

## O 5: Adsorption on semiconductors, oxides and insulators I

Time: Monday 10:30–13:15

Location: MA 042

O 5.1 Mon 10:30 MA 042

**Tailoring Hybrid States at Inorganic/Organic Interfaces: Pyridine/ZnO(10-10)** — ●OLIVER T. HOFMANN, YONG XU, PATRICK RINKE und MATTHIAS SCHEFFLER — FHI, Berlin

Hybrid inorganic/organic systems (HIOS) have opened up new opportunities for the development of optoelectronics due to their potential of achieving synergy beyond simply combining the best features of two distinct material classes. Even new physics and thus added value could be achieved if new quantum mechanical states occur at the interface, provided their energetic position is readily controllable. Theory and experiment indicate that such states can be found for a pyridine monolayer adsorbed on the transparent conductive oxide ZnO. We employ density functional theory, augmented with the electron-density dependent vdW-TS scheme, to investigate the nature of these states and the factors governing their energetic position. We find that conventional semi-local functionals give the wrong ordering of the pyridine orbitals and underestimate the bond strength between adsorbate and substrate, favoring an incorrect morphology. Both issues are ameliorated by incorporating exact exchange. The hybrid states, found approximately 1eV above the valence band edge and within the conduction band, originate from the ZnO conduction band and the pyridine LUMO. The large adsorption-induced interface dipole responsible for the energetic alignment is attributed to strong charge rearrangement within the subsystems. Having identified the interaction mechanism, we propose tailoring the energetic position of the interface state by controlling the interface dipole, e.g. by pre-covering ZnO with small molecules.

O 5.2 Mon 10:45 MA 042

**DFT study of the interaction of hydrogen with stepped ZnO surfaces** — ●JAKUB GOCLON and BERND MEYER — Interdisziplinäres Zentrum für Molekulare Materialien und Computer-Chemie-Centrum, Universität Erlangen-Nürnberg

The nature of the interaction of hydrogen with ZnO surfaces, which is a very important process in heterogeneous catalysis, is still mostly unresolved. While our previous study [1] was devoted to hydrogen adsorption on the ideal ZnO(10 $\bar{1}$ 0) surface in comparison with experimental observations [2], we will present here results on hydrogen interaction with stepped surfaces. The steps were represented by (10 $\bar{1}$ 1) and (20 $\bar{2}$ 1) crystal cuts, considering both Zn and O terminations.

Using DFT calculations in combination with a thermodynamic analysis we have calculated the relative stability of various structural models representing surface steps as function of hydrogen and water chemical potentials. Different surface coverages of hydrogen on O and Zn sites formed by homolytic, heterolytic, and mixed types of adsorption were considered. Based on the phase diagrams from our thermodynamic analysis we find that at low hydrogen chemical potential only OH groups are present, while with increasing hydrogen partial pressure heterolytic adsorption becomes more favorable. For the O-terminated steps the onset of zinc hydroxide formation, which was found to be a stable configuration on the flat ZnO(10 $\bar{1}$ 0) surface, is observed.

[1] J. Goclon, B. Meyer, *in preparation*[2] Y. Wang, B. Meyer, X. Yin, M. Kunat, D. Langenberg, F. Traeger, A. Birkner, Ch. Wöll, *Phys. Rev. Lett.* 95 (2005) 266104

O 5.3 Mon 11:00 MA 042

**Theoretical Investigations of the Interface between Copper and Zinc Oxide** — ●BJÖRN HILLER and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Universitätsstraße 150, 44801 Bochum, Germany

Heterogeneous catalysis is used in many industrial processes for production of main base chemicals. For instance, in methanol synthesis copper clusters on a zinc oxide support are used. Although this process is of great importance, the microscopic structure of the catalytic system is not known.

In experiments it has been found, that there are strong interactions between the copper particles and the support as the copper entrenches into zinc oxide. A theoretical treatment of interface systems is elaborate due to differences in cell dimensions of the subsystems. This leads to either very large calculations or an artificial stress in the system. Furthermore the entrenching increases the number of possible interfaces which have to be investigated in order to fully understand the system.

To identify the most stable interfaces we need to obtain reliable geometries. For this we suggest an approach that finds possible matching cells and also fully relaxed geometries. Using this technique we present energies for interfaces between low-index copper surfaces and ZnO(10 $\bar{1}$ 0) and ZnO(11 $\bar{2}$ 0), respectively.

O 5.4 Mon 11:15 MA 042

**New mechanism for work-function tuning: ZnO surfaces modified by a strong organic electron acceptor** — ●YONG XU<sup>1</sup>, OLIVER T. HOFMANN<sup>1</sup>, PATRICK RINKE<sup>1</sup>, MATTHIAS SCHEFFLER<sup>1</sup>, RAPHAEL SCHLESINGER<sup>2</sup>, NORBERT KOCH<sup>2</sup>, and ANTJE VOLLMER<sup>3</sup> — <sup>1</sup>Fritz Haber Institute Berlin — <sup>2</sup>Humboldt-Universität zu Berlin — <sup>3</sup>Helmholtz-Zentrum Berlin

A key task for optimizing optoelectronic devices comprising hybrid inorganic/organic systems is to control the energy level alignment at interfaces. The use of interlayers provides a pathway to solve this challenge. To demonstrate the concept we investigated the polar surfaces of ZnO, modified by the prototypical organic electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) theoretically and experimentally. DFT-PBE  $\Delta$ SCF calculations of the O 1s surface core-level shifts combined with XPS measurements suggest that ZnO(000-1)/ZnO(0001) are H/OH covered. Depositing F4TCNQ on these surfaces considerably increases the work function that is shown to be insensitive to the doping level. F4TCNQ on ZnO(0001) exhibits an extraordinary high work function due to the appearance of upright adsorption. The PBE+vdW results are in line with the UPS data that shows work-function increases up to 1.4/2.8 eV on ZnO(000-1)/ZnO(0001). In contrast to F4TCNQ on metals, where pronounced bidirectional charge transfer occurs, the charge transfer to F4TCNQ is small, pinning the LUMO close to the Fermi level. The polarization of the system, caused by strong charge rearrangement within the adsorbate, is the main mechanism for the large work-function increase.

O 5.5 Mon 11:30 MA 042

**Adsorption and laserinduced desorption of CO on a rutile(110)-surface** — ●HENDRIK SPIEKER and THORSTEN KLÜNER — Theoretical Chemistry, Carl von Ossietzky Universität, PO Box 2503, 26111 Oldenburg

The CO/TiO<sub>2</sub>-system – being a model system for surface chemistry – is experimentally as well as theoretically of very high interest. To understand and compute the interaction of a CO molecule with titanium dioxide a Ti<sub>9</sub>O<sub>18</sub>Mg<sub>7</sub><sup>14+</sup>-cluster, which is embedded within a finite point charge field, is used to approximate the rutile(110)-surface. [1] Thus, we are now able to calculate the first two-dimensional potential energy surfaces representing the ground state and the first excited state of the CO molecule on MP2-level which are corrected for the basis set superposition error. Applying wave packet propagation methods to these potential surfaces yields a quantum state resolved description of laserinduced desorption of CO from the rutile(110)-surface and reveals a completely new, mixed desorption mechanism. Dependent on the angle between the surface normal and the CO bond axis, a transition from a MGR- to an Antoniewicz-like desorption can be observed. In addition, a negative correlation between the rotational and translational degrees of freedom of the CO molecule was found. Finally, this leads to a desorption probability of the CO molecule in accordance with the expected value for metal oxides like TiO<sub>2</sub>.

[1] M. Mehring, T. Klüner, *Chem. Phys. Lett.* **513**, 212 (2011).

O 5.6 Mon 11:45 MA 042

**Adsorption of amino acids on the TiO<sub>2</sub> (110) surface** — ●RALF TONNER — Fachbereich Chemie, Philipps-Universität Marburg, Germany

The optimal adsorption modes for amino acids glycine and proline on the ideal TiO<sub>2</sub>(110) surface have been investigated using density functional theory (PBE) applying periodic boundary conditions (VASP). Binding modes with anionic acid moieties bridging two titanium atoms after transferring a proton to the surface are the most stable configurations for both molecules investigated similar to previous results for carboxylic acids. In contrast to the latter, amino acids can form hydrogen bonds via the amino group towards the surface-bound proton which provide an additional stabilization of 15-20 kJ mol<sup>-1</sup>.

Calculations of vibrational frequencies complement the adsorption

study and provide guidance for future experimental investigations. Dispersion effects can influence the relative stabilities of adsorption modes considerably.

O 5.7 Mon 12:00 MA 042

**The adsorption of H<sub>2</sub>O on TiO<sub>2</sub>(110) investigated by Helium Atom Scattering** — ●NIKLAS OSTERLOH<sup>1</sup> and FRANZISKA TRAEGER<sup>2</sup> — <sup>1</sup>Physical Chemistry 1, Ruhr-University Bochum, Germany — <sup>2</sup>Institute for Business Engineering, University of Applied Science Gelsenkirchen, Germany

Previously reported experimental and theoretical studies disagree on, whether or not water on a defect free rutile TiO<sub>2</sub>(110)-surface adsorbs dissociative. The experimental results showed almost no dissociative behavior, but theoretical studies predicted exactly the opposite. [1,2] To clarify this question, we investigated water on rutile(110) by helium atom scattering (HAS), a most surface sensitive and non-destructive method, as well as by thermal desorption spectroscopy (TDS). The angular distributions of the helium atoms clearly show a (1x1) superstructure for temperatures between 130 and 300 K. While a fully dissociated layer was ruled out by previous studies [3], this symmetry rules out any half-dissociated layer. Neither the angular distribution nor the curves of specular intensity versus temperature showed any indications for a phase transition. In this talk we will present and discuss this results.

[1] Diebold, U., The surface science of titanium dioxide. Surface Science Reports, 2003. 48: p. 53-229 [2] Pang, C.L., R. Lindsay, and G. Thornton, Chemical reactions on rutile TiO<sub>2</sub>(110). Chemical Society Reviews, 2008. 37(10): p. 2328-2353 [3] Henderson, M.A., An HREELS and TPD study of water on TiO<sub>2</sub>(110): The extent of molecular versus dissociative adsorption. Surface Science, 1996. 355(1-3): p. 151-166

O 5.8 Mon 12:15 MA 042

**Ab initio calculations on the adsorption of water on rutile (110)** — ●JAN MITSCHKER and THORSTEN KLÜNER — Theoretical Chemistry, Carl von Ossietzky Universität Oldenburg, PO Box 2503, 26111 Oldenburg

Despite its apparent simplicity, the adsorption and photoreaction of water on surfaces is still a very challenging task. However, a fundamental understanding of the interaction is of great importance for a systematic surface modification. Furthermore, many substrates reveal interesting photochemical properties. As an example system, H<sub>2</sub>O on titanium dioxide has attracted a great deal of attention, especially, because of its ability to split water under light irradiation. Though many theoretical and experimental studies have been performed, there is no satisfying agreement on how the process actually takes place. We address this problem by combining highly accurate *ab initio* potential energy surfaces (obtained on MP2 and CASPT2 level) with an explicit quantum dynamical treatment of the reaction in all relevant degrees of freedom. Such a procedure is indispensable to account for the quantum mechanical character of reactions involving hydrogen. The rutile(110) surface is modeled by a TiO<sub>2</sub> cluster embedded in a finite point charge field. The dynamics after an electronic excitation is simulated within the jumping wave packet model. In our talk, we present first results for the adsorption on the rutile(110) surface.

O 5.9 Mon 12:30 MA 042

**Cu induced morphology changes at Pb/Si (111) interface: separation of "5x5"-Cu structure into individual domains.** — ●PAVEL SHUKRYNAU<sup>1,2</sup>, PINGO MUTOMBO<sup>2</sup>, LARS SMYKALLA<sup>1</sup>, VLADIMIR CHAB<sup>2</sup>, and MICHAEL HIETSCHOLD<sup>1</sup> — <sup>1</sup>Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group. D-09107 Chemnitz, Germany. — <sup>2</sup>Institute of Physics Academy of Sciences of the Czech Republic, Cukrovarnická 10. CZ 162 53 Prague,

Czech Republic

The adsorption of small amount of Cu onto Pb covered Si (111-7x7) surface was studied with the variable temperature scanning tunnelling microscopy and spectroscopy. We observe many small clusters that appear on flat surface of 1x1-Pb islands upon RT deposition of copper. The behaviour of the clusters indicates that they are anchored to the underlying silicon substrate. Following temperature treatment fastens chemical reaction and transforms the clusters into shallow depressions of variable shape and size. Tunnelling spectra taken over the depressions suggest the formation of the copper silicides. Moreover, new objects having pronounced hexagonal form appear on rt3xrt3R30-Pb surface upon annealing. The filled and the empty state STM images of the hexagons differ strongly giving the evidence of an electronic effect. The hexagons are coalesced with the increase of Cu concentration and/or with the temperature rise. Detailed analysis of such agglomerate reveals hexagonal-like symmetry of pseudo-5x5 Cu structure. We suppose, that hexagonal objects are, possibly, individual "5x5"-Cu domains surrounded by the border made of Pb atoms.

O 5.10 Mon 12:45 MA 042

**Reflectance anisotropy spectroscopy of clean and adsorbate-covered Si(111) surfaces: comparison of experiment and hybrid density functional theory** — SOUMYA BANERJEE, SOFIA GIORGI, JOHN F. MCGILP, and ●CHARLES H. PATTERSON — School of Physics, Trinity College Dublin, Dublin 2, Ireland.

Reflectance anisotropy (RA) at surfaces of cubic semiconductors provides a means of probing the electronic structure and optical transitions of their outermost atomic layers. We present experimental data and hybrid density functional theory (DFT) calculations for RA spectra of the clean Si(111)-2x1, Si(111)-3x1-Ag and Si(111)-5x2-Au surfaces. We test several structural models for the metal adsorbate covered surfaces as their exact structures are not known. Models which consist of linear regions of pi-bonded Si in honeycombs, which are separated by metal-rich rows give good agreement with experimental RA data. The exchange functional in these hybrid DFT calculations is adjusted so that the bulk Si band gap agrees with the experimental band gap. There is no need for a 'scissors' shift of the conduction band in these calculations.

O 5.11 Mon 13:00 MA 042

**Interaction of Ta with Si (100) surface: Intermixing at the interface.** — ●PAVEL SHUKRYNAU<sup>1,2</sup>, PINGO MUTOMBO<sup>2</sup>, LARS SMYKALLA<sup>1</sup>, and MICHAEL HIETSCHOLD<sup>1</sup> — <sup>1</sup>Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group. D-09107 Chemnitz, Germany. — <sup>2</sup>Institute of Physics Academy of Sciences of the Czech Republic, Cukrovarnická 10. CZ 162 53 Prague, Czech Republic.

The adsorption of small amounts of tantalum on Si (100)-2x1 reconstructed surface was investigated systematically using scanning tunneling microscopy/spectroscopy combined with first-principles density functional calculations. We found that the room temperature deposition of Ta on to Si (100)-2x1 surface followed by moderate annealing results in the formation of the short nanochains running perpendicular to the silicon dimer rows of the substrate. The chains are sporadically distributed over the surface and their density is metal coverage dependent. Filled and empty state images of the chains differ strongly giving the existence of covalent bonds within a particular chain. Careful analysis of these images allowed us to build up several structural models. Simulating the STM images on the base of these models and consequently comparing them with experiment, one of the proposed geometries is confirmed to match best the Ta chains. Tunneling spectra taken over each individual protrusion within a chain reveal small energy gap, showing semiconductor-like behavior of constituent atoms.