O 46 Adsorption an Oberflächen V

Zeit: Dienstag 15:45–18:30 Raum: TU EB420

O 46.1 Di 15:45 TU EB420

Investigation of water adsorption on different low index ZnO surfaces — •Tilo Plake, Stefan Andres, and Christian Pettenkofer — Hahn-Meitner-Institut, Glienicker Straße 100, 14109 Berlin

The influence of $Zn(OH)_x$ is reported to play a considerable role regarding the electronical properties of ZnO semiconductor structures. We present x-ray and ultraviolet photoelectron spectroscopy data of ZnO (0001), (000$\bar{1}$), (10$\bar{1}$0), and (11$\bar{2}$0) surfaces that have been cleaned under ultrahigh vacuum conditions by Ar^+ sputtering and subsequent annealing. Adsorption of H_2O is performed on the samples which have been cooled down to 77 K. Temperature is gradually raised until all water desorbes completely. The changes in the spectral emissions are discussed with respect to the formation of a hydroxide capping. Alternatively, samples are exposed to water at temperatures ranging from 300 K to 600 K. Adsorbate spectra are compared to data obtained from hydroxide exposed samples. Decomposition of $Zn(OH)_x$ to ZnO and H_2O during annealing is monitored and compared to data obtained from polycrystalline samples.

O 46.2 Di 16:00 TU EB420

Partial Dissociation of Water on the ZnO(10$\bar{1}$0) Surface — •B. Meyer[1], D. Marx[1], O. Dulub[2], U. Diebold[2], M. Kunat[3], D. Langenberg[3], and Ch. Wöll[3] — [1]LS für Theoretische Chemie, Ruhr-Universität Bochum — [2]Dept. of Physics, Tulane University, New Orleans, USA — [3]LS für Physikalische Chemie I, Ruhr-Universität Bochum

The delicate interplay between chemical bonding, van der Waals forces, and hydrogen bonding gives rise to complex phenomena such as complete dissociation, partial dissociation at defects, molecular adsorption, and multilayer formation when H_2O interacts with solid surfaces. Recently, an intriguing, yet controversial, intermediate scenario was advanced, where the interaction between water molecules results in a partial dissociation of H_2O on perfect surfaces, leading to superlattices with long-range order. In a combined theoretical and experimental study, applying DFT calculations, Car-Parrinello molecular dynamics simulations, and STM computations, together with diffraction (He-atom scattering, LEED), STM, and thermodynamic measurements we give conclusive evidence that such a phenomenon is encountered for H_2O on the perfect ZnO(10$\bar{1}$0) surface. At monolayer coverage, every second water molecule is found to auto-dissociate, subject to a low activation barrier, upon a favorable hydrogen-bonding interaction with a neighboring water molecule, i.e. without the need to invoke defects or impurities. This process leads to a (2×1) superlattice with long-range order which is stable from below 200 K up to temperatures close to the boiling point of liquid water. [1] B. Meyer, D. Marx, O. Dulub, U. Diebold, M. Kunat, D. Langenberg, Ch. Wöll, Angew. Chem., in print.

O 46.3 Di 16:15 TU EB420

Alternative Gate Oxide Pr_2O_3: Growth characterization on Si(111) and Si(113) — •N.M. Jeutter[1], M. Hennemeyer[1], L. Libralesso[2], T.-L. Lee[2], J. Zegenhagen[2], A. Stierle[3], and W. Moritz[1] — [1]Dept. of Earth- and Enviromental Sciences, LMU Munich, Germany — [2]ESRF, Grenoble, France — [3]MPI MF, Stuttgart, Germany

GIXRD measurements of a 0.6 nm thick Pr_2O_3 -layer on Si(111) show that the interface is formed by an Pr-O-Si bond with oxygen on top of Si. Evidence is found from XRD and LEED measurements that Pr_2O_3 grows at 500 ° C in double layers, corresponding to one unit cell of the hexagonal Pr_2O_3 bulk phase. Annealing up to 760 ° C of the thicker layers leads to island growth and formation of $PrSi_2$. The p(2x1) and the coexisting p($\sqrt{3}x\sqrt{3}$) structures, occurring in the LEED pattern after annealing, are probably due to submonolayer coverage of Pr on Si (111)[1].
The growth of Pr_2O_3 on Si(113) has been investigated by LEED and X-ray diffraction. Pr_2O_3 was evaporated at a substrate temperature of 600 ° C. After deposition of 0.2 nm of Pr_2O_3, the reconstruction of the clean surface is removed and the LEED pattern exhibits a streaky (4x1) superstructure. AFM images show flat islands of triangular to trapezoid form. First GIXRD measurements did not show any superstructure reflections indicating that the (4x1)pattern seen in LEED arises from the oxygen ordering.

[1] L. Grill, M.G. Ramsey, J.A.D. Matthew, F.P. Netzer, Surface Science 380 (1997) 324-334

O 46.4 Di 16:30 TU EB420

Towards ultimate resolution in surface stress measurements — •Peter Kury and Michael Horn-von Hoegen — Institut für Laser- und Plasmaphysik, Universität Duisburg-Essen, 45141 Essen

Surface stress is one of the most important physical quantities for the evolution of structure and morphology on the surfaces of solids due to its large contribution to the total energy. Unfortunately, the direct measurement of surface stress is not possible, but it can be determined via the elastic response of a thin substrate as utilized in bending sample techniques like surface stress induced optical deflection (SSIOD) [1]. A sensitivity in the order of 1N/m, corresponding for example to a biaxially by 4.2% compressed germanium film of one monolayer thickness, can be easily achieved if proper mechanical isolation of the system and vibration damping are implemented. To reach an instrumental resolution in the order of 0.01N/m, however, it is necessary also to consider effects which are far from obvious in this context. Here we present modifications of SSIOD that allow the determination of surface stress with a resolution of 0.005N/m [2] corresponding to a sensitivity of less than 1% of a monolayer in typical adsorbate systems. Experimental results are shown for Sb/Si(001), Cs/Si(001) and Si/Si(111).
[1]: A. Schell-Sorokin et al., Phys. Rev. Lett. **64**(9), 1039 (1990)
[2]: P. Kury et al., Rev. Sci. Instrum., in press (2004)

O 46.5 Di 16:45 TU EB420

Nanostructuring with silver on Au-Si(111) — •C. Seifert, C. Wiethoff, F.-J. Meyer zu Heringdorf und M. Horn-von Hoegen — Universität Duisburg-Essen, Standort Essen

Self-assembly of 1D nanostructures on surfaces usually requires anisotropic qualities of the substrate e.g. vicinial cut of the surface. Gold adsorption over 350°C on the non-anisotropical Si(111) surface produces anisotropically formed (5x2) domains, with domain shapes rounding up at higher temperatures. Adsorption or annealing in temperature regions of around 750 °C, well below the transition of the (5x2) to (1x1) reconstructed areas, leads to creation of a surface with the 2-fold direction mainly aligned along the step direction of the remaining steps. In order to use these surfaces as template for silver wire growth - atoms diffuse faster along the 2-fold direction of the (5x2) reconstruction - the alloying of silver with gold on this surface has to be understood better. Measurements on the formation of Ag/Au alloys have been done with RT-STM and high resolution LEED. A phasediagram for Silver on Au(5x2)-Si(111) is provided.

O 46.6 Di 17:00 TU EB420

Photodesorption of molecules adsorbed on ultrathin Au — •Claudia Wesenberg and Eckart Hasselbrink — FB Chemie, Universitaet Duisburg-Essen, Universitaetstr. 5, 45117 Essen, Germany

Ultrathin Au films (20-100ML) deposited on Si(100) are suited to study the electron dynamics in such films and the influence of the film thickness on charge transfer to the adsorbate and subsequent photodesorption. In our experiments, NO is chosen as the probe molecule. Its adsorbtion is performed at 100K on the Au-covered Si(100) surface. Photodesorption is induced using a Nd:YAG laser and the desorbed molecules are detected by QMS. The film thickness is varied in order to obtain information about the charge transfer dynamics between the ultrathin Au film and the NO adsorbate. The photodesorption crosssection of NO is expected to decrease with increasing film thickness.

O 46.7 Di 17:15 TU EB420

CO-Adsorption auf der Pt(111)-Oberfläche: Vergleich eines gradientenkorrigierten Funktionals und eines Hybridfunktionals — •Klaus Doll — Institut für Mathematische Physik, TU Braunschweig, Mendelssohnstraße 3, D-38106 Braunschweig

Die CO-Adsorption auf der Pt(111)-Oberfläche in einem ($\sqrt{3} \times \sqrt{3}$)-Muster wurde mit dem gradientenkorrigierten Funktional von Perdew und Wang (PW91) und dem Hybridfunktional B3LYP studiert. Dazu wurde das System mit einem Modell mit Periodizität in zwei Raumrichtungen beschrieben. Das PW91 Funktional gibt den falschen Adsorptionsplatz (fcc), in Übereinstimmung mit einer Reihe früherer Rechnungen [1]. Das B3LYP-Funktional gibt den top site als den bevorzugten Platz

an. Dies bestätigt Resultate von Cluster-Rechnungen, wo vorgeschlagen wurde, dass die unterschiedliche (je nach Funktional) Energielücke zwischen höchstem besetzten und tiefsten unbesetzten Orbital verantwortlich sein könnte für diese Veränderung [2]. Die Resultate werden unterstützt durch projezierte Zustandsdichten und Populationsanalysten.

[1] P. J. Feibelman, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe and J. Dumesic, J. Phys. Chem. **105**, 4018 (2001).
[2] A. Gil, A. Clotet, J. M. Ricart, G. Kresse, M. García-Hernández, N. Rösch, and Ph. Sautet, Surf. Sci. **530**, 71 (2003).

O 46.8 Di 17:30 TU EB420

A comparative study of prenal on Pt(111), Pt_2Sn(111) and Pt_3Sn(111) surface alloys — •Jan Haubrich, Alexander Krupski, Conrad Becker und Klaus Wandelt — Inst. f. Phys. u. Theo. Ch., Wegeler. 12, D-53115 Bonn

It is known that the selectivity of the hydrogenation processes of α,β-unsat. aldehydes like acrolein or prenal depends not only on the molecule itself, but also on the catalyst employed. To understand the different selectivities, the adsorption of prenal on Pt(111) and two Pt-Sn surface alloys is investigated with HREELS, TPD and LEED.

After adsorption of prenal at 100K the desorption of fragments up to 100 amu is studied with TPD. While on Pt(111) the desorption of prenal is detected at 160K (Multilayer), 177K and 199K, also a fragmentation reaction is observed giving rise to desorption of H_2 and CO in several peaks. On Pt_2Sn and Pt_3Sn surface alloys this fragmentation process is suppressed. HREELS experiments carried out between 100K and 500K on the three surfaces show highly complex spectra of adsorbed prenal. On Pt(111) also the fragmentation process starting at 300K can be examined with HREELS. Also on the Pt_xSn surfaces complex HREEL spectra of prenal are recorded.

O 46.9 Di 17:45 TU EB420

CO adsorption on stepped Pt(355) and Pt(644) - the dissimilar twins — Barbara Tränkenschuh, Thomas Fuhrmann, Christian Papp, Junfa Zhu, •Reinhard Denecke, and Hans-Peter Steinrück — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

The adsorption and thermal desorption of CO on stepped Pt surfaces was studied by the combination of a supersonic molecular beam and in-situ high resolution XPS. Using synchrotron radiation as excitation source, we are able to clearly distinguish between adsorption sites at steps and at terraces in C 1s spectra, even at fast measuring times (about 4 s per spectrum). Both surfaces studied contain five atom wide (111) terraces separated by monatomic steps. While on Pt(355) these steps have (111) orientation, they are in (100) orientation on Pt(644). Interestingly, these very similar surfaces exhibit differences in CO adsorption behaviour not only at step sites, as expected, but also on the nominally equal terraces. Here, the distribution between bridge and on-top bound species on Pt(644) is quite similar to the situation found for Pt(111)[1], whereas for the (355) surface the adsorbate-adsorbate interactions modify the occupation ratio significantly. Thus, an influence on surface reactions such as the CO oxidation, can be expected. Supported by the DFG (STE 620/4-2). [1] M. Kinne et al., J. Chem. Phys. 117, 10852 (2002).

O 46.10 Di 18:00 TU EB420

Accurate prediction of the CO adsorption site on Cu(111) from first-principles calculations — •Qing-Miao Hu, Karsten Reuter, and Matthias Scheffler — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin

It is well known that density-functional theory (DFT) with present-day jellium-based local or gradient-corrected exchange-correlation (xc) functionals fails to predict the correct adsorption site of CO on most close-packed metal surfaces, including Pt(111) and Cu(111). Motivated by earlier findings, e.g. [1], that showed that the error of these functionals is "nearsighted", we present here a systematic study of the correction of the xc energy for CO adsorption. The clue is to use appropriate *energy differences* and appropriately chosen clusters around the adsorption site. Again [1] we find that *the xc correction* (not the total energy) converges rapidly with cluster size. Calculations using DFT-LDA, PBE, and B3LYP as well as HF+MP2 are presented.

For the example of low-coverage adsorption of CO at Cu(111) we therewith indeed obtain the correct on-top adsorption site. We also explain our results, as well as the failure of standard DFT calculations in a simple physical picture.

[1] C. Filippi, S.B. Healy, P. Kratzer, E. Pehlke, and M. Scheffler, Phys. Rev. Lett. **89**, 166102 (2002)

O 46.11 Di 18:15 TU EB420

MIES (=Metastable Induced Electron Spectroscopy) als Methode zur mechanistischen Untersuchung der heterogenen Katalyse — •YanChun Liu, Andrea Berlich und Harald Morgner — Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie der Universität Leipzig, Linnestr.2, 04103 Leipzig

Der Mechanismus von Reaktionen an Metall-Träger-Katalysatoren ist bis heute nicht eindeutig verstanden. Insbesondere ist zu klären, welchen Einfluß die Belegung von Metallclustern mit Molekülen und Oxidpartikeln hat. Die perfekt oberflächenempfindliche Methode MIES (=Metastable Induced Electron Spectroscopy) kann einen Beitrag zur Aufklärung zu leisten. Wir haben begonnen mit Arbeiten an dem System Nickel/Nickeloxid. MIES erlaubt die Aussage, dass dabei das NiO teilweise zu Metall reduziert wird. Dies ist im Einklang mit früheren Befunden, dass der Übergang zwischen Oads/Ni(100) und NiO reversibel ist und von der Sauerstoffkonzentration abhängt[1]. Unter welchen Umständen sich auf der Oxidschicht Ni-Cluster bilden können, wird untersucht. Das Angebot von CO zur Adsorption zeigt kaum einen merkbaren Einfluss zwischen Raumtemperatur und ca. 200°C. Experimente zur Adsorption von NH3 sind in Vorbereitung. Die quantitative Analyse der Oberflächenbeschaffenheit in allen Stadien der Präparation mit Hilfe von MIES wird präsentiert[2]. [1]R.Kubiak, H.Morgner and O.Rakhovskaia, Surf. Science 321 (1994) 229-36 [2]H. Morgner, Adv. At. Mol. Opt. Physics 42B (2000) 387-488