

## O 67: Metal surfaces: Adsorption of H/O and inorganic molecules

Time: Thursday 10:30–12:45

Location: MA 043

O 67.1 Thu 10:30 MA 043

**Two-Level Conductance Fluctuations of a Single-Molecule Junction** — ●NICOLAS NÉEL<sup>1,2</sup>, JÖRG KRÖGER<sup>2</sup>, and RICHARD BERNDT<sup>1</sup> — <sup>1</sup>Christian Albrechts Universität zu Kiel — <sup>2</sup>Technische Universität Ilmenau

The conductance of a single-molecule junction in a low temperature scanning tunneling microscope has been measured at nanosecond time resolution. In a transition region between tunneling and contact the conductance exhibits rapid two-level fluctuations which are attributed to different geometries of the junction. The voltage dependence of the fluctuations indicates that electrons injected into the lowest unoccupied molecular orbital may efficiently couple to molecular vibrations. Financial support through SFB 677 is acknowledged.

N. Néel, J. Kröger, and R. Berndt, *Nano Lett.* **11**, 3593 (2011)

O 67.2 Thu 10:45 MA 043

**Tilting, bending and nonterminal sites in CO on Cu(001)** — ●HOLGER L. MEYERHEIM<sup>1</sup>, RAMESH THAMANKAR<sup>1</sup>, ARTHUR ERNST<sup>1</sup>, SERGEI OSTANIN<sup>1</sup>, IGOR V. MAZNICHENKO<sup>2</sup>, ELENA SOYKA<sup>1</sup>, INGRID MERTIG<sup>2</sup>, and JÜRGEN KIRSCHNER<sup>1</sup> — <sup>1</sup>Max-Planck-Institut f. Mikrostrukturphysik, D-06120 Halle — <sup>2</sup>Institut f. Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle

Carbon monoxide (CO) adsorbed on metals represents an archetype system in surface science. In the case of CO on Cu(001) it is undisputed that the ( $\sqrt{2}\times\sqrt{2}$ ) structure is characterized by  $\theta=0.5$  monolayers (MLs) of CO molecules located on top of every other Cu atom with carbon bonded to the metal.

We have studied the geometric structure of the compressed  $c(7\sqrt{2}\times\sqrt{2})$  anti-phase domain structure of CO on Cu(001) by using scanning tunnelling microscopy experiments in combination with first principles calculations. We find direct evidence for structural relaxations involving an inhomogeneous CO-environment characterized by molecular tilting, bending and non-terminal sites [1]. Our study resolves the so far unresolved problem to explain coverage dependent changes in RAIRS spectra reported previously [2,3].

[1] R. Thamankar, H. L. Meyerheim, A. Ernst, S. Ostanin, I.V. Maznichenko, E. Soyka, I. Mertig, and J. Kirschner, *Phys. Rev. Lett.* **106**, 106101 (2011); [2] C.J. Hirschmugl et al., *Phys. Rev. Lett.* **65**, 480 (1990); [3] J.C. Cook et al., *J. Chem. Soc. Faraday Trans.* **93**, 2315 (1997)

O 67.3 Thu 11:00 MA 043

**Ab-initio study of the stability of Fe<sub>3</sub>Al surfaces in contact with an oxygen atmosphere** — ●AFSHIN IZANLOU, MIRA TODOROVA, MARTIN FRIAK, and JÖRG NEUGEBAUER — Department for Computational Materials Design, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf

Iron-aluminides are potential candidates for high temperature applications, but their deformability, which is necessary for manufacturing processes, is reduced by hydrogen diffusion at room temperature. The presence of passive surface films has been reported to reduce H embrittlement [1] by lowering the H liberation rate at the surface. It has been further suggested that addition of passivity inducing alloying elements would have a beneficial effect on their thermo-mechanical and electro-chemical behaviour, as well [2].

In a first step towards the identification of suitable alloying elements that reduce H liberation over a wide range of environmental conditions, we study by density functional theory both clean and oxygen covered low index Fe<sub>3</sub>Al surfaces. We find the mixed FeAl termination to be most stable on the [001] and [110] clean surfaces, while an Fe-termination is most favourable on the [111] surface. Having identified the likely clean surface terminations, we study low coverage oxygen structures and assess the impact the environment has on surface structure and stability by employing thermodynamic concepts.

[1] C.T. Liu *et al.*, *Scr. Metall. Mater.* **24** (1990) 385.

[2] R. Balasubramaniam, *Bull. Mater. Sci.* **3** (1999) 571; D.G. Morris and M. A. Muñoz-Morris, *Adv. Eng. Mater.*, **13** (2011) 43.

O 67.4 Thu 11:15 MA 043

**Iodine on Pt(110) - competing phases** — ●NADJA OBERKALMSTEINER, MICHAEL CORDIN, and ERMINALD BERTEL — Institute of Physical Chemistry, University of Innsbruck, Innsbruck, Austria

The adsorption of halogens on Pt(110) leads to an exceedingly rich phase diagram. This is due in part to the competition between different ordered phases at the same coverage of  $\Theta=0.5$  ML. In previous experiments with Br/Pt(110) a  $c(2\times 2)$  structure was observed at room temperature, while a small excess coverage led to the appearance of a threefold periodicity. The latter structure however, was strongly fluctuating, thus neither the exact coverage nor the structure could be determined unambiguously. Here we present STM data on the  $\Theta=0.5$  ML room temperature phase of Iodine on Pt(110). Similarly to Bromine, a long-range ordered  $c(2\times 2)$  structure is observed. A minute excess coverage leads to nucleation of a  $(3\times 1)$  structure with local coverage of  $\Theta=0.66$  ML. The presence of such a few highly dispersed  $(3\times 1)$  nuclei, however, switches the rest of the surface with  $\Theta=0.5$  ML local coverage into a global  $(3\times 2)$  structure. Since the Iodine adlayer does not fluctuate at room temperature, one can determine precisely the excess coverage required to switch the whole surface to the threefold periodicity. The observed transition clearly demonstrates the long-range nature of the interaction in real space, thus arguing for an electronically driven phase transition. Remarkably, the  $(3\times 2)$  structure involves a considerably buckling of the substrate pointing towards an inherent instability of the Pt(110) surface. Apparently both halogens promote a charge density wave/periodic lattice distortion transition of Pt(110).

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**Structure and characterization of the hydrogen-bonded NH<sub>3</sub>-NO coadsorption on Pt(111): an ab-initio study.** — ●ANDREA CEPELLOTTI<sup>1</sup>, ANGELO PERONIO<sup>2</sup>, and MARIA PERESSI<sup>3</sup> — <sup>1</sup>Theory and Simulation of Materials, École Polytechnique Fédérale de Lausanne — <sup>2</sup>IOM-CNR Laboratorio TASC, Trieste — <sup>3</sup>Dipartimento di Fisica, Università di Trieste

The study of coadsorption states is an important subject in heterogeneous catalysis, since interactions between adsorbates can inhibit or allow specific reaction pathways. As such the coadsorption of NH<sub>3</sub> and NO on Pt(111) is an interesting system that still lacks a satisfactory characterization both on theoretical and experimental grounds. Early EELS and TDS experiments [1] and recent STM measurements have suggested the formation of complexed structures composed by the two molecules.

Available observations are not able to unambiguously characterize the observed structures, therefore we employ density functional theory to demonstrate the existence of two stable structures, determining the geometrical structure by means of total energy minimization and reproducing the available experimental data. The electronic structure has been characterized, proving that the interaction between adsorbates arises from a hydrogen bond between each H and O. Such interaction suggests an explanation for the high selectivity of NH<sub>3</sub> in the reduction with NO on platinum-based catalysts, which makes this class of systems suitable for combustion-gas treatment.

[1] J. L. Gland and B. A. Sexton, *J. Catal.* **68**, 286 (1981)

O 67.6 Thu 11:45 MA 043

**Ordered domain-wall structure of Ir(100)-(2×1)-O** — ●PASCAL FERSTL, TOBIAS SCHMITT, LUTZ HAMMER, and M. ALEXANDER SCHNEIDER — LS f. Festkörperphysik, Universität Erlangen-Nürnberg, Germany

Oxygen adsorption on Ir(100) leads to the formation of a  $(2\times 1)$  superstructure, whereby 0.5 ML of oxygen atoms are adsorbed in bridge positions [1,2]. A recent SXRD study [2] found an additional partial occupation of the hollow sites in the centres of the  $(2\times 1)$  cell by oxygen atoms. This finding is now validated by our STM measurements where we could directly image these extra atoms, which, however, are still very mobile at room temperature.

A slight reduction of the amount of oxygen adsorbed by heating the sample to the onset of oxygen desorption does not depopulate the hollow sites but creates light domain walls perpendicular to the oxygen rows instead. The mutual spacing of the domain walls is rather regular and decreases with coverage eventually leading to a  $(2\times n)$  superstructure. The occurrence of such a superstructure has been inferred from very early LEED work [3], but its origin remained unclear. We argue that the domain walls already exhibit the hexagonal reconstruction of the clean surface.

[1] K. Johnson *et al.*, *J. Chem Phys.* **112** (2000) 10460;

- [2] D. Sander *et al.*, Phys. Rev. B **81** (2010) 153403;  
 [3] J. Küppers & H. Michel; Appl. Surf. Sci. **3** (1979) 179

O 67.7 Thu 12:00 MA 043

**Interactions of 2nd row high electron affinity elements with Mg(0001)** — •SU-TING CHENG, MIRA TODOROVA, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

The high corrosion susceptibility of magnesium can be either beneficial or detrimental, depending on the application. For use in biodegradable implants fast, but controllable, degradation behavior is desirable. However, in engineering applications the low corrosion resistance of magnesium and its alloys is a considerable drawback.

Aiming to gain a better understanding of the corrosion behavior of Mg and its alloys we investigate the interaction of oxidizing species such as O, F, N and Cl with the Mg (0001) surface using density functional theory calculations. Accounting for the effect of the environmental conditions within a thermodynamic picture we find that adsorbate phases can only be stable kinetically and are always thermodynamically unstable with respect to the corresponding bulk compounds.

O 67.8 Thu 12:15 MA 043

**Coadsorption of deuterium and CO on PtRu/Ru(0001) model surfaces - The influence of surface structure** — •THOMAS DIEMANT, HEINRICH HARTMANN, JOACHIM BANSMANN, and ROLF JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

The study of the interaction of hydrogen (deuterium) and/or CO with bimetallic PtRu surfaces is of high interest for an improved understanding of the chemistry of low temperature Polymer Electrolyte (PE) fuel cells. Studies with structurally well-defined model surfaces can contribute significantly in this respect. In our study, we used PtRu/Ru(0001) model surfaces of two distinct structural configurations: (i) monolayer Pt islands on a Ru(0001) substrate and (ii)

PtRu/Ru(0001) surface alloys with almost random distribution of the two metal components in the surface layer. We studied the coadsorption of deuterium and CO on these bimetallic model surfaces using temperature-programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS). We will show how the adsorption properties of both species are affected by the deposition of Pt, the metal distribution in the surface and the presence of the co-adsorbed species.

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**Exceptionally low friction of CrN/TiN multilayer coatings – a combined experimental and theoretical study** — •DAVID HOLEC, JÖRG PAULITSCH, and PAUL H. MAYRHOFER — Department of Physical Metallurgy and Materials Testing, University of Leoben, Leoben, Austria

Recently we have demonstrated that CrN/TiN multilayer coatings, deposited using the hybrid high power impulse magnetron sputtering (HIPIMS)/direct current magnetron sputtering (DCMS), exhibit extremely low friction coefficients below 0.1 when tested at room temperature and ambient air conditions. By performing dry-sliding tests in an atmosphere with reduced humidity we identified relative humidity of approximately 13% as the necessary condition for the friction to drop to values below 0.1. Density functional theory was used to study the properties of the CrN/TiN system. While the surface energy of the (100) surface is lower than that of (111) in TiN, the situation reverses in CrN. Subsequently we studied the binding energies of H and O atoms on the (100) surfaces. It has turned out that both atoms are weaker bonded on TiN than on CrN. Moreover, the barrier for surface diffusion of H on TiN is significantly lower ( $\sim 0.5\text{eV}$ ) than on CrN ( $\sim 0.8\text{eV}$ ), thus suggesting that H atoms are more mobile on TiN surfaces while stronger bonded on CrN surfaces. Based on both evidences we therefore speculate that the extraordinary low friction coefficient of the CrN/TiN multilayer may be related to accumulation of water molecules from humid air (creation of water droplets) on the CrN on the expense of the TiN surfaces, thus providing a bearing-like effect.