

## O 82: Metal Substrates II

Time: Thursday 16:00–19:00

Location: WIL A317

O 82.1 Thu 16:00 WIL A317

**Measuring the mode-selective e-ph interaction constant on Sb(111) using Helium atom scattering** — ●PATRICK KRAUS<sup>1</sup>, MICHAEL MAYRHOFER-R.<sup>1</sup>, FLORIAN APOLLONER<sup>1</sup>, CHRISTIAN GÖSWEINER<sup>1</sup>, GIORGIO BENEDEK<sup>2</sup>, SALVADOR MIRET-ARTÉS<sup>3</sup>, and WOLFGANG E. ERNST<sup>1</sup> — <sup>1</sup>IEP, University of Technology, Graz, Austria — <sup>2</sup>DIPC, San Sebastián, Spain — <sup>3</sup>C.S.I.C, Madrid, Spain

As one of the essential components in the recently discovered group of topological insulators [1], the semimetal antimony (Sb) is an attractive candidate for studying the properties of its surface. Quite recently the surface phonon dispersion curve of Sb(111) as well as the influences of e-ph interaction were calculated using DFPT [2]. Helium Atom Scattering allows to investigate elastic as well as inelastic phenomena associated with structure and dynamics of the electronic corrugation slightly above the Sb(111) surface. Using exact approaches such as the Close-Coupling-Method, a fundamental analysis of the surface corrugation is possible. Furthermore, this approach can be extended to include inelastic interactions [3,4], rendering the measurement of the mode-selective electron-phonon interaction constant possible. The complete procedure, beginning with the determination of the three dimensional static interaction potential to the evaluation of the mode-selected electron-phonon interaction, will be presented. [1] H. Zhang et al., Nature Physics 5 (2009) 438-442 [2] D. Campi et al., Phys. Rev. B. 86 (2012) 075446 [3] A.S. Sanz and S. Miret-Artés, Phys. Rep. 451 (2007), 37-154 [4] M. Mayrhofer-R. et. al., Phys. Rev. B. 88 (2013), 205425

O 82.2 Thu 16:15 WIL A317

**Reinvestigation of the Acoustic Surface Plasmon Dispersion on Cu(111) by HREELS** — ●JAN PISCHEL, EMANUEL WELSCH, OLAF SKIBBE, and ANNEMARIE PUCCI — Kirchhoff-Institut für Physik, Im Neuenheimer Feld 227, D-69120 Heidelberg

During the past decade, the existence of the acoustic surface plasmon (ASP, [1]) on various single crystal metal surfaces has been established experimentally, see e.g. [2]. Its low energy in the meV range and a linear dispersion near  $\Gamma$  make it interesting for a wide range of phenomena and applications reaching from superconductivity to nano-optics. Only recently, it was reported that the ASP on Au(111) disperses into the electron-hole (e-h) pair continuum [3], which is in contrast to the theoretical prediction [1]. This unexpected behaviour could be traced back to the fact that the majority of bulk electrons around the Fermi level move slower than the electrons of the Shockley surface state and are hence screened by the latter rather than the other way around.

We used HREELS with low impact energies down to 2eV and an angular resolution of  $1.4^\circ$  to reinvestigate the situation on Cu(111). As shown here, the ASP turned out to be only one of multiple contributions to the broad excitation feature that was earlier exclusively ascribed to the ASP [2] and to disperse into the e-h pair continuum. These results suggest that a situation similar to the Au(111) case must be present on the Cu(111) surface, too.

[1] Silkin et al., Europhys. Lett. **66**(2):260–264, 2004.[2] Pohl et al., Europhys. Lett. **90**:57006, 2010.[3] Vattuone et al., Phys. Rev. Lett. **110**:127405, 2013.

O 82.3 Thu 16:30 WIL A317

**Probing Two-Band Superconductivity by Scanning Tunneling Spectroscopy** — ●MICHAEL RUBY<sup>1</sup>, BENJAMIN W. HEINRICH<sup>1</sup>, JOSE I. PASCUAL<sup>1,2</sup>, and KATHARINA J. FRANKE<sup>1</sup> — <sup>1</sup>Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — <sup>2</sup>CIC nanoGUNE and Ikerbasque, Basque Foundation for Science, Tolosa Hiribidea 78, Donostia-San Sebastian 20018, Spain

Recent DFT simulations have shown that the two separated Fermi-surfaces of the strong-coupling s-wave BCS superconductor lead (Pb) exhibit different character in momentum space, namely s-p- and p-d-like [1]. The two Fermi-surfaces make Pb a two-band superconductor with different gap parameter for each band. Using scanning tunneling spectroscopy (STS) we observe an energy difference of the gap parameters of  $\approx 150 \mu\text{V}$ , and different intensity for each of the BCS resonances. We use the high spacial resolution of STS measurements to further investigate the influence of surface defects, adsorbates, and impurities on the density of states of the two-band superconductor.

[1] A. Floris et al., Phys. Rev. B **75**, 054508, (2007)

O 82.4 Thu 16:45 WIL A317

**Electromechanical coupling coefficients of sp-bonded metals from first principles** — ●ANJA MICHL<sup>1,2</sup>, SANDRA HOPPE<sup>2</sup>, CHANDRAMOULI NYSHADHAM<sup>2</sup>, JÖRG WEISSMÜLLER<sup>1,3</sup>, and STEFAN MÜLLER<sup>2</sup> — <sup>1</sup>Institute of Materials Research, Materials Mechanics, Helmholtz-Zentrum Geesthacht, Germany — <sup>2</sup>Institute of Advanced Ceramics, Hamburg University of Technology, Germany — <sup>3</sup>Institute of Materials Physics and Technology, Hamburg University of Technology, Germany

The coupling between mechanical stress or strain of a surface and its electronic properties is relevant for various applications ranging from sensors and actuators to catalysis. In experiment, coupling coefficients are determined via electrochemical experiments, e.g. by measuring the variation of the electrode potential upon applying tangential strain  $\epsilon$  to the electrode surface. Theoretically, this coupling strength is accessible as the response of the electronic work function  $W$  to strain. Using density functional theory, we calculate such strain response parameters  $dW/d\epsilon$  for sp-bonded metals. While for Al we find an abnormal positive sign for the coupling coefficient [1], all other investigated metals show the usual negative response parameter (in their natural crystal structure). We analyze trends of the coupling coefficients with respect to valence electron density, crystal structure and work function of the unstrained surface and discuss the identified correlations.

[1] A. Michl, J. Weissmüller and S. Müller, J. Phys.: Condens. Matter **25**, 445012 (2013)

O 82.5 Thu 17:00 WIL A317

**Ground-state structures for oxygen adsorption on Ir(100)-(1×1) investigated via the cluster-expansion method** — ●ANJA MICHL<sup>1,2</sup>, PASCAL FERSTL<sup>3</sup>, LUTZ HAMMER<sup>3</sup>, M. ALEXANDER SCHNEIDER<sup>3</sup>, and STEFAN MÜLLER<sup>2</sup> — <sup>1</sup>Institute of Materials Research, Materials Mechanics, Helmholtz-Zentrum Geesthacht, Germany — <sup>2</sup>Institute of Advanced Ceramics, Hamburg University of Technology, Germany — <sup>3</sup>LS f. Festkörperphysik, Universität Erlangen-Nürnberg, Germany

The interaction of oxygen with transition metal surfaces is of fundamental importance for a variety of processes in heterogeneous catalysis. In the case of iridium, oxygen exposure lifts the (5×1)-hex reconstruction of the (100) surface leading to a (1×1) structure.

We performed an exhaustive ground-state search for the O/Ir(100)-(1×1) system by using the cluster-expansion formalism in conjunction with first-principles calculations. Our study reveals ( $n \times 1$ )- $mO$  superstructures as the dominant structural motif of energetically favorable structures, where the periodicity  $n$  and the number of oxygen atoms in the unit cell  $m$  vary with the coverage. Bridge site occupation is preferred and the most pronounced ground state is the well-known (2×1)-br superstructure. At low coverage, structures formed by an alternation of (2×1)-br stripes and a shifted row reconstruction have lower formation energies than the corresponding structures on a merely (1×1) ordered substrate. Our findings are in agreement with experimental data obtained by STM and LEED.

O 82.6 Thu 17:15 WIL A317

**Origin of unexpected attractive adsorbate-adsorbate interactions between negatively charged ions on Mg(0001) surfaces** — SU-TING CHENG, ●MIRA TODOROVA, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung, Düsseldorf

Electrostatic repulsion usually leads to an increase in work function and a decrease in binding energy when the coverage of electronegative elements adsorbed on a metal surface is increased. Using density-functional theory we investigate the adsorption of {N,O,F,Cl} on Mg(0001) and find that only Cl complies with this expectations. All the considered 2<sup>nd</sup> row elements cause a decrease in work-function and an increase in binding energy with increasing coverage. We show that these counter-intuitive phenomena can be understood in terms of an efficient embedding of the adsorbate atoms into the unusually large electronic surface spill-out of Mg(0001). The described mechanism is based on purely electrostatic arguments and thus expected to be a generic feature on surfaces consisting of highly electropositive elements.

O 82.7 Thu 17:30 WIL A317

**Local Adsorption Sites of Oxygen and Hydrogen on the Ir(100) surface** — ●PASCAL FERSTL<sup>1</sup>, LUTZ HAMMER<sup>1</sup>, M. ALEXANDER SCHNEIDER<sup>1</sup>, FLORIAN MITTENDORFER<sup>2</sup>, MD. ALIF ARMAN<sup>3</sup>, EDVIN LUNDGREN<sup>3</sup>, and JAN KNUDSEN<sup>3</sup> — <sup>1</sup>Lst f. Festkörperphysik, FAU Erlangen-Nürnberg, Germany — <sup>2</sup>Inst. f. Angewandte Physik & CMS, TU Wien, Austria — <sup>3</sup>Synchrotron Radiation Research, Lund, Sweden

The adsorption behavior of oxygen and hydrogen on transition metal surfaces is of fundamental importance for heterogeneous catalysis. In this high-resolution X-ray photoelectron spectroscopy study we investigated their adsorption on the Ir(100) surface in the whole accessible coverage range  $\Theta = 0 - 1.0$ . The investigation is complemented by LEED, STM and TDS measurements, as well as by DFT calculations, allowing the clear identification of different components in the XP-spectra of the various phases.

A detailed investigation of the Ir 4f<sub>7/2</sub> line reveals that on the unreconstructed Ir(100)-1×1 surface both adsorbates are found to occupy exclusively bridge sites of the substrate. For the maximum coverage  $\Theta = 1.0$  – in case of oxygen this can only be achieved by offering atomic species – every Ir surface atom is connected to two adsorbate atoms while for  $\Theta = 0.5$  every two substrate atoms have to share one adsorbate. This leads to clear shifts in the Ir 4f<sub>7/2</sub> core level energies. Series of spectra taken for various coverages achieved via successive thermal desorption can be explained by a superposition of spectra of these limiting structures and that for the finally reached clean, reconstructed 5×1 phase discarding any further local binding configuration.

O 82.8 Thu 17:45 WIL A317

**Au-Ag(110) Alloy Surfaces: Surface Restructuring and Oxygen Chemistry** — ●MARTIN SCHMID, JOSHUA KLOBAS, ROBERT J. MADIX, and CYNTHIA M. FRIEND — Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA, USA

We investigated the morphology and oxygen chemistry of thin film Au-Ag(110) alloy surfaces. The alloys were prepared by deposition of Au onto an Ag(110) single crystal under UHV conditions. The initial deposition was followed by several steps of moderate annealing in order to fabricate a thin, homogeneous surface alloy. Examination of the Au-Ag(110) surfaces with Scanning Tunneling Microscopy (STM) showed a substantial surface restructuring on the submicrometer scale, which is associated with the onset of gold diffusion into the Ag(110) bulk, starting at 400K. After repeated moderate annealing steps to 630K, an apparently constant thin film composition could be established, as confirmed with angle resolved X-ray Photoelectron Spectroscopy (XPS). The oxygen chemistry of the thin film alloys was monitored with Temperature Programmed Desorption (TPD) experiments. Exposing the thin film alloys to O<sub>2</sub> (pressure range of 1×10<sup>-6</sup> mbar) showed a linear dependence between the oxygen uptake of the thin film at 300K and its gold content. Furthermore, probing the adsorption sites of chemisorbed O<sub>2</sub> at low temperatures (125K) showed strong indications that gold atoms, while being unreactive themselves, control the oxygen uptake by shaping the size, amount, and distribution of reactive Ag sites.

O 82.9 Thu 18:00 WIL A317

**Investigation of ice on Ag(111) via scanning tunneling microscopy: Kinetics and thermodynamics**

— ●CORD BERTRAM, KARSTEN LUCHT, and KARINA MORGENSTERN — Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum

As a member of the dipolar liquids and a well-known solvent, water is a very important component in electro-catalysis. For a further understanding of the microscopic processes taking part in electro-catalytic reactions, the local rearrangement of molecules in frozen water on Cu(111) in presence of an electrical field has recently been studied by scanning tunneling microscopy<sup>1</sup>. However, the local rearrangement depends highly on the coordination of the water molecules within the ice structure, which largely influences its ability to solvate ions or electrons. Therefore water structures on Cu(111) and on Ag(111) are studied. These surfaces with a difference in adsorption energy show substrate-mediated structure formation due to lattice mismatch effects. Additionally different preparation procedures result in structural differences, which can be explained by kinetic and thermodynamic processes. The consideration of these effects leads to new candidates for the microscopic observation of ion solvation.

<sup>1</sup>Mehlhorn et al.: Chem Electro Chem (2013) *in print*

O 82.10 Thu 18:15 WIL A317

**The CO adsorption on Ru(0001) and bimetallic PtRu/Ru(0001) surfaces at elevated pressures (from 10<sup>-3</sup> to 100 mbar)** — ●THOMAS DIEMANT, JOACHIM BANSMANN, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

PtRu catalysts are, due to their superior CO tolerance, a promising material for the anodic hydrogen oxidation reaction in low-temperature polymer electrolyte fuel cells in the presence of small amounts of CO. After studying the adsorption of CO and hydrogen on structurally well-defined PtRu/Ru(0001) surfaces under UHV conditions, we extended our studies to catalytically relevant conditions (atmospheric pressure and RT), investigating the CO adsorption on Ru(0001) and bimetallic surfaces at elevated CO pressure, using polarization-modulated IR reflection absorption spectroscopy (PM-IRAS).

On unmodified Ru(0001), we find a gradual blue-shift of the peak position with increasing pressure, which stops at a wave number higher than the value found for UHV CO saturation. In agreement with a recent XPS study on this topic [1], we explain this finding by a higher CO saturation coverage than obtained under UHV conditions. For CO adsorption on a Pt/Ru(0001), we find a comparable wave number. In this case, however, it resembles the value obtained for UHV adsorption at 150 K, supporting our previous model of a kinetic barrier for direct CO adsorption on Ru(0001) at high CO coverages, which can be circumvented by spillover from Pt monolayer islands.

[1] D. E. Starr, H. Bluhm, Surf. Sci. 608 (2013) 241.

O 82.11 Thu 18:30 WIL A317

**Spontaneous step creation during NO reduction on Pt surfaces: a high-pressure STM study** — ●MATTHIJS VAN SPRONSEN, QIAN LIU, and JOOST FRENKEN — Kamerlingh Onnes Laboratory, Leiden University, Leiden, P.O. Box 9504, 2300 RA, The Netherlands

When atoms and molecules adsorb on surfaces, they can introduce significant changes in the surface stress, for example when an overlayer is formed of dipolar molecules that strongly repel each other. This may have dramatic consequences for the structure of catalysts that have dense overlayers due to high gas pressures. We have used a scanning tunneling microscope (STM), dedicated for atomic-scale, high-pressure, high-temperature observations of active catalysts, to investigate the structural changes that occur on a Pt(110) surface when this is active as a catalyst for NO reduction by H<sub>2</sub>. To our surprise we find that atmospheric pressures of (NO,H<sub>2</sub>) gas mixtures lead to the spontaneous creation of regular step arrays on the initially flat surface. We propose that the step creation is a pathway for the surface to relax part of the high, adsorption-induced stress. This interpretation finds support in DFT calculations.

O 82.12 Thu 18:45 WIL A317

**Pt-coverage dependence and adsorption kinetics of the coadsorption of CO and deuterium on bimetallic Pt/Ru(0001) surfaces** — HEINRICH HARTMANN, ●JOACHIM BANSMANN, THOMAS DIEMANT, and R. JÜRGEN BEHM — Institut für Surface Chemistry and Catalysis, Ulm University, D-89081 Ulm

The interaction of hydrogen and CO with bimetallic PtRu surfaces as technological promising materials is of high interest for the understanding of the chemistry in low temperature Polymer Electrolyte (PE) fuel cells. In the present TPD and IR study we investigated the coadsorption of CO and deuterium at 100 K (subsequently exposed) on sub-monolayer Pt films on Ru(0001) as model systems.

The total coverage of adsorbates (CO<sub>ad</sub> and D<sub>ad</sub>) on the bimetallic Pt/Ru(0001) surface depends not only on the amount of Pt on the surface, but also strongly on the sequence in the coadsorption process. Deuterium adsorption followed by high CO exposures results in very high coverages, whereas, in the opposite case, no further D<sub>2</sub> adsorption is possible on a saturated CO layer and the total coverages are smaller. Here, we will additionally analyze the influence of pre-adsorbed D<sub>ad</sub> species on the CO adsorption kinetics and the total adsorbate coverage compared to pure CO and deuterium adsorption on bimetallic Pt/Ru(0001) [1] and PtRu/Ru(0001) surfaces alloys [2].

[1] H. Hartmann et al., Phys. Chem. Chem. Phys. 14 (2012) 10919.

[2] T. Diemant et al., Chem. Phys. Chem. 11 (2010) 1482.