O 27: Metal subtrates: Adsorption of O and/or H

Time: Tuesday 10:30–12:30 Location: H42

O 27.1 Tue 10:30 H42

New Surfaces Stabilized by Adsorbate-Induced Faceting of Ir(210) — •Payam Kaghazchi[1], Ivan Ermanoski[2], Wenhua Chen[3], and Timo Jacob[1] — [1]Universität Ulm, Albert-Einstein-Allee 47, D-89069 Ulm, Germany — [2]Sandia National Laboratories, USA — [3]Rutgers University, Piscataway, NJ 08854, USA

When atomically-rough Ir(210) is exposed to more than 0.5 ML of oxygen and annealed to 600 K, nanoscale three-sided pyramidal facets grow and cover the surface. Experimental measurements revealed that these facets expose faces of Ir(311), Ir(31$\bar{1}$), and Ir(110) orientation. Furthermore, while the (311) and (31$\bar{1}$) faces are always smooth, some (110) faces were found to be partially rough [1]. As a combined effort of experiment (STM) and theory (DFT) we investigated the nature of these rough areas on the (110) faces. It was found that these regions consist of a complicated Ir(110) reconstruction, leading to a stepped double-missing-row (110) superstructure. Interestingly, while this structure is not observable on a Ir(110) single crystal surface, it only becomes thermodynamically favorable on the (110) faces of the nanopyramids formed after the oxygen-induced faceting of Ir(210). This indicates that with the aid of facet formation one can stabilize new surfaces, which cannot be stabilized neither by cleavage of a crystal nor through by reconstruction. [1] T. E. Madey, W. Chen, H. Wang, P. Kaghazchi, T. Jacob, *Chem. Soc. Rev.*, **37**, 2310 (2008).

O 27.2 Tue 10:45 H42

The interaction of oxygen with AgPd/Pd(111) surface alloys - A case study for ensemble effects on bimetallic surfaces — •Thomas Diemant, Joachim Bansmann, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

AgPd/Pd(111) surface alloys, which consist of a reactive and an inert metal, represent an ideal test case for the study of ensemble effects on bimetallic surfaces. The structural properties of these planar model systems (surface contents and atom distribution) are accessible by high-resolution scanning tunnelling microscopy (STM), while the chemical/adsorption properties can be studied by a combination of temperature-programmed desorption (TPD) and vibrational spectroscopy, such as high-resolution electron energy loss spectroscopy (HREELS). We have used this approach to correlate the structural properties of structurally well-defined AgPd/Pd(111) surface alloys to their oxygen adsorption behaviour. The modification of the oxygen adsorption properties can be attributed predominantly to ensemble effects. Ligand effects only play a minor role. The results will be compared to findings on the interaction of CO with these surface alloys.

[1] Yunsheng Ma et al., Surf. Sci. 603 (2009) 1046.

O 27.3 Tue 11:00 H42

Oxidation kinetics of Ru(0001) — •Marius Ernst[1] and Wim Sloof[2] — [1]Universität Würzburg, Experimentelle Physik 7 — [2]Delft University of Technology, Department of Materials Sciences

Ru is a candidate material to be used as protective capping layers on mirrors for extreme ultraviolet (EUV) lithography. These mirrors are subject to contamination due to reaction of the mirror surface with hydrocarbons and oxygen under influence of the EUV radiation. In order to find a method of mitigating the effects of this contamination, it is necessary to understand the interaction process of the contaminating species and the Ru mirror surface. In this study the oxidation kinetics of a monocrystalline Ru(0001) surface was studied with ellipsometry and XPS. During the oxide growth, first a monolayer of chemisorbed oxygen was formed on the surface. After this monolayer was formed in its entirety, ruthenium dioxide could start to grow. The change from the chemisorbed oxygen layer to RuO_2 is related to a phase transition from a (1x1) overlayer structure to the (110) plane of RuO_2 and only occurs after a constant exposure of the Ru(0001) surface to oxygen. In the second stage the growth of RuO_2 is linear with time, indicating an adsorption limited growth mode. Finally, in the third stage, the growth levels off due to a transport limited behavior. The EUV light can accelerate the transition from the chemisorbed monolayer to RuO_2 but has no significant effect on the thickness and structure of the oxide after longer oxidation times.

O 27.4 Tue 11:15 H42

Surface stress driven population of an "unusual" adsorption site — •Zhen Tian[1], Dirk Sander[1], Holger Meyerheim[1], Larissa Niebergall[1], Nikolay Negulyaev[2], Katayoon Mohseni[1], Valeriy Stepanyuk[1], and Jürgen Kirschner[1] — [1]Max-Planck-Institute of Microstructure Physics,Halle, Germany — [2]Fachbereich Physik,Martin-Luther-Universität, Halle

Adsorption on (001) surfaces of fcc metals often leads to the population of the fourfold hollow site. This is not the case for small coverage of O on Ir(001), where adsorption on bridge sites is observed[1]. We perform combined surface X-ray diffraction (SXRD) [2], and adsorbate-induced surface stress measurement to elucidate the correlation between structure, stress and adsorption site. We find from SXRD that at 550 K up to a coverage of 0.5 O adsorbs in the unusual bridge site, whereas for $\theta_O > 0.5$, the hollow sites are populated in addition. Our calculations offer an explanation for hollow site adsorption, as O-adsorption for $\theta_O > 0.5$ in bridge sites would induce a prohibitively large lattice corrugation. Our stress measurements reveal a compressive surface stress change of -2.2 N/m for the population of both p(1×2) and hollow sites at a total coverage of 0.75. Our experimental results on the atomic structure and the O-induced surface stress change are supported by ab initio calculations. [1] K. Johnson, Q. Ge, S. Titmus, and D. A. King, J. Chem. Phys. 112 (2000) 10460. [2] We thank the staff at ID-03, E.S.R.F., Grenoble for expert support.

O 27.5 Tue 11:30 H42

Dispersion effects in the dissociative adsorption of O_2 on Al(111) — •Christian Carbogno[1], Jörg Behler[2], Karsten Reuter[3,4], and Axel Gross[1] — [1]Universität Ulm, Germany — [2]Ruhr-Universität Bochum, Germany — [3]Fritz-Haber-Institut, Berlin, Germany — [4]Technische Universität München, Germany

We have recently shown that the low sticking probability of thermal O_2 molecules at Al(111) can be reproduced from first principles if spin selection rules are explicitly accounted for [1,2]. These hinder transitions from the initial O_2 gas-phase triplet state to the singlet state of the adsorbed O atoms. In spite of the good agreement with the experimental sticking coefficient at normal incidence, its non-monotonic dependence on the incidence angle [3] is only partially reproduced by our calculations. A possible explanation for this discrepancy is the lack of dispersion forces in such a pure DFT approach. As a consequence, the calculated potential energy surfaces do not feature a physisorbed precursor state whose existence is assumed to lead to the observed non-monotonic dependence [3]. We inspect if and how various semi-empirical dispersion corrections (DFT-D) can compensate for this flaw in the description of this system. In addition, we discuss the implications of such corrections on the molecule-metal surface interaction.

[1] J. Behler *et al.*, Phys. Rev. Lett. **94**, 036104 (2005).

[2] C. Carbogno *et al.*, Phys. Rev. Lett. **101**, 096104 (2008).

[3] O. Weiße *et al.*, J. Chem. Phys. **118** 8010 (2003).

O 27.6 Tue 11:45 H42

Growth and morphology of ultrathin TiOx films on Pt3Ti(111) — •Marco Moors[1], Séverine Le Moal[2,3], Jan Markus Essen[1], Conrad Becker[2], and Klaus Wandelt[1] — [1]Institut für phys. und theoret. Chemie, Universität Bonn — [2]Centre Interdisciplinaire de Nanoscience de Marseille — [3]Technische Universität München

The morphology as well as the surface composition of ultrathin titanium oxide films grown on a Pt3Ti(111) single crystal surface have been investigated as a function of oxidation temperature (700 K to 1000 K) and oxygen exposure (up to 4500 L) using LEED, HREELS and AES. The oxidation of the alloy surface starts at sample temperatures over 500 K but ordered phases are not formed below 800 K. Depending on the used preparation conditions four different ordered oxide phases with both rectangular and hexagonal symmetry have been observed caused by the competitive influence of the hexagonal symmetry of the substrate and the favoured rectangular oxide symmetry. The found structures show a high degree of surface order. Our studies indicate the preference for a two dimensional oxide growth despite very high oxygen exposures (> 900 L). The thicker films are only metastable in a rather small temperature range between 800 and 900 K. Annealing to higher temperatures results in an immediate surface reduction. A complete oxidation to TiO2 is not possible under UHV conditions (p(O2) up to 10-5 mbar). By comparison with the parameters of known stable bulk oxide surfaces a structure proposal of the found oxide phases can be made.

O 27.7 Tue 12:00 H42

The molecular structure of ice on Pt(111) — •Sebastian Standop[1], Alex Redinger[1], Markus Morgenstern[2], Thomas Michely[1], and Carsten Busse[1] — [1]II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, D-50937 Köln — [2]II. Physikalisches Institut (IIB), RWTH Aachen, D-52056 Aachen

Using Scanning Tunneling Microscopy the molecular arrangement of the wetting layer of H_2O on Pt(111) is resolved. The water molecules arrange in a hexagonal pattern resembling the (0001) surface of ice I_h. The dense packed molecular rows are slightly rotated with respect to the dense packed rows of the underlying metal. This leads to a complex superstructure in accordance with scattering experiments [1]. Due to the tendency of single water molecules to adsorb flat on Pt(111) the structure is geometrically frustrated as each monomer donates two hydrogen bonds but can in turn accept only one. The system escapes this frustration by the introduction of a disordered arrangement of vacancy clusters.

Our results show that the degree of order in the globally disordered phase may be increased artificially. On an appropriate substrate both the $\sqrt{39} \times \sqrt{39}$ R16.1° structure for a full monolayer as well as the $\sqrt{37} \times \sqrt{37}$ R25.3° structure for submonolayer water islands could be identified. Based on the well known binding mechanism of single molecules we propose criteria for the structure formation, domain size enhancement and thermodynamic stability of these high order commensurate phases.

[1] A. Glebov *et al.*, Journal of Chemical Physics 106 (1997) 9382

O 27.8 Tue 12:15 H42

Effects of substituted palladium on hydrogen adsorption to stepped Au(111) surfaces — •Jonathan E. Mueller[1,2], Sudha Venkatachalam[1], and Timo Jacob[1] — [1]Ulm University, Albert-Einstein-Allee 47, D-89069 Ulm, Germany — [2]Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, United States of America

Configurations of different Pd-containing Au(111) bimetallic surfaces with Pd substituents varying from one to three atoms have been studied using density functional theory. The stability of the so-formed Pd monomers, dimers or trimers in the surface and subsurface layers of a Au(111) terrace and their influence on the adsorption of hydrogen have been investigated [1]. We find that before hydrogen adsorption the surface prefers to form Pd monomers over dimers or trimers located in subsurface positions, which is in agreement with experimental observations. However, adsorption of atomic hydrogen reverses this trend, leading to a stabilization of Pd trimers over dimers or monomers all located in the surface layer. Since realistic surfaces usually contain step edges, we extended our studies to the (100) and (111) steps of Au(111), finding that Pd does prefer substituting Au at bulk sites over edge sites, a behavior again modified by the presence of surface hydrogen [2].

[1] S. Venkatachalam, T. Jacob, Phys. Chem. Chem. Phys., 11, 3263-3270 (2009) [2] J. E. Mueller, S. Venkatachalam, T. Jacob, in preparation.