

O 81: Oxide and Insulator Surfaces III

Time: Thursday 16:00–19:00

Location: PHY C 213

O 81.1 Thu 16:00 PHY C 213

Surface core-level shifts of zinc oxide — ●NAVID ABEDI KHALEDI and GEORG HEIMEL — Institut für Physik, Humboldt Universität zu Berlin, Brook-Taylor-Straße 6, 12489 Berlin, Germany

X-ray photo-emission spectroscopy (XPS) is an extremely useful tool for understanding the chemical composition of any surface. However, interpretation of experimental results is not always straightforward. To this aim, we perform density functional theory (DFT) based calculations of the most probable structures of Zinc oxide's complex (0001), (000-1) and (10-10) surfaces. Chemical core-level shifts are then obtained from total-energy differences and Slater's transition-state theorem. XPS intensities are estimated from tabulated values for electron mean free paths. In the end, we produce peak shapes with a combination of Lorentzian and Gaussian functions, allowing direct comparison with experimental spectra.

O 81.2 Thu 16:15 PHY C 213

Tuning amorphous network structures — ●CHRISTIN BÜCHNER, STEFANIE STUCKENHOLZ, MARKUS HEYDE, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

A bilayer silica film system has been presented, exhibiting amorphous and ordered regions [1]. Noncontact atomic force microscopy (nc-AFM) and scanning tunneling microscopy (STM) with atomic resolution reveal a network of different ring sizes. The structure can be described in terms of ring size occurrence, neighborhoods and pair distance histograms, which are directly derived from atomic coordinates. In the study of the ring size arrangements of the amorphous region, valuable insights can be gained concerning formation principles of vitreous or amorphous structures. On the basis of knowing these structural properties, tuning the network structures is endeavored. Introducing Al as a dopant, combined with subsequent annealing, results in film structures with new characteristics [2]. Ring size distribution and film growth properties in particular are influenced by the element composition. A study of different networks is presented, focusing on the network features studied with SPM.

[1] L. Lichtenstein, C. Büchner, B. Yang, S. Shaikhutdinov, M. Heyde, M. Sierka, R. Włodarczyk, J. Sauer and H.-J. Freund, *Angewandte Chemie International Edition* 51 (2012) 404

[2] J. A. Boscoboinik, X. Yu, B. Yang, F. D. Fischer, R. Włodarczyk, M. Sierka, S. Shaikhutdinov, J. Sauer and H.-J. Freund, *Angewandte Chemie International Edition* 51 (2012) 6005

O 81.3 Thu 16:30 PHY C 213

Importance of Space-Charge effects for the Concentration of Defects at Metal-Oxide Surfaces — NORINA A. RICHTER¹, SABRINA SICOLÒ², ●SERGEY V. LEVCHENKO¹, JOACHIM SAUER², and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft — ²Humboldt Universität zu Berlin

We consider the charge-carrier conductivity induced by doping as a thermodynamic factor in the context of defect formation. As a technologically relevant example, we study surface oxygen vacancies (F centers) in MgO. Defect formation energies are determined using *ab initio* atomistic thermodynamics in combination with hybrid density-functional theory (DFT), with parameters of the exchange-correlation functional optimized according to a condition on DFT ionization energies. Formation energies for neutral defects are validated by coupled-cluster CCSD(T) calculations for embedded clusters. The virtual-crystal approximation [1] is used for a realistic modeling of doping. We find that at catalytically relevant conditions charge transfer between surface defects and dopants in deeper layers leads to formation of a macroscopically extended space-charge region. The concentration of F_s^{2+} centers at the (100) terrace of *p*-type MgO can be as high as 1%, while F_s^+ and F_s^0 concentrations are negligible in both *p*-type and *n*-type MgO [2].—[1] L. Vegard, *Z. Phys.* 5, 17 (1921); M. Scheffler, *Physica B+C*, 146, 176 (1987); [2] N.A. Richter, *et al.*, *Phys. Rev. Lett.* 111, 045502 (2013).

O 81.4 Thu 16:45 PHY C 213

Metal nucleation and clusters on ultrathin ZrO₂ films — JOONG-IL J. CHOI¹, ILARIA VALENTI², WERNFRIED MAYR-SCHMÖLZER¹, FLORIAN MITTENDORFER¹, JOSEF REDINGER¹, ULRIKE

DIEBOLD¹, and ●MICHAEL SCHMID¹ — ¹Institut f. Angewandte Physik, TU Wien, Austria — ²Università degli Studi di Modena e Reggio Emilia, Modena, Italia

Zirconia (ZrO₂) is used as a catalyst support and solid-state electrolyte in gas sensors and solid-oxide fuel cells. Nevertheless, its surface properties are insufficiently understood, mainly due to its insulating nature. To overcome this problem, we use ultrathin ZrO₂ films [1,2], which are accessible to scanning tunneling microscopy (STM). We have studied nucleation and growth of Ag, Au and Pd on these ZrO₂ films at room temperature. Compared to other ultrathin oxides like alumina or FeO, we find a high density of metal clusters or even single metal adatoms. Comparison between ZrO₂ grown on Pd₃Zr(0001) and Pt₃Zr(0001) indicates that the buckling of the Zr atoms in these oxide films plays an important role, which means that metal atoms can easily bind to Zr in the oxide, as already suggested in Ref. [1]. This explains the high nucleation density and also suggests that the various crystallographic phases of bulk ZrO₂ differ significantly in their surface properties.

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

[2] J.I.J Choi et al., submitted (2013)

O 81.5 Thu 17:00 PHY C 213

Ultra-thin zirconia films on Zr-alloys — ●JOONG IL JAKE CHOI¹, WERNFRIED MAYR-SCHMÖLZER¹, HAO LI², GÜNTHER RUPPRECHTER², FLORIAN MITTENDORFER¹, JOSEF REDINGER¹, ULRIKE DIEBOLD¹, and MICHAEL SCHMID¹ — ¹Institute of Applied Physics, Vienna University of Technology, Austria — ²Institute of Materials Chemistry, Vienna University of Technology, Austria

Zirconia ultra-thin films have been prepared by oxidation of Pt₃Zr(0001) and showed a structure equivalent to (111) of cubic zirconia[1]. Following previous work, we have prepared ultra-thin zirconia by oxidation of a different alloy, Pd₃Zr(0001), which resulted in a similar structure with a slightly different lattice parameter, 351.2±0.4 pm. Unlike the oxide on Pt₃Zr, where Zr of the oxide binds to Pt in the substrate, here the oxide binds to substrate Zr via oxygen. This causes stronger distortion of the oxide structure, *i.e.* a stronger buckling of Zr in the oxide. After additional oxidation of ZrO₂/Pt₃Zr, a different ultra-thin zirconia phase is observed. A preliminary structure model for this film is based on (113)-oriented cubic zirconia. 3D oxide clusters are also present after growing ultra-thin zirconia films. They occur at the step edges, and the density is higher on Pd₃Zr. These clusters also appear on terraces after additional oxidation. XPS reveals different core level shifts of the oxide films, bulk, and oxide clusters.

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

O 81.6 Thu 17:15 PHY C 213

Ordered Phases of Reduced Ceria as Epitaxial Films on Cu(111) — TOMÁŠ DUCHOŇ, FILIP DVOŘÁK, MARIE AULICKÁ, VITALII STETSOVYCH, MYKHAILO VOROKHTA, DANIEL MAZUR, KATEŘINA VELTRUSKÁ, TOMÁŠ SKÁLA, ●JOSEF MYSLIVEČEK, IVA MATOLÍNOVÁ, and VLADIMÍR MATOLÍN — Charles University in Prague, Faculty of Mathematics and Physics, Department of Surface and Plasma Physics, V Holešovičkách 2, 18000 Praha 8, Czech Republic

We study the relationship between the stoichiometry and the structure in thin epitaxial films of reduced ceria, CeO_x, 1.5≤x≤2, prepared via an interface reaction between a thin ceria film on Cu(111) and a Ce metal deposit. We show that the transition between the limiting stoichiometries CeO₂ and Ce₂O₃ is realized by equilibration of mobile oxygen vacancies near the surface of the film, while the fluorite lattice of cerium atoms remains unchanged during the process. We identify three surface reconstructions representing distinct oxygen vacancy ordering during the transition, $\sqrt{7} \times \sqrt{7}R19.1^\circ$, 3×3 , and 4×4 corresponding to bulk phases of ceria *l*-Ce₇O₁₂, CeO_{1.67}, and *c*-Ce₂O₃ [1], respectively. Due to the special property to yield ordered phases of reduced ceria the interface reaction between Ce and thin film ceria represents a unique tool for oxygen vacancy engineering. The perspective applications include advanced model catalyst studies with both the concentration and the coordination of oxygen vacancies precisely under control.

[1] Stetsovyh, V.; *et al.*, Epitaxial Cubic Ce₂O₃ Films via Ce-CeO₂ Interfacial Reaction. *J. Phys. Chem. Lett.* 2013, 4, 866-871.

O 81.7 Thu 17:30 PHY C 213

Surface phonons of titanium oxide ultrathin films on Pt(100) — ●FLORIAN SCHUMANN¹, KLAUS MEINEL¹, JOHANNES LOTZE¹, and WOLF WIDDRA^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Max-Planck Institut für Mikrostrukturphysik, Halle, Germany

Phonons and their softening are key elements for the understanding of the long-range coupling in ferroelectric and multiferroic materials. Titanium oxide is a relevant part and one possible termination in many perovskites like BaTiO₃ and SrTiO₃. In thin films, structure and lattice dynamics can be modified due to the interaction at the interfaces. Here we study the surface phonons of ultrathin titanium oxides grown by MBE on Pt(100). Three different well-ordered TiO_x phases have been identified as (4×13), (3×5) and (2√2×2√2)R45° structures based on their LEED pattern [1,2]. The three phases can be distinguished by their characteristic phonon frequencies at 1020, 755 and 625 cm⁻¹, respectively. The stability of the three phases as function of temperature and oxygen pressure will be discussed based on the phonon spectroscopy.

[1] T. Matsumoto et al., Surf. Sci. 572: 127, 2004.

[2] T. Matsumoto et al., Surf. Sci. 572: 146, 2004.

O 81.8 Thu 17:45 PHY C 213

Development of a new Phase on TiO₂ (101) Anatase with Reduced Bandgap — ●CHRISTIAN DETTE¹, CHRISTOPHER S. KLEY¹, MIGUEL A. PEREZ², PAUL PUNKE¹, CHRISTOPHER PATRICK², FELICIANO GIUSTINO², SOON J. JUNG¹, and KLAUS KERN^{1,3} — ¹MPI for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany — ²University of Oxford, 16 Parks Road, Oxford OX1 3PH, United Kingdom — ³EPF Lausanne, IPCM, 1015 Lausanne, Switzerland

Nanosized TiO₂ photocatalytic water-splitting technology has great potential for low-cost, environmentally friendly solar-hydrogen production to support the future hydrogen economy. Presently, the solar-to-hydrogen energy conversion efficiency is too low for the technology to be economically sound. The main barriers are the poor activation of TiO₂ by visible light. Hence, our research is focused on the reduction of the band gap to increase the photocatalytic activity in the visible.

We have created a reduced band gap phase (phase II) on the standard surface (phase I) of a natural grown TiO₂ (101) Anatase crystal by a combination of standard cleaning processes. The creation processes are fully reversible. We have taken detailed topography and spectroscopy data at various positions of each phase by using scanning tunnelling microscopy (STM) and spectroscopy (STS). We found a similarity in the electronic configuration between phase II and the [-111] oriented edge of phase I, since both show a reduced band gap due to a band gap state near the valence band maximum. We will present a structural model of phase II consistent with the experimental data and first-principle density functional theory based calculations.

O 81.9 Thu 18:00 PHY C 213

Small and Large Polarons in TiO₂ Rutile and Anatase — ●MARTIN SETVIN¹, CESARE FRANCHINI², XIANFENG HAO¹, BENJAMIN DANIEL¹, MICHAEL SCHMID¹, GEORG KRESSE², and ULRIKE DIEBOLD¹ — ¹TU Wien, Vienna, Austria — ²Universität Wien, Vienna, Austria

TiO₂ is a prototypical metal oxide and used in photocatalysis, photoelectrochemical (Grätzel) solar cells, and transparent optical conductors. Industrially two forms of TiO₂ are used, rutile and anatase. The behavior of charge carriers is of key importance in virtually all applications of these materials. When excess electrons are added to the conduction band of an oxide, the electron-phonon interaction may result in electron trapping – the formation of either localized (small) or delocalized (large) polarons.

We used a combination of STM, STS and DFT+U to investigate the nature of electron polarons in rutile and anatase. The excess electrons in rutile can localize at any lattice Ti atom, forming a small polaron. The polarons in rutile can easily hop to neighboring sites. Electrons in a perfect anatase lattice prefer delocalized (band-like) solution, while small polarons can only be formed at defects. Large polarons were observed in Nb-doped anatase in vicinity of subsurface Nb dopants. Our results help to understand the different behavior of TiO₂ rutile and anatase in applications.

Work supported by ERC Advanced Research Grant Oxide Surfaces.

O 81.10 Thu 18:15 PHY C 213

In-situ characterization of ferroelectric domains of epitaxially BaTiO₃(100) ultrathin films on Pt(100) by STM and STS

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The understanding of ferroelectric domain properties of ultrathin films is of fundamental interest with regard to interface effects and smallest domain dimensions [1]. To address these issues the widely used piezoresponse force microscopy is not a suitable tool due to its limited resolution and the low mechanical stability of the ultrathin films.

Alternatively, we apply scanning tunneling microscopy (STM) and spectroscopy (STS) for writing and reading of ferroelectric domains in BaTiO₃(100) thin films. The films were grown pseudomorphically on a Pt(100) substrate with compressive strain of 2% [2]. A voltage dependent contrast between positively and negatively poled areas appears in dI/dV maps. In particular a contrast inversion at 1 V between different domains is observed. This inversion results from a characteristic shift of the density of states between c⁺ and c⁻ domains as confirmed by dI/dV point spectra. For ultrathin films of 2 and 3 unit cell thickness, we find different ferroelectric switching behaviors.

[1] J. F. Scott, *J. Phys.: Condens. Matter* 18, 2006

[2] S. Förster et al., *J. Chem. Phys.* 135, 104701 2011

O 81.11 Thu 18:30 PHY C 213

Stress measurements during PLD growth of BaTiO₃ and SrTiO₃ films on single crystal metal substrates — ●JÖRG PREMPER¹, DIRK SANDER¹, and JÜRGEN KIRSCHNER^{1,2} — ¹Max-Planck-Institut für Mikrostrukturphysik, D-06120 Halle — ²Institut für Physik, Martin-Luther-Universität, Halle, Germany

The in situ measurement of film stress by the optical 2-beam cantilever deflection technique [1] is used to study the correlation between stress and strain in BaTiO₃ and SrTiO₃ monolayers on Fe, Pd and Pt single crystal surfaces of different orientations. These films are grown by pulsed laser deposition (PLD). We find that the deposition of 18 uc (unit cells) BaTiO₃ on Pt(001) (misfit = -2.3%) leads to a compressive film stress of -4.2 GPa, whereas the deposition of SrTiO₃ (misfit = +0.4%) induces a tensile stress of +1.5 GPa. On Pd(001) the measured film stress for BaTiO₃/Pd(001) is -2.6 GPa (misfit = -3.0%) and for SrTiO₃/Pd(001) -2.0 GPa (misfit = -0.4%). The comparison between measured stress and calculated misfit-induced stress in the framework of continuum elasticity, considering elastic anisotropy, reveals a qualitative agreement between experiment and stress calculations. This identifies epitaxial misfit as one decisive contribution to film stress in BaTiO₃ and SrTiO₃ atomic layers. In contrast, no epitaxial order of BaTiO₃ and SrTiO₃ films on Fe(001) was observed for PLD at 420°C by LEED. Still film stress of +2.1 GPa and +3.8 GPa is measured. The results are discussed in view of substrate-mediated strain and the influence of growth conditions.

[1] J. Prempfer, D. Sander, and J. Kirschner, *RSI* 83, (2012), 073904

O 81.12 Thu 18:45 PHY C 213

Structure, stress and magnetism of CoO(111) monolayers on Ir(001) — ●SUMALAY ROY¹, HOLGER MEYERHEIM¹, KATAYOON MOHSEN¹, ZEHN TIAN¹, DIRK SANDER¹, ARTHUR ERNST^{1,2}, MARTIN HOFFMANN^{1,3}, WAHEED ADEAGBO³, WOLFRAM HERGERT³, ROBERTO FELICI⁴, and JÜRGEN KIRSCHNER^{1,3} — ¹Max-Planck-Institute of Microstructure Physics, Halle, Germany — ²Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Leipzig, Germany — ³Martin-Luther-University Halle-Wittenberg, Halle, Germany — ⁴European Synchrotron Radiation Facility, Grenoble, France

To investigate the structural depolarization [1] and its correlation with magnetic properties [2] in ultrathin (111) oriented CoO films, 1.6 and 2 monolayers of CoO were deposited on Ir(001) using molecular beam epitaxy of Co followed by subsequent annealing in ambient oxygen. An in-situ Surface X-ray diffraction (SXRD) measurement and analysis of the so prepared CoO(111) films reveals the coexistence of wurtzite and rocksalt structure involving strong vertical relaxations, which is attributed to the reduction of the dipole moment in the polar CoO (111) film which in the bulk renders the structure unstable. The measured stress change (+2.1 N/m) during epitaxial growth can be attributed to the epitaxial misfit between the c-(10×2) CoO(111) film and the Ir(001) substrate. Ab-initio calculations using the SXRD structure parameters as input reveal an anti-ferromagnetic order (below 150K) in the CoO film. [1] P. W. Tasker *J. Phys. C: Solid State Phys.* 12, 4977 (1979). [2] F. Mittendorfer et. al., *Phys. Rev. Lett.* 109, 015501 (2012).