuss possible relations of surface properties to structural elements like number of broken bonds or missing oxygen atoms to complete the coordination.

DS 29.11 Wed 17:30 MA 042

Surface Adsorbates and Defects on the Subsurface Cation Vacancy Stabilized Surface of Magnetite (001) — ●EAMON MCDERMOTT¹, ROLAND BLIEM², GARETH PARKINSON², ULRIKE DIEBOLD², and PETER BLAHA¹ — ¹Institute for Material Chemistry, TU Wien, Vienna, Austria — ²Institute of Applied Physics, TU Wien, Vienna, Austria

Having proposed a new surface reconstruction for the magnetite (001) surface which is stabilized by a subsurface cation vacancy, we are now studying the extended properties of this reconstruction, including its preferred adsorption sites for various metals, the properties of oxygen vacancies at the structure and the adsorption of CO and OH groups. The surface structure has interesting chemistry, due to the presence of an oxygen site with a +1 oxidation state. In particular, we are interested in understanding our database of known magnetite surface defects as observed by STM. Progress on several ongoing investigations will be reported.

DS 29.12 Wed 17:45 MA 042

The Structure of Magnetite(100)-c(2x2) revisited — ●LUTZ HAMMER¹, PASCAL FERSTL¹, M.ALEXANDER SCHNEIDER¹, ROLAND BLIEM², ULRIKE DIEBOLD², and GARETH PARKINSON² — ¹Solid State Physics, FAU Erlangen-Nürnberg — ²Inst. Appl. Physics, TU Wien

The widely accepted "Distorted-Bulk-Truncation" model [1,2] for the c(2x2) surface reconstruction of $\text{Fe}_3\text{O}_4(100)$ fails to explain recent STM results for the adsorption and nucleation behaviour of metal adatoms on this surface [3,4]. We have therefore revisited the surface structure by means of a full-dynamical LEED intensity analysis. We tested in particular a new model of subsurface cation vacancies and interstitials [5], which was not yet considered in a former LEED analysis [2]. This new model led to a remarkably better correspondence between experimental and calculated spot intensities expressed by a Pendry R-factor of 0.125 (compared to 0.34 of ref.[2]). The new analysis is based on a very large experimental data base of 11300 eV allowing a safe determination of as much as 59 structural parameters. The atomic coordinates derived from the LEED analysis are in excellent agreement with predictions from DFT for this structure [5]. This study also proves that there are no inherent problems in the LEED I-V methodology to properly determine the structure of oxide surfaces as frequently claimed in literature.

[1] R. Pentcheva *et al.*, PRL 94, 126101 (2005); [2] R. Pentcheva *et al.*, Surf. Sci. 602, 1299 (2008); [3] Z. Novotny *et al.*, PRL 108, 216103 (2013); [4] G.S. Parkinson *et al.*, Nat. Mater. 12, 724 (2013); [5] R. Bliem *et al.* Science, accepted

DS 29.13 Wed 18:00 MA 042

Surface structure of Fe_3O_4 under varying conditions studied by surface x-ray diffraction — ●BJÖRN ARNDT^{1,2}, ROLAND BLIEM³, HESHMAT NOEI¹, OSCAR GAMBA³, JESSICA VAN DER HOVEN³, GARETH PARKINSON³, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektron-Synchrotron (Desy), D-22607 Hamburg, Germany — ²Fachbereich Physik, Universität Hamburg, D-20355 Hamburg, Germany — ³Institute of Applied Physics, Vienna University of Technology, 1060 Vienna, Austria

Magnetite (Fe_3O_4) exhibits interesting material properties which makes it attractive for industrial applications as a catalyst for the water-gas shift reaction. Therefore, it is important to understand its surface structure under different conditions. The (001) surface of magnetite shows a $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstruction in UHV which gets lifted at around 450°C as well as upon water adsorption at room temperature. To clarify the recent controversy about the atomic structure of the reconstruction and to get insight into it at different conditions, we performed a surface x-ray diffraction experiment on a natural $\text{Fe}_3\text{O}_4(001)$ single-crystal. The experiment was carried out at the ESRF ID03 beamline using an UHV-ambient pressure flow reaction chamber at 11 keV photon energy. Our data support the recently proposed surface model¹ with overstoichiometric oxygen concentration. Upon heating and upon water adsorption, the surface reconstruction van-

ishes.

[1] R. Bliem et al., submitted