

O 14: Adsorption on semiconductors, oxides and insulators II

Time: Monday 16:00–19:00

Location: MA 041

O 14.1 Mon 16:00 MA 041

Gold adsorption on pristine and defective ceria films — ●YI PAN, NIKLAS NILIUS, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

Scanning tunnelling microscopy and spectroscopy have been employed to study the adsorption of individual Au adatoms on well defined CeO₂(111) films grown on Ru(0001). In correspondence with recent DFT calculations, the Au adatoms can be stabilized in two charge states on the oxide surface, giving rise to the appearance of features with different size and bias-dependent contrast in the STM. The relative abundance of the two species sensitively depends on the reduction state of the surface, i.e. on the density of oxygen vacancies. This interrelation suggests that an exchange of electrons between the adatoms and the Ce 4f states is responsible for the bi-modal charge distribution. Moreover, the Au charge state can be switched reversibly via electron injection from the STM tip, providing insight into the nature of the participating Au electronic states.

O 14.2 Mon 16:15 MA 041

Nucleation, growth and shape of Au clusters on CeO₂ (111) — ●HANS HERMANN PIEPER and MICHAEL REICHLING — Universität Osnabrück, Germany

Gold nano-clusters of variable size on CeO₂ (111) are investigated by non-contact atomic force microscopy (NC-AFM) and Kelvin probe force microscopy (KPFM). The cluster size and nucleation behaviour is controlled by means of sample temperature during deposition and post-deposition annealing. The exact cluster shape is revealed by Kelvin compensated NC-AFM and measurements in the constant height mode, thus eliminating tip convolution effects and image distortion due to electrostatic forces.

Furthermore, we establish a relation between the KPFM contrast and the cluster size and demonstrate charging of individual clusters to an equivalent of a few electrons.

O 14.3 Mon 16:30 MA 041

Adsorption of Metallophthalocyanines on thin CoO(111) films on Ir(100) — ●TOBIAS SCHMITT, MARTINA REUSCHL, CARSTEN TRÖPPNER, LUTZ HAMMER, and M.ALEXANDER SCHNEIDER — LS f. Festkörperphysik, Uni. Erlangen, Germany

Cobalt oxide is technologically relevant as a low-temperature catalyst for carbon monoxide oxidation and is often used as a substrate for other oxidic and metallic catalysts. Also of particular interest is the functionalisation of catalytic surfaces by functional organic molecules or the preparation of molecular layers for organic electronics. For these applications an understanding of the interaction of large molecules with the cobalt oxide surface is needed.

On Ir(100) thin films of cobalt oxide can be grown in a variety of structures and surface terminations[1,2] that allow a systematic study with surface science methods in UHV. We investigated the adsorption of large metallophthalocyanine molecules by low-temperature scanning tunneling microscopy. As an example we identified different adsorption geometries of iron-(II)-phthalocyanine on the CoO(111)-c(10x2)-phase on Ir(100). It appears that the most favourable adsorption geometry leads to a maximisation of the interaction of the carbon pi-system with the oxygen atoms at the surface and hence the interaction of the central metal ion of the molecule with the substrate is less important.

[1] M. Gubo, et al., Phys. Rev. B 83, 075435 (2011) [2] W. Meyer, et al., Phys. Rev. Lett. 101, 016103 (2008)

O 14.4 Mon 16:45 MA 041

Adsorbate-induced reconstructions of the polar NiO(111) surface — ●CHRISTINA EBENSPEGER and BERND MEYER — Interdisziplinäres Zentrum für Molekulare Materialien und Computer-Chemie-Centrum, Universität Erlangen-Nürnberg

Bulk-truncated structures of polar surfaces are intrinsically unstable and especially susceptible to reconstructions and reactions with adsorbates. Indeed, our DFT+U calculations show that the adsorption of small molecules (H₂, O₂, H₂O, CO, CO₂) on NiO(111) alters the surface structure considerably. Phase diagrams of the energetically most stable surface reconstructions depending on temperature and pressure conditions exhibit a wide variety of configurations with different degree of surface hydroxylation and carbonate formation. An adsorbate free

(2x2)-O-octopolar structure, a fully hydroxylated (1x1)-OH surface and tridentate carbonate complexes including O surface atoms are energetically most favorable. Interestingly, in many cases the transformation between different stable phases does not only involve adsorption or desorption of molecules and the rearrangement of Ni and O surface atoms, but also requires mass transport/diffusion of NiO units. NEB calculations for reaction barriers of subprocesses of transformations between surface structures explain the observed high thermal stability of surface carbonates and hydroxyl groups.

[1] C. Ebensperger, B. Meyer, *phys. stat. sol. (b)* 248 (2011) 2229

O 14.5 Mon 17:00 MA 041

Tuning the growth geometry of metal ad-particles by doping the oxide support — ●NIKLAS NILIUS, XIANG SHAO, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Doping is a versatile yet little examined approach to tailor the physical and chemical properties of oxide thin films. By means of scanning tunnelling microscopy, we demonstrate that small amounts of Mo embedded in a CaO matrix change the growth behaviour of gold. While 3D deposits are formed on the pristine oxide, strictly 2D growth prevails on the doped films. The crossover in particle shape is driven by charge transfer processes from the Mo d-states into the Au islands. The negatively charged gold exhibits a larger adhesion and therefore tends to wet the oxide surface. The Mo d-states that are responsible for the electron exchange are identified inside the CaO band gap via tunnelling spectroscopy. The impact of the Mo dopants on the Au growth is suppressed by Li co-doping, which provides traps for the Mo electrons in the CaO film.

O 14.6 Mon 17:15 MA 041

LEED I(V) analysis of oxygen physisorption on the rumpled NaCl(100) surface — ANNE MÖLLER, STEPHAN HÄRTEL, ●JOCHEN VOGT, and HELMUT WEISS — Chemisches Institut der Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany

Among the diatomic molecules, O₂ is unique due to its magnetic properties in the gas phase and in the bulk[1]. The structure of O₂ adsorbed on the NaCl(100) surface is of interest in many respects, e. g. for studies of the surface aligned photochemistry of O₂. We have characterized the physisorption of O₂ using low-energy electron diffraction (LEED) with primary electron currents in the nA range and electron energies above 70 eV. No signs of electron beam induced charging of the NaCl surface were perceptible even at cryogenic temperatures. A saturated 2D phase O₂-p(1x1)/NaCl(100) was prepared at temperatures below 31 K. LEED diffraction spot intensities were recorded as a function of electron energy. The subsequent determination of the adsorbate structure based on a full-dynamical LEED-I(V) analysis reveals that O₂ is bound on top of the Na⁺ cations. The rumpling of the NaCl(100) surface [2] appears to be unaffected by the adsorbed O₂, consistent with its very weak interaction with the substrate. The details of the adsorbate structure will be discussed and compared with the results of model calculations.

[1] Y. A. Freiman, H. J. Jodl, Phys. Rep. **401** (2004), 1

[2] J. Vogt, H. Weiss, Surf. Sci. **491** (2001), 155

O 14.7 Mon 17:30 MA 041

Optical spectroscopy of PTCDA molecules on a KCl (100) surface in the limit of ultralow densities — ●A. PAULHEIM, M. MÜLLER, C. MARQUARDT, and M. SOKOŁOWSKI — Institute for Chemistry, University of Bonn

We use fluorescence spectroscopy as a tool to study aggregation and structural site transitions of molecules in the limit of isolated entities on surface. For this purpose submonolayers of PTCDA were vacuum deposited on thin epitaxial KCl films grown on the Ag(100) surface. The structural and optical properties were investigated by SPA-LEED and by fluorescence(FL) and FL excitation spectroscopy, respectively. For the limit of isolated molecules (1% ML coverage), we observed an irreversible transition in the FL spectra, if the intensity of the exciting light is increased by an additional focussing optics. The FL spectra of this novel phase is blue shifted with respect to that of the original phase by 130 cm⁻¹ and the vibronic modes exhibit a smaller

FWHM due to reduced inhomogeneous site broadening. In addition, we analysed the polarization of the emitted light and were able to determine the azimuthal orientation of the molecules with respect to the substrate. In both phases, the original and the novel phase, the molecules show the same orientation. So far, the origin of the blue shift is unknown. A possible reason may be photo-induced diffusion of the molecules to surface step sites. This demonstrates that photo-induced heating in combination with FL spectroscopy can be used as a technique for studying the diffusion of molecules on surfaces and the optical properties of molecules depending on the respective adsorption sites.

O 14.8 Mon 17:45 MA 041

NEXAFS/XPS Study of Azobenzene adsorbed on metal oxide structure — •MICHAEL NABOKA, ALEXEI NEFEDOV, and CHRISTOF WÖLL — Karlsruhe Institute of Technologies

In recent years, molecular switches have attracted considerable attention because of the high potential application in electronic and photonic devices. The molecular switches enable the storage of information on a molecular level, and may find a numerous application in nanotechnology, and molecular electronics. The integration of molecular switches with inorganic surfaces has recently become a hot topic as it can give rise to novel hybrid materials in which the properties of the two components are mutually affected or even enhanced in a reversible fashion. One of the candidates for such a molecular switch can be azobenzene, a chemical compound composed of two phenyl rings linked by a N=N double bond. Here we present some results of the NEXAFS/XPS study of the Azobenzene molecule adsorbed on metal oxide surfaces.

O 14.9 Mon 18:00 MA 041

Adsorption Properties of a Thin Vitreous Silica Film on Ru(0001) — •LEONID LICHTENSTEIN, CHRISTIN BÜCHNER, STEFANIE STUCKENHOLZ, MARKUS HEYDE, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Silica is a technologically very important material. Particularly, it is widely used as a support for metal nanoparticles in catalysis. However, neither the exact atomic structure nor the precise adsorption properties of the silica substrate are well known. Therefore, our goal is to study the adsorption of metal particles on a well defined thin film of vitreous silica by using low temperature dynamic force microscopy (DFM, also known as nc-AFM) in combination with scanning tunneling microscopy (STM) in ultra-high vacuum.

Recently, we resolved the atomic structure of a vitreous silica film on Ru(0001) [1]. Our results showed good agreement with the postulated glass model from Zachariasen [2] and diffraction experiments on silica glass [3,4]. Herein, we use this film as a template for the adsorption of metal single atoms and nanoparticles. Studying the exact adsorption geometry provides insight into the catalytic properties of this combined sample system.

[1] L. Lichtenstein *et al.*, *Angew. Chem. Int. Ed.*, **in press** (2011), DOI: 10.1002/anie.201107097

[2] W. H. Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932)

[3] R. L. Mozzi *et al.*, *J. Appl. Crystallogr.* **2**, 164 (1969)

[4] D. I. Grimley *et al.*, *J. Non-Cryst. Solids* **119**, 49 (1990)

O 14.10 Mon 18:15 MA 041

Submonolayers of Au/Pd on the hematite (0001) and magnetite (111) surfaces — •ADAM KIEJNA, TOMASZ PABISIAK, and TOMASZ OSSOWSKI — Institute of Experimental Physics, University of Wrocław, plac M. Borna 9, Wrocław, Poland

Ultra-thin films and nanostructures formed by noble metals on oxide surfaces exhibit enhanced catalytic activity for the CO oxidation. Iron oxide-based catalysts are superior to other oxides, at least for several reactions. We applied the spin-polarized density functional theory (DFT) and the DFT+U method, accounting for the effect of strong on-site Coulomb correlations, to study the submonolayer adsorption

of Au/Pd atoms on two stable iron-oxide surfaces: hematite (0001) and a magnetite (111). For each surface, adsorption on two terminations has been studied: one terminated with iron and the other with oxygen. Both Au and Pd bind strongly to hematite and magnetite surfaces and induce large changes in their geometry. DFT and DFT+U provide qualitatively similar surface geometries but they differ much in the prediction of the surface energetics and the electronic and magnetic properties of the oxides. Pd binds stronger than Au both to hematite and magnetite surfaces and the Au/Pd bonding to the O-terminated surface is distinctly stronger than that to the Fe-terminated one. For hematite, the DFT+U bonding is by 0.3-0.6 eV weaker than DFT on the Fe-terminated surface and about 2 eV stronger on the O-terminated one. For magnetite, in each case, DFT+U gives stronger bonding than DFT. The differences between DFT and DFT+U results are discussed based on the calculated electronic structure.

O 14.11 Mon 18:30 MA 041

The relevance of surface defects for the adsorption of pyrrole on GaAs(001)-c(4x4) surfaces — •THOMAS BRUHN¹, BJØRN-OVE FIIMLAND³, MICHAEL KNEISSL¹, NORBERT ESSER^{1,2}, and PATRICK VOGT¹ — ¹TU Berlin, Institut für Festkörperphysik, Hardenbergstr.36, 10623 Berlin, Germany — ²Leibniz-Institut für Analytische Wissenschaften, ISAS e.V., Berlin, Albert-Einstein-Str.9, 12489 Berlin, Germany — ³NTNU, NO-7491 Trondheim, Norway

The basic principles that determine the adsorption mechanisms of organic materials on solid surfaces are still not sufficiently understood and represent a key issue for recent semiconductor research. In our work we have investigated the adsorption of the aromatic molecule pyrrole (C₄H₄NH) on the GaAs(001)-c(4 × 4) reconstruction. The samples were prepared under UHV conditions and the adsorption process was monitored in-situ with a reflectance anisotropy spectroscopy (RAS) setup operating from 1.5 to 8 eV. At sub-monolayer coverage, single adsorbed pyrrole molecules were investigated by scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) and photoelectron spectroscopy (XPS). Our results reveal that pyrrole predominantly physisorbs on As-rich c(4 × 4) reconstruction and essentially retains its initial electronic structure. Additional, however, we could identify a significant amount of molecules which are chemisorbed at surface defects. Our results demonstrate that the occurrence of surface defects plays an important role for the reactivity of the As-rich GaAs c(4 × 4) surface to the adsorption of pyrrole.

O 14.12 Mon 18:45 MA 041

Adsorption of Au atoms on the h-BN/Rh(111) nanomesh — •HANS PETER KOCH, ROBERT LASKOWSKI, and PETER BLAHA — Institute of Material Chemistry, University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria

The h-BN/Rh(111) nanomesh [1] consists of a highly corrugated single layer of h-BN on a Rh(111) surface. Due to the lattice mismatch a nanostructure with a periodicity of 3.2 nm is formed. In this nanostructure BN forms “pores” of about 2 nm, which are separated by “wires”, where BN is 0.1 - 0.2 nm further away from the transition metal than in the “pores”. The “pores” of the nanomesh show the extraordinary ability to trap molecules and metallic clusters - forming well-ordered arrays and prohibiting aggregation.

We have theoretically studied the adsorption of Au atoms on bulk h-BN and on various models of the h-BN/Rh(111) nanomesh. While Au binds only weakly to bulk h-BN and h-BN/Rh(111) at the “wire” configurations, the underlying Rh atoms in the “pores” modify considerably the electronic structure of h-BN and Au adsorbs strongly on top of the B atoms. The adsorption is accompanied by a strong outward relaxation of the B atoms and a significantly charging of the Au atoms [2].

Furthermore, we will present first results of the adsorption of small Au[n] clusters (n=2-4) in the “pores”. Their adsorption properties show similar trends as observed for single Au atoms.

[1] M. Corso *et al.*, *Science* **303**: 217 (2004)

[2] HP. Koch *et al.*, *Phys. Rev. B* **in print**