

O 17: Oxides and insulators III

Time: Tuesday 10:30–13:00

Location: SCH A01

O 17.1 Tue 10:30 SCH A01

Oxygen adatoms at SrTiO₃(001): A density-functional theory study — ●HANNES GUHL¹, WOLFRAM MILLER¹, and KARSTEN REUTER² — ¹Institut für Kristallzüchtung, Max-Born-Str. 2, D-12489 Berlin, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Apart from its use in photo-catalytic and sensing applications, the SrTiO₃(001) surface is also receiving increasing attention as a suitable substrate material for thin film growth. For the latter context the numerous reported surface reconstructions, partly in sensitive dependence of the applied annealing temperature, indicate a complex surface kinetics, which needs to be understood and controlled when aiming at growth experiments tailored to the atomic-scale. As a first step in this direction we carry out density-functional theory calculations addressing the energetics and electronic properties of adsorbed oxygen atoms at both regular terminations of SrTiO₃(001). With the bonding at the SrO-termination in general stronger than at the TiO₂-termination, we find in both cases that the most stable adsorption site does not correspond to the one expected from a continuation of the perovskite lattice. Instead, the ad-atom forms a strong bond to a surface oxygen atom that is reminiscent of the oxygen-oxygen bond in SrO₂. Mapping the potential energy surface for lateral adatom motion away from the stable site, the obtained diffusion barriers are about 0.8 eV in the isolated ad-atom limit. This suggests that, at least at the studied ideal terminations, oxygen mobility is not a major bottleneck under typical growth conditions.

O 17.2 Tue 10:45 SCH A01

Adsorption of benzoic acids on NaCl surface — ●WEI CHEN¹, CHRISTOPH TEGENKAMP¹, HERBERT PFNÜR¹, and THOMAS BREDOW² — ¹Institut fuer Festkörperphysik, Leibniz Universität Hannover, Hannover, Germany — ²Institut für Physikalische und Theoretische Chemie, Universität Bonn, Bonn, Germany

The adsorptions of benzoic acid (BA) and its OH-substituted derivatives, salicylic acid (SA) and para-salicylic acid (p-SA) on NaCl surfaces have been investigated by periodic DFT. On NaCl(100) these molecules bond to the surface weakly with binding energies of around 0.4 eV (in the absence of van der Waals interaction), through the electrostatic interaction between oxygen and surface sodium. The band gap is reduced to the HOMO-LUMO separation of the adsorbate (4.86 eV for SA). In existence of surface anion vacancy, the unpaired electron localized in the vacancy transfers to the molecules after adsorption. As a result the LUMO of the adsorbate is partially occupied. Larger increase of adsorption energies have been found due to stronger bonding between oxygen and sodium, as well as the interaction between the transferred unpaired electron over the benzene ring and surface sodium. On (001)-like step site, it shows a stronger binding than on NaCl(100) surface, with adsorption energies of around 0.8 eV, whereas the electronic structure remains similar. On (011)-like step site the adsorption energy further increases to about 1.0 eV. Interestingly, due to the 1.5 eV upward shift of 2p state from step edge Cl atoms, the band gap is effectively reduced (2.97 eV for SA). Implication of these results to the contact charging effect will be discussed.

O 17.3 Tue 11:00 SCH A01

Correlation between bonding geometry and band gap states at organic-inorganic interfaces: catechol on rutile TiO₂(110) — ●ANNABELLA SELLONI¹, JIAN-GUO WANG¹, SHAO-CHUN LI², PETER JACOBSON², XUE-QING GONG¹, and ULRIKE DIEBOLD² — ¹Department of Chemistry, Princeton University, Princeton NJ 08544 — ²Department of Physics, Tulane University, New Orleans, LA 70118 (USA)

Adsorbate-induced band gap states in semiconductors are of particular interest due to the potential of increased light absorption and photoreactivity. A combined theoretical and experimental (STM, photoemission) study of the molecular-scale factors involved in the formation of gap states in TiO₂ is presented. Using the organic catechol on rutile TiO₂(110) as a model system it is found that the bonding geometry strongly affects the molecular electronic structure. At saturation catechol forms an ordered 4 × 1 overlayer. This structure is attributed to catechol adsorbed on rows of surface Ti atoms with the molecular plane tilted from the surface normal in an alternating fashion. In the

computed lowest-energy structure one of the two terminal OH groups at each catechol dissociates and the O binds to a surface Ti atom in a monodentate configuration, while the other OH group forms a H-bond to the next catechol neighbor. Through proton exchange with the surface this structure can easily transform into one where both OH groups dissociate and the catechol is bound to two surface Ti in a bidentate configuration. Only bidentate catechol introduces states in the band gap of TiO₂.

O 17.4 Tue 11:15 SCH A01

Understanding the Accuracy of Density-Functional Theory Exchange-Correlation Functionals for Adsorption at Ionic Substrates: Water on salt and some other examples — ●BO LI¹, ANGELOS MICHAELIDES^{1,2}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6 Berlin, Germany — ²London Centre for Nanotechnology and Department of Chemistry, University College London, London UK

The interaction of water with salt (NaCl) is of widespread importance. Although numerous theoretical studies have been reported (see Ref. [1] and references therein), none has provided a reliable estimate of the strength of the bond between water and NaCl(001). Moreover, the adsorption energies predicted by density-functional theory (DFT) range from 0.2 to 0.7 eV/H₂O depending on exchange-correlation (xc) functional. Here, we address this through a set of second order Møller-Plesset perturbation theory and coupled cluster calculations on a series of Na_xCl_x (x = 5 to 25) clusters to arrive at a reliable estimate of the H₂O adsorption energy on NaCl(001). This is then used to *understand* the performance of a range of xc functionals in treating this and related adsorption systems. Further, through symmetry-adapted perturbation theory the relative importance of electrostatics, covalency, and van der Waals forces in water adsorption on ionic substrates is unraveled.

[1] A. Verdaguer, G. M. Sacha, H. Bluhm, and M. Salmeron, Chem. Rev. **106**, 1478 (2006).

O 17.5 Tue 11:30 SCH A01

Theoretical evidence for mixed adsorption of water on Fe₃O₄(001) — ●NARASIMHAM MULAKALURI^{1,2}, ROSSITZA PENTCHEVA¹, MARIA WIELAND¹, WOLFGANG MORITZ¹, and MATTHIAS SCHEFFLER² — ¹Section Crystallography, Dept. for Earth and Environmental Sciences, University of Munich — ²Fritz-Haber-Institut der MPG, Berlin

The interaction of water with a mineral surface is a fundamental process towards understanding surface reactivity. Based on density functional theory (DFT) calculations we investigate the adsorption of water and its influence on the electronic properties and surface reconstruction of Fe₃O₄(001). Starting from a single water molecule per ($\sqrt{2} \times \sqrt{2}$)R45° unit cell, we vary the concentration and configuration of water and hydroxyl groups. The surface phase diagram compiled within the framework of *ab-initio* thermodynamics indicates that a clean wave-like distorted bulk termination (*modified* B-layer) [1] is favorable over a substantial range of O₂ and H₂O partial pressures, but competes with a B-layer with oxygen vacancies in the oxygen poor limit. Such vacancies can promote dissociation of isolated water molecules. With increasing pressure in the gas phase there is a crossover to a mixed molecular and dissociative adsorption mode. A quantitative low energy electron diffraction (LEED) analysis confirms two distinct Fe-O-distances. DFT and LEED results indicate a suppression of the ($\sqrt{2} \times \sqrt{2}$)R45°-reconstruction.

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

O 17.6 Tue 11:45 SCH A01

Tailoring the adsorption properties of SiO₂ thin films — ●JAN-FREDERIK JERRATSCH, NIKLAS NILIUS, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der MPG, D14195 Berlin, Germany

An ultra-thin silica film grown on Mo(112) can be chemically modified by inserting Li atoms into the nano-pores of the oxide material. The Li becomes cationic upon incorporation and considerably reduces the silica/Mo work function by creating a positive surface dipole. The smaller work function facilitates charge transfer processes from the Mo support into adsorbates on the surface. The hence negatively charged ad-

species have a much larger binding energy due to Coulomb interactions with the support. This principle is demonstrated for gold deposited onto Li/silica/Mo(112) using a low temperature STM. Whereas single Au atoms and small clusters are anchored on the Li-modified surface, they are unable to bind to the pristine oxide film.

O 17.7 Tue 12:00 SCH A01

Structure of CO₂ adsorbed on the KCl(100) single crystal surface — ●JOCHEN VOGT, MILICA HADNADIEV, and HELMUT WEISS — Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany

Self-organization phenomena in two dimensions are a hallmark of systems with weak molecule-surface interaction in gas adsorption. On insulator single crystal surfaces, such systems can be ideally studied experimentally, e. g. by means of polarization infrared spectroscopy (PIRS) and low-energy electron diffraction (LEED). On the KCl(100) surface at a temperature of 80 K, the first layer of carbon dioxide grows in three different phases: firstly a lattice-gas, secondly a disordered phase at submonolayer coverage, which thirdly undergoes a phase-transition to a highly ordered $(6\sqrt{2} \times \sqrt{2})R45^\circ$ structure, if the CO₂ partial pressure exceeds a critical temperature-dependent value. So far, not much was known about the structure of the 237 Å² unit cell of the high-order phase which in absolute terms offers place for up to 14 inequivalent CO₂ molecules. Total energy minimizations and Monte Carlo Simulations based on pair-potentials favor a structure containing 12 inequivalent molecules. Using a vibrational exciton approach, simulated infrared spectra based on this structure are in very satisfactory agreement with experimental IR spectra. According to theory, 10 molecules are stabilized on the surface due to a predominant molecule-molecule interaction, while only two molecules are "pinned" onto the surface at sites with favorable molecule-surface interaction. This might explain the rapid aging of the structure observed in the experiments.

O 17.8 Tue 12:15 SCH A01

An Azobenzene Derivate on NaCl/Ag(111): Surface Structure, Molecule Adsorption, and Electron-Induced Switching — ●ALI SAFIEI, JÖRG HENZL, and KARINA MORGENSTERN — Leibniz University of Hannover, Institute of Solid State Physics, Appelstraße 2, 30167 Hannover

Thin NaCl films on metallic substrates offer the possibility of investigating the conformational, mechanical and electronic structure and thus functionalities of molecules with low coupling to the substrate. We first studied the growth of NaCl islands by scanning tunnelling microscopy and spectroscopy on the clean Ag(111) surface. On this surface the islands grow epitaxially in double layers, are atomically flat and nearly defect-free. Spectroscopic dI/dV measurements show that the surface state of Ag on NaCl double layer is shifted to higher energies than on the pure Ag(111) surface. Amino-nitro-azobenzene molecules

(ANA) are adsorbed on the NaCl islands at very low temperatures. We found the trans-configuration of ANA on the ultra-thin insulating layers and realized a reversible switching process by electron-induced manipulation. In contrast to the switching processes on Au(111) [1], these conformational changes resemble the trans-cis isomerisation of the ANA molecule in the gas phase. The reason is that the molecules on NaCl islands are less coupled to the substrate. The shift of the surface state of Ag on NaCl, the switching process and the energy barrier of the reversible switching will be discussed in this talk.

[1] Jörg Henzl, Michael Mehlhorn, Heiko Gawronski, Karl-Heinz Rieder, Karina Morgenstern, *Angew. Chem. Int.* 45 (2006) 603-606.

O 17.9 Tue 12:30 SCH A01

The resonant x-ray absorption coefficient by diffraction peak widths — ●VICTOR SOLTWISCH, YEVGEN GOLDSHTEYN, ENRICO SCHIERLE, DETLEF SCHMITZ, and EUGEN WESCHKE — Helmholtz-Zentrum Berlin für Materialien und Energie

The (010) structural reflection of multiferroic DyMnO₃ was measured for photon energies across the *M*₅ absorption edge of Dysprosium by resonant soft x-ray diffraction. It is found that the width of this diffraction peak exactly tracks the x-ray absorption spectrum obtained from the same sample by measurement of the total electron yield (TEY). While such a connection has been anticipated, we provide a direct experimental proof. The method is more bulk sensitive than TEY and avoids the problem of self absorption present in fluorescence-yield data. Furthermore, it provides an excellent tool for measurements of the absorption coefficient in insulators at low temperatures or in strong magnetic fields.

O 17.10 Tue 12:45 SCH A01

Ferroelectric domain structures on BaTiO₃(100) observed by Laser-excited PEEM — ●ANKE HÖFER, KLAUS DUNCKER, STEFAN FÖRSTER, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, Halle, Germany

The ferroelectric domain structure at a single crystal BaTiO₃(100) surface is imaged by photoelectron emission microscopy (PEEM) using a fully tunable femtosecond laser source. For a BaTiO₃(100) surface which is prepared under UHV conditions by sputtering and annealing in an oxygen atmosphere, at room temperature a stripe like domain pattern is observed with high contrast aligned in the high symmetry [100] direction of the substrate. The PEEM pattern is explained by sequences of 90°-a-c domains.

Wavelength-dependent images with UV excitation in the range of 290 - 330 nm show a varying domain contrast and allow the determination of the local photoemission threshold for one ferroelectric domain. For higher laser pulse energies and for wavelengths below the onset of one-photon photoemission, two-photon PEEM images show the ferroelectric domain structure as well.