O 18 Adsorption an Oberflächen II

Zeit: Samstag 10:45–13:00 Raum: TU EB301

O 18.1 Sa 10:45 TU EB301

Experimental determination of surface stress of H/Si(001) — •Peter Kury[1], Jan van Heys[2], Eckhard Pehlke[2], and Michael Horn-von Hoegen[1] — [1]Institut für Laser- und Plasmaphysik, Universität Duisburg-Essen, 45141 Essen — [2]Institut für Theoretische Physik und Astrophysik, Universität Kiel, 24098 Kiel

The adsorption of hydrogen on Si(100) is one of the most profoundly investigated model systems for the study of reaction dynamics on semiconductor surfaces. The interest in this system, however, is not only motivated by fundamental questions regarding the chemisorption dynamics, but also by the technologically relevant epitaxial growth by means of chemical vapor deposition using silanes. Surface stress is an important surface property, intimately linked to the electronic structure of the surface, which is known to provide the driving force for structure formation on mesoscopic length scales, e.g. in case of the clean Si(100) surface. In the system H/Si(100), however, the role of surface stress is yet unknown. We present stress data for this system as a function of hydrogen coverage measured by SSIOD (surface stress induced optical deflection [1]) and compare to the theoretical surface stress tensor for various partially hydrogen-covered Si(100) surfaces predicted by density-functional total-energy calculations. [1] P. Kury et al., Rev. Sci. Instrum., in press.

O 18.2 Sa 11:00 TU EB301

Structure and Stability of the H / Ir (100) Adsorbate System — •Lutz Hammer, Daniel Lerch, Andreas Schmidt, Andreas Klein, Stefan Müller und Klaus Heinz — Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr.7, D-91058 Erlangen

The structure and energetics of hydrogen adsorption on the $Ir(100)-1\times1$ and -5×1 surface phases were studied by LEED, STM and first-principles calculations. For the metastable $Ir(100)-1\times1$ surface ab-initio DFT calculations surprisingly find the bridge site as the energetically stable adsorption site for all H-coverage values considered. A LEED structure analysis performed for this system confirms both this adsorption site and the substrate multilayer relaxation predicted by DFT. For the $5\times1-hex$-phase, the reconstructed ground state of $Ir(100)$, again an excellent agreement between the geometrical results of LEED and DFT was achieved. For this phase the heat of adsorption for the bridge and hollow site is degenerate and about 0.2 eV less than for the 1×1-phase. The heat of adsorption values computed for other sites point towards a one-dimensional diffusion of hydrogen on the quasi-hexagonal surface. The structural modifications induced by H can be regarded as a precursor state for the lifting of the reconstruction. As the hydrogen induced $5\times1-hex\rightarrow1\times1$ deconstruction is kinetically hindered, a new 1×1-like phase $(5\times1-H)$ is formed instead. The bridge site is again the favoured adsorption site, with a heat of adsorption equivalent to that of the 1×1-phase. Again the structural parameters revealed from LEED and DFT agree in all details.

O 18.3 Sa 11:15 TU EB301

Einfluss von Oberflächenverunreinigungen auf die Speicherung von Wasserstoff in Form von Metallhydriden — •Mark Schülke[1], Hubert Paulus[2], Karl-Heinz Müller[1,2] und Martin Lammers[2] — [1]Hochschule für Technik und Wirtschaft Südwestfalen — [2]Institut für Technologie- und Wissenstransfer an der Hochschulabteilung Soest

Die Wasserstoffspeicherung in Metallhydriden ist auf Grund der hohen Sicherheit und der hohen volumenbezogenen Speicherdichte eine viel versprechende Alternative zu den herkömmlichen Speicherformen. Das H-Absorptionsvermögen von Metallhydriden hängt in hohem Maße von Oberflächenkontaminationen ab. Im Rahmen der Untersuchungen an verschiedenen AB_2-Legierungen auf Ti-Zr-Basis wurden Oberflächenkontaminationen durch definierte Präparationsschritte eingestellt und deren Einfluss auf die H-Absorption untersucht. Hierzu wurden die Oberflächen mit AES, XPS und SNMS charakterisiert und Beladungsexperimente in einer KDI-Anlage durchgeführt. Die Untersuchungen zeigen, wie sich Variationen in den Legierungszusammensetzungen auf das Kontaminationsverhalten auswirken. So besitzen die Legierungen auch nach mehrwöchiger Lagerung an Luft nur eine wenige Atomlagen dicke Kontaminationsschicht, die durch Sputtern bzw. durch Aktivierungsprozesse (Tempern in H-Atmosphäre) entfernt werden kann. Nach wenigen Aktivierungszyklen besitzen sie wieder ihre volle Kapazität. Ziel der Untersuchungen ist/war es, am Beispiel ausgesuchter Metalllegierungen den Einfluss von Verunreinigungen in der Gasphase und im Material auf wichtige Prozesse bei der H-Absorption zu untersuchen.

O 18.4 Sa 11:30 TU EB301

H on Pt(110): Atypical chemisorption site at low coverages, typical at high covarages? — •Rinaldo Zucca and Josef Redinger — Center f. Computational Materials Science, Vienna University of Technology, Getreidemarkt 9/134, A-1060 Vienna, Austria

A recent analysis of an hydrogen-modified Pt(110) surface with quantitative LEED and DFT calculations established a strong dependence of (1x2) missing row surface Pt lattice relaxations on the H atom coverage. Contrary to former assignments, both experiment and DFT calculations agree that at low coverages (β_2-state) H occupies adsorption sites above the outermost close-packed rows. A careful theoretical study of possible sites and trajectories revealed the short-bridge site on the outermost row, and not the fcc pseudo-threefold site at the (111) microfacets of the missing row surface's deep troughs as the preferred chemisorption site. Possible adsorption sites and adsorbate structures at higher coverages, such as found in the β_1-state, are presently under investigation.

O 18.5 Sa 11:45 TU EB301

Analyzing the order-disorder transition in hydrogen adsorption on Pd(111) with a first-principles lattice gas hamiltonian approach — •Cesar Lazo[1], Karsten Reuter[2], Volker Blum[2], Frerich Keil[1], and Matthias Scheffler[2] — [1]TU Hamburg-Harburg, Eissendorfer Str. 38, D-21071 Hamburg — [2]Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin

The interaction of hydrogen with Pd surfaces is of particular interest in many industrial reactions, including hydrogenation and fuel cell technologies. We set out to study the mesoscopic ordering behavior of hydrogen on Pd(111) from first-principles by parametrizing a lattice gas Hamiltonian (LGH) with density-functional theory (DFT) data. The subtle energy differences involved in the hydrogen bonding make this a critical test case, and we discuss the present methodological limitations with respect to basis set, exchange-correlation functional, and LGH expansion. Using our LGH model we then carry out Monte Carlo simulations in order to obtain the (T,p)-phase diagram, as well as the configurational energy density of states (DOS) using the Wang-Landau algorithm. With this DOS we calculate the configurational entropy and can correlate it with the experimentally observed low critical temperatures for the order-disorder transition in the H/Pd(111) system.

O 18.6 Sa 12:00 TU EB301

PM-IRAS and XPS studies of methanol oxidation on Pd model catalysts — •Marta Borasio, Oscar Rodríguez de la Fuente, Günther Rupprechter, and Hans-Joachim Freund — Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin

Methanol decomposition and oxidation on Pd(111) and Al_2O_3 supported Pd nanoparticles were studied by Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS) and X-ray Photoelectron Spectroscopy (XPS) from ultrahigh vacuum (UHV) to 15 mbar, at temperatures up to 450 K. Under high pressure these processes were also followed by gas chromatography (GC).

Methanol decomposition proceeds via dehydrogenation to CO and hydrogen or via methanolic C-O bond scission producing carbonaceous species (CH_x or C), which deactivate the catalyst. The kinetics of the evolution of these species and their preferred binding sites were analyzed. During methanol oxidation at mbar pressure surface species (CO, CH_xO) and products (CO_2, H_2O, CH_2O) were detected by PM-IRAS and GC, respectively, with XPS being utilized for pre- and post-reaction surface analysis.

O 18.7 Sa 12:15 TU EB301

Adsorbate induced surface stress for $(2\times1)O$ on Cu(110) measured with an STM — •Christian Bombis, Marina Moiseeva, and Harald Ibach — Institut für Schichten und Grenzflächen ISG 3, Forschungszentrum Jülich GmbH, 52425 Jülich

The formation of the so-called (2×1) oxygen stripe phase on Cu(110) is imaged in situ with an STM and simultaneously a quantitative determination of the induced surface stress is accomplished. For this intention the bending bar technique is utilized with the bending measured by the STM. Due to the anisotropy of the Cu(110) surface, two experiments, one with the $[1\bar{1}0]$-direction and a second with the [001]-direction along the bar have to be carried out for a quantitative analysis of the induced surface stress. From the two experiments we calculate the induced surface stress. We find that the difference $\Delta\tau$ of the surface stresses of the $(2 \times 1)O$ phase on Cu(110) and the clean Cu(110) surface is compressive for both directions, in accordance with the adsorption of oxygen on other surfaces. The stress depends significantly on the coverage. Orthogonal to the oxygen stripes ($[1\bar{1}0]$-direction) the data can be fitted to $\Delta\tau_{[1\bar{1}0]} \approx (-0,24 - 1,7 \times e^{-2,5\times\theta_s})Nm^{-1}$ and parallel to the stripes ([001]-direction) to $\Delta\tau_{[001]} \approx (-0,37 - 2,65 \times e^{-2,52\times\theta_s})Nm^{-1}$.

O 18.8 Sa 12:30 TU EB301

When Seeing is Not Believing: The case of O on Ag(111) — •Angelos Michaelides, Karsten Reuter, and Matthias Scheffler — Fritz-Haber-Institut, Faradayweg 4-6, D-14195, Berlin

A number of recent studies indicate that, under the oxygen rich conditions of oxidation catalysis, some transition metal catalysts are covered in thin oxide overlayers. Moreover, it has been suggested that such 'surface-oxide' layers are catalytically active, and that this role is not performed by the pure metal surfaces as was traditionally assumed. This contemporary picture can be traced back to Ag catalysis, where over 30 years ago it was suggested that the top layer of Ag(111) reconstructed to an epitaxial Ag_2O overlayer upon exposure to oxygen. Extensive experimental work, including scanning tunnelling microscopy studies in which the oxide was apparently imaged with atomic resolution [1], and density functional theory calculations [2,3] largely confirmed this interpretation. However, subsequent density functional theory results, presented here, augmented with thermodynamic calculations, indicate that previous conclusions are significantly incomplete and that the structure of this original surface-oxide must be reconsidered.

[1] C. Carlisle *et al.*, Phys. Rev. Lett. **84**, 3899 (2000).
[2] A. Michaelides, M.-L. Bocquet, P. Sautet, A. Alavi, and D.A. King, Chem. Phys. Lett. **367**, 344 (2003).
[3] W.X. Li, C. Stampfl, and M. Scheffler, Phys. Rev. Lett. **90**, 256102 (2003).

O 18.9 Sa 12:45 TU EB301

High pressure STM for atomic resolution studies of surface reactions under realistic conditions — •A. Männig, H. Hoster, H. Rauscher, and R. J. Behm — Abt. Oberflächenchemie und Katalyse, Universität Ulm, D-89096 Ulm

We describe the design and the performance of a high pressure video STM (HP-STM), which allows the atomically resolved analysis of adsorption processes and reactions in a pressure range from ultra high vacuum (10^{-10} mbar) up to atmospheric pressure (1000 mbar). The HP-STM was designed to investigate catalytic reactions under steady state conditions over the so called 'pressure gap'. The high pressure cell with a volume of about 2.5 liters is attached to a UHV preparation / analysis chamber. First atomic resolution results on the oxygen adsorption, e.g. on pure and modified Ru(0001) surfaces are presented.