O 32: Oxides and Insulators: Clean Surfaces

Time: Tuesday 13:00–16:45 Location: MA 042

O 32.1 Tue 13:00 MA 042

Structure of the rutile TiO_2(011)-(2x1) surface — •Navid Khorshidi[1], Andreas Stierle[1], Vedran Vonk[1], Claus Ellinger[1], Helmut Dosch[1], Ulrike Diebold[2], Xueqing Gong[3], and Annabella Selloni[3] — [1]Max-Planck-Institut für Metallforschung, Stuttgart, Germany — [2]Tulane University, New Orleans, USA — [3]Princeton University, Princeton, USA

TiO_2 has various applications in technology and is one of the most investigated metal oxides. It is used in solar cells and its photocatalytic activity makes an understanding of the structure of diverse surface orientations desirable. Although there are many studies on TiO_2 surfaces, the (011) surface has been rarely investigated. First principal DFT calculations predict the (011)-(1x1) face to have the third lowest energy and in a Wulff Construction a large part of the surface is (011) oriented. TiO_2 nano particles exhibit preferentially (011) oriented facets. Therefore a structure model of this surface is required to understand the photocatalytic processes on an atomic scale.

We have investigated the TiO_2(011)-(2x1) surface using Surface X-Ray Diffraction (SXRD), Scanning Tunnelling Microscopy (STM) and Low Energy Electron Diffraction (LEED). From our data we are able to derive a novel model for the (011) surface in combination with DFT calculations. The new model has a much lower surface energy than the one suggested previously and fits the X-Ray data very well.

O 32.2 Tue 13:15 MA 042

Structure determination of clean V_2O_3(0001) and TiO_2(110) surfaces — •Werner Unterberger[1], Emily A. Kröger[1], Tsenolo J. Lerotholi[2], Francesco Allegretti[2], David I. Sayago[1], Matthew Knight[2], and Phillip Woodruff[1,2] — [1]Fritz-Haber-Institute — [2]Physics Department, University of Warwick

Scanned-energy mode photoelectron diffraction (PhD) is a well-established method to determine quantitatively the local structure of adsorbates at surfaces. Here we describe its application to the clean surfaces of TiO_2(110) and thin epitaxial films of V_2O_3 on Pd(111).

For V_2O_3(0001) key questions are termination and relaxation of the clean surface; current understanding is based only on theoretical calculations and STM imaging. While the PhD technique is more naturally suited to studies of adsorbate structures, here we report its application to the clean surfaces of V_2O_3 and TiO_2. The TiO_2(110) surface is in principle well-known, and so provides a valuable test of the methodology, although the sign and magnitude of the relaxation of the bridging O atoms has been the subject of recent controversy. The PhD analysis for this surface yields relaxation parameter values in good agreement with the most recent results giving some confidence in the method. For the V_2O_3(0001) surface the results clearly favour the "half-metal"termination with a strongly relaxed outermost layer, as found in published theoretical total energy calculations. However, the PhD results prove inconclusive regarding the presence or absence of surface vanadyl (V=O) species favoured by theory.

O 32.3 Tue 13:30 MA 042

Direct Observation of d^2L^2 Charge Transfer States in TiO_2 thin films by Resonant Photoelectron Spectroscopy — •Sebastian Müller and Dieter Schmeisser — Brandenburgische Technische Universität Cottbus, Angewandte Physik - Sensorik, Konrad-Wachsmann-Allee 17, 03046 Cottbus, Germany

We investigate the electronic structure of TiO_2 thin films by SR-PES, NEXAFS and ResPES. The films are prepared in a combined in-situ/ex-situ process that leads to stoichiometric thin films ($\approx$ 10 nm) in Rutile structure. We focus on ResPES at the Ti 2p edge. When the photon energy is close to the Ti 2p absorption edge we observe additional features about 13 eV below the valence band main features. These features show clear spectator auger decay at the resonance leading to d^0 final state. From this, we deduce the existence of the d^2L^2 initial charge transfer state as this is the only possible channel that enables the corresponding spectator auger decay. These features have the same origin as the satellite structures observed in core level spectra, esp. 2p and 3p.

O 32.4 Tue 13:45 MA 042

Tensor LEED study of the surface relaxation and lattice dynamics of RbI(100) and RbBr(100) — •Stephan Härtel, Jochen Vogt, and Helmut Weiss — Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg

During the last decade the surfaces of several alkali halides were investigated by LEED and other experimental techniques. In good agreement with theoretical predictions for many compounds a rumpling as well as a contraction of the first interlayer distance was found. Up to now no LEED data of the rubidium halides were available. In the present work RbI(100) and RbBr(100) were investigated by means of LEED in an energy range from 30 to 220 eV. The recorded I(E) data were analyzed using the tensor LEED approach. RbI(100) exhibits a slight rumpling where the Rb^+ are shifted inward by 0,07±0,03 Å and the I^- outward by 0,02±0,01 Å. There is no significant contraction of the interlayer distance. In contrast to theoretical calculations [1] the lattice amplitudes of the ions of the two topmost layers are not enlarged significantly compared to the bulk values. For RbBr(100) also a rumpling was observed which is however smaller than that of RbI. The first interlayer distance is reduced by about 1.5%. Different from RbI the lattice amplitudes in the two topmost layers are enlarged by a factor of 1.3 for Rb^+ and 1.25 for Br^-.

[1] de Wette, F.W. et al.: New surface mode on the (001) surfaces of RbBr and RbI, Physical Review B, **35**, 5 (1987)

O 32.5 Tue 14:00 MA 042

Lattice Dynamics of Cu_2O: Bulk and (110) Surface — •Klaus-Peter Bohnen[1], Rolf Heid[1], Aloysius Soon[2], and Catherine Stampfl[2] — [1]Forschungszentrum Karlsruhe, Institut für Festkörperphysik — [2]School of Physics, The University of Sydney

A number of theoretical studies have been carried out in the past to investigate the stability of various surface oxides for the O/Cu system however despite the fact that catalytic processes usually proceed at elevated temperatures stability at finite temperatures has never been studied for these systems. Modern ab-initio methods however allow for the determination of the lattice dynamics and the phononic contribution to the free energy. Using density functional perturbation theory we have studied the lattice dynamics of Cu_2O-bulk as well as Cu_2O(110). In calculating the free energy as function of lattice constant we obtained for the bulk a negative thermal expansion up to roughly 300 K in excellent agreement with experiments. This is due to anomalous mode Grüneisen parameters for vibrational modes in the low energy regime. Due to the anomalous behavior of the mode Grüneisen parameter the bulk system is highly unstable against variations of the lattice constant by more than 2%. To investigate the stability of the O/Cu surfaces we have investigated the lattice dynamics of Cu_2O(110) as a prototype. Despite a large number of low lying modes no instability has been found. These calculations allow also for the O/Cu system for the first time for a realistic estimation of the surface free energy which is important for the determination of surface thermodynamic properties.

O 32.6 Tue 14:15 MA 042

Electronic structure and thermodynamic stability of cubic $La_xSr_{1-x}MnO_3$ (001) surfaces: First-principles calculations by means of hybrid density-functional theory — •Sergejs Piskunovs[1], Eckhard Spohr[1], and Timo Jacob[2] — [1]Lehrstuhl fuer Theoretische Chemie, Universitaet Duisburg-Essen, Campus Essen, S05 V06 E15, Universitaetsstr. 5, D-45141 Essen, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Surface properties of $La_xSr_{1-x}MnO_3$ (LSM) are of high scientific and technological interest due to potential application of these materials in magnetoresistive devices, spintronics, and high-temperature fuel cells. Using the hybrid exchange-correlation functional within density functional theory, we calculated the electronic structure for a wide range of cubic LSM(001) surfaces at low doping $x \sim 1/8$. The layered antiferromagnetic structure is found to be the most energetically favorable for all LSM(001) surfaces under study. Stability of the considered LSM surfaces has been predicted by means of the atomistic thermodynamics. Our calculations show that segregation of Sr at La(Sr)-terminated surface does not lead to its stabilization and thus is thermodynamically unlikely. On the other hand, MnO_2-terminated LSM(001) can be stabilized through adsorption of atomic oxygen atop of Mn sites.

O 32.7 Tue 14:30 MA 042

Preparation of model single crystalline aluminium oxide films suitable for scanning tunnelling microscopy — •Sergiy Borodin and Michael Rohwerder — Max-Planck-Institut für Eisenforschung, Düsseldorf, Deutschland

Self assembly of organic molecules on aluminium or aluminium alloys is of increasing technical importance, e.g. for adhesion promotion and corrosion protection. For the performance of the SAMs in many cases their defect structure is of importance. However, it is difficult to obtain detailed information about the nanoscopic defect structure, as it is difficult to prepare suitable atomically flat samples that can be scanned by STM.

In this work a model thin film aluminum has been prepared under UHV conditions, whose surface is suitable for a scanning tunneling microscopy investigation, e.g. of phosphonate self-assembly on aluminium. This surface is stable even upon contact at high water exposures and hence much superior to model aluminium oxide surfaces prepared on NiAl.

O 32.8 Tue 14:45 MA 042

Work function measurements with a combined AFM/STM setup under ultrahigh vacuum conditions at 5K on thin MgO films grown on Ag(001) — •Thomas König, Georg Hermann Simon, Violeta Simic-Milosevic, Markus Heyde, and Hans-Joachim Freund — Fritz-Haber-Institute of the Max-Planck-Society, Faradayweg 4-6, 14196 Berlin, Germany

For many years metal supported thin oxide films have been investigated in the research field of heterogeneous catalysis. The properties of the thin films depend strongly on both the support and the film thickness. While thick films approach the properties of bulk material thin films exhibit their own characteristics. It has been proposed by Pacchioni et al. [1] that charging can occur by depositing metal atoms on ultrathin MgO films grown on metal supports. The charging of Au atoms on top of a thin MgO film grown on Ag(001) has been confirmed by STM measurements done by Sterrer et al. [2]. The MgO film on top the metal support leads to a compression of the metal electrons which for a free metal spill over into the vacuum. The compression results in a reduction of the surface dipole and thus to a decrease of the work function. Here we present work function measurements on different MgO film thicknesses grown on Ag(001). The measurements have been done with our combined AFM/STM setup operating under UHV conditions at 5K. The results will be discussed and compared with theoretical calculations.

[1] L. G. Giordano et al., Phys. Rev. B 73, 045414, 2005. [2] M. Sterrer et al., Phys. Rev. Lett. 98, 096107, 2007.

O 32.9 Tue 15:00 MA 042

Stress of CoO(111) on Ir(100) — •Zhen Tian, Dirk Sander, and Juergen Kirschner — Max-Plank Institute of Microsctructure Physics

An important aspect of epitaxial oxide films is that the growth of (111) oriented films with rock salt structure leads to polar surfaces, where adjacent layers are composed of either anions or cations only. Considerable repulsive Coulomb interaction within the oxide (111) layers are therefore expected [1]. We measured the stress change during the formation of CoO(111) on Ir(100) by post-oxidation of Co films [2]. Combined structural investigations by LEED and stress measurements by the crystal curvature technique are performed. The formation of the CoO(111)-c(10×2) structure by post-oxidation of 2 monolayers Co induces a compressive surface stress change of −0.5 N/m. The epitaxial Co film prior to oxidation is under a tensile stress of +16 GPa, which is induced by the lattice misfit between fcc-Co and Ir. The formation of the CoO(111) film induces a tensile stress change of +2.1 N/m, as compared to the clean Ir(100) surface. This stress change is quantitatively ascribed to the anisotropic misfit between the c(10×2) structure of CoO(111) and Ir(100) of +0.22 % and +4.2 % along Ir[110] and Ir$[1\bar{1}0]$, respectively. Our stress measurements indicate that charge depolarization effects [3] might be operative on the CoO(111)-c(10×2) film.

[1] C. Noguera, J. Phys.: Condens. Matter 12 (2000) R367-R410.

[2] C. Giovanardi, L. Hammer, and K. Heinz, Phys. Rev. B 74, 125429 (2006).

[3]C. Tusche, H. L. Meyerheim, and J. Kirschner, Phys. Rev. Lett. 99 (2007) 026102.

O 32.10 Tue 15:15 MA 042

Metal-insulator transition on the V_2O_5(001) surface: Theory and experiment — •Maria Veronica Ganduglia-Pirovano[1], Remy Fortrie[1], Joachim Sauer[1], Ralf-Peter Blum[2], Horst Niehus[2], Carsten Hucho[3], Shamil Shaikhutdinov[4], and Hans-Joachim Freund[4] — [1]Inst. für Chemie, HU-Berlin — [2]Inst. für Physik, HU-Berlin — [3]Paul-Drude-Institut Berlin — [4]FHI Berlin

Several vanadium oxides undergo a metal-to-insulator transition (MIT) in the bulk, e.g., V_2O_3 at $\sim$150 K, VO_2 at 340 K, whereas V_2O_5 is a semiconductor. Experimental evidence for a thermally induced *surface* insulator-metal transition (MIT) at the V_2O_5(001) surface at 350-400 K is presented. This surface exposes vanadyl (V=O) double rows along the [010] direction. Using density functional theory (DFT) in combination with statistical thermodynamics, the facile reduction along the rows was predicted.[1] The experimentally observed MIT transition expands preferentially in the direction of these rows. We then used the Monte Carlo method to simulate the reduced V_2O_5(001) surface at a given temperature and defect concentration. We typically find areas with a random distribution of isolated defects and others with up to 5 sites forming [010] oriented trenches. Using calculated band gaps for reduced V_2O_5 structures as obtained with DFT+U, we construct band gaps maps which agree with those derived from scanning tunneling spectroscopy data; only the areas with defective rows are metallic.

[1] M. V. Ganduglia-Pirovano and J. Sauer, PRB **70**, 045422 (2004).

[2] R.-P. Blum, H. Niehus, C. Hucho et al., PRL. in press.

O 32.11 Tue 15:30 MA 042

Structural arrangement of room temperature ionic liquids at a hard wall — •Heiko Schröder, Markus Mezger, Sebastian Schramm, Harald Reichert, John Okasinski, and Helmut Dosch — Max-Planck-Institut für Metallforschung, Stuttgart

Interfacial phenomena in physical, chemical, and biological systems are of increasing relevance in many of today's technological applications. In order to access solid-liquid interfaces and extract microscopic details of their local structure with high resolution, we have employed high energy x-ray microbeam reflectivity. Here, we discuss the analysis and interpretation of reflectivity data recorded at the interface between different room temperature ionic liquids (RTIL) and a hard wall (sapphire). Real space structures could be resolved with Å-resolution. Although crucial for the understanding of solvent properties, only little is known about the structural arrangement of anions and cations in RTILs at solid interfaces. We systematically examined different parameters altering the interfacial properties. By choosing different combinations of anions and cations, the ion-ion and ion-substrate interaction as well as the size ratio of the involved ions could be varied. By modifying the temperature, the ratio between entropy and interfacial energy can be tuned as well, favoring a disordered liquid or interfacial layering, respectively. This results in different structural arrangements at the molecular level.

O 32.12 Tue 15:45 MA 042

The Au(111) Electrolyte Interface: A DFT Investigation — Sudha Venkatachalam[1], Felice C. Simeone[1], Dieter M. Kolb[1], and •Timo Jacob[1,2] — [1]Institut für Elektrochemie, Universität Ulm, D-89081 Ulm — [2]Fritz-Haber-Institut der MPG, D-14195 Berlin

Density functional theory calculations have been performed to derive a detailed model of the electric double layer for Au(111) in contact with an aqueous H_2SO_4 electrolyte. At potentials of $E \geq +0.8\,V$ vs. SCE various surface sensitive techniques found evidence for a $(\sqrt{3} \times \sqrt{7})$R19.1° (bi)sulfate structure, but the nature of coadsorbates remains still unclear. Focusing on a sulfate adlayer, the coadsorption of H_3O^+ and/or H_2O has been studied [1]. The calculated binding energies show that the coadsorption of a single H_3O^+ per sulfate (stabilizing the adlayer by hydrogen bonds) is the most stable configuration. In addition, the charge density distribution within the adlayer well agrees with effective barrier heights deduced from recent distance tunnelling spectroscopy measurements [2].

Afterwards we studied the interfacial structure that forms at negative electrode potentials and found that water arranges near the electrode in an ice-like hexagonal structure with hydronium ions being located in the second water layer and non-specifically adsorbed. Again the calculated charge density distribution shows a perfect correspondence to distance tunnelling spectroscopy measurements.

[1] S. Venkatachalam, T. Jacob, Z. Phys. Chem., **221**, 1393 (2007).

[2] S. Venkatachalam *et al.*, Angew. Chem. Int. Ed., DOI: 10.1002/anie.200702868.

O 32.13 Tue 16:00 MA 042

Surface Stress Variation as a Function of Charge for the Metal

at Metal - Electrolyte Interface — •Maxim Smetanin[1], Raghavan N Viswanath[1], Dominik Kramer[1], and Joerg Weissmueller[1,2] — [1]Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany — [2]Universität des Saarlandes, Saarbruecken, Germany

During the last decade, there has been considerable progress in measuring and understanding the capillary forces on metal surfaces. The present work revisits the question, what is the magnitude of the surface stress charge coefficient(SSCC) for the gold in an electrolyte near the potential of zero charge, in particular in respect to comparison to numerical computation. We report in-situ measurements of f(q) for planar gold electrodes in weakly adsorbing electrolytes, using a cantilever bending technique with optical detection. We used 40 nm thick, (111)-textured gold films on 100 *m thick (100)-oriented silicon wafers in aqueous NaF and HClO4. The films were characterized in respect to roughness (using a scanning probe microscopy) and to contamination (using Auger microscopy). Their pzc value was determined in 7 mM NaF using the minimum of the differential capacitance, it is ca. 0.20 V vs. SCE. The wafer bending results testify to an essentially linear f(q) near the pzc and electrode charging occurs mainly within the diffuse double layer at minimum influence of specific ions adsorption. SSCC was found to be of the order of -1.95 V for 7 mM NaF and -2.02 V for 10 mM HClO4.

O 32.14 Tue 16:15 MA 042

STM of superstructures and surface transformations on Pt(111) in a sulfuric acid electrolyte — •Björn Braunschweig and Winfried Daum — Institut für Physik und Physikalische Technologien, TU-Clausthal, Leibnizstrasse 4, D-38678 Clausthal-Zellerfeld

Imaging of weakly chemisorbed species on Pt surfaces with the STM in electrochemical environments and with molecular resolution is a challenge to the experimenter as these electrode surfaces are very susceptible to contaminations at a level well below the sensitivity of cyclic voltammetry. We have investigated the surface structure of Pt(111) in a 0.1 M H_2SO_4 electrolyte in the potential range of sulfate adsorption. In agreement with a previous study [1] we observe a disorder-order transitions at a potential of 0.5 V versus the reversible hydrogen electrode (RHE). For potentials between 0.5 and 0.8 V RHE we identified two distinctly different sulfate superstructures: the well-known $(\sqrt{3} \times \sqrt{7})$R19.1° superstructure and a new (3x1) superstructure. We were able to simultaneously image the sulfate and the Pt surface lattice and to determine the registry of the sulfate anions with the substrate. The structure in the unit cell of the (3x1) superstructure indicates the presence of an additional molecular component, possibly hydronium or water molecules. For potential sweeps to 0.8 V RHE and above the ordered sulfate overlayer changes instantaneously to a more disordered structure presumably due to adsorption of OH^- ions.

[1] A.M. Funtikov, U. Linke, U. Stimming and R. Vogel; Surf.Sci. <u>324</u>, L343 (1995) and J. Electroanal. Chem. <u>428</u>, 147 (1997)

O 32.15 Tue 16:30 MA 042

The quest for ZnO$(11\bar{2}0)$ surface states – an ARPES study — •Christian Pettenkofer and Stefan Andres — Hahn-Meitner-Institut, Glienicker Str. 100, D-14109 Berlin

We present angle resolved photoemission data from differently prepared ZnO$(11\bar{2}0)$ single crystals and epitaxially grown thin films. ZnO$(11\bar{2}0)$ single crystal surfaces were prepared by both cleaving in vacuum and sputtering-annealing cycles of pre-polished crystals. ZnO$(11\bar{2}0)$ thin films were grown heteroepitaxially on the r-face of sapphire by MOMBE using diethylzinc and water as precursor molecules. The ARUPS-spectra were recorded at the TGM7 beamline at BESSY-II synchrotron light facility in Berlin.

The band dispersion along $k_\parallel$ and $k_\perp$ is discussed in accordance with theoretical band structure calculations of the bulk electronic states within the GGA-DFT framework. An excellent agreement between the theoretically and experimentally determined band structure is achieved for the upper valence bands. Furthermore the surface electronic structure of both the epitaxially grown thin films and the single crystals coincide very well with each other.

It is shown, that despite the very different nature of the surface preparation methods no surface states could be observed. Therefore different effects such as hydrogen adsorption, surface defects and lattice relaxation will be discussed with regard to the specific surface preparation method.