

## O 45: Metal Substrates II

Time: Wednesday 10:30–12:45

Location: H42

O 45.1 Wed 10:30 H42

**Coadsorption of deuterium and CO on submonolayer Pt films on Ru(0001) model surfaces** — HEINRICH HARTMANN, •JOACHIM BANSMANN, THOMAS DIEMANT, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

Pt surfaces modified by Ru are of high interest for applications in low temperature Polymer Electrolyte (PE) fuel cells. Here, we report on a combined TPD/IRAS study of coadsorbed hydrogen (deuterium) and CO and their interaction with model surfaces, e.g., submonolayer Pt films on Ru(0001) with varying Pt coverages. The experimental results show that a closed CO layer completely blocks the adsorption of D<sub>2</sub>. On a surface partly covered by CO, D<sub>2</sub> adsorption is still possible, however a considerable decrease of the D<sub>ad</sub> adsorption energy is observed. In the reverse case, pre-adsorbed D<sub>ad</sub> also reduces the amount of subsequently adsorbed CO, although CO adsorption is possible even on a closed D<sub>ad</sub> layer. This phenomenon leads to very high total coverages (exceeding 1 ML) and an additional destabilization of the coadsorbed species. Pre-adsorbed D<sub>ad</sub> has the strongest influence on the CO adsorption on Pt films with low Pt coverage (< 0.3 ML Pt). This trend can be explained by the considerably weaker D<sub>ad</sub> binding energy on Pt islands compared to the Ru surface) which leads to a decreasing initial D<sub>ad</sub> coverage and facilitates the displacement of D<sub>ad</sub> by post-adsorbed CO. For the same reason the influence of pre-adsorbed CO on D<sub>2</sub> adsorption considerably increases with increasing Pt coverage, since D<sub>ad</sub> is displaced to the less favorable Pt sites.

O 45.2 Wed 10:45 H42

**Bimetallic PtAg/Pt(111) surfaces and their interaction with CO** — •THOMAS DIEMANT, JOACHIM BANSMANN, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

The growth of Ag films on a Pt(111) substrate at room temperature and the formation of PtAg/Pt(111) surface alloys by annealing to higher temperature (up to 900 K) was studied by a combination of X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) measurements. XPS measurements indicate a modification of the electronic properties of both components in the bimetallic surface layer; most prominently the binding energy of the Ag peaks shifts compared to pure Ag.

In the next step, the interaction of CO with structurally well-defined PtAg/Pt(111) surface alloys was studied by TPD and high resolution electron energy loss spectroscopy (HREELS). These alloys were formed by annealing to 900 K; their structural properties had already been clarified before by scanning tunneling microscopy (STM) measurements in our institute. Both on the low as well as on the high temperature side of the platinum related CO TPD peak additional features arise after alloy formation. Furthermore, a peak related to CO adsorption on Ag sites is detected at 150 K in the CO TPD spectra.

O 45.3 Wed 11:00 H42

**DFT-studies of interfacial processes in fluoride ion batteries** — •KATRIN FORSTER-TONIGOLD<sup>1</sup> and AXEL GROSS<sup>1,2</sup> — <sup>1</sup>Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, 89069 Ulm, Germany — <sup>2</sup>Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany

Fluoride ion batteries (FIBs) are highly attractive systems for electrochemical energy storage as they offer substantially larger theoretical energy densities compared to conventional lithium ion batteries. The basic electrochemical reaction underlying FIBs is the conversion reaction:  $mM + nM'F_m \rightleftharpoons mMFn + nM'$  with fluoride anions acting as charge transfer ions [1].

The performance of FIBs crucially depends on the fluoride ion transport through the electrolyte. As a possible route towards fluoride ion conducting, liquid electrolytes might be the use of shuttle molecules, that collect fluoride ions from the metal fluoride and release them at the metal. Therefore, molecules with a well-balanced fluoride binding energy are needed. Especially the first step of the conversion reaction, i.e. the adsorption and desorption of the shuttle molecule at the metal and metal fluoride substrate, could be crucial. To provide an insight into these initial processes occurring at the electrode-electrolyte interface of FIBs, we employ DFT calculations. We aim to find trends

among different main group elements used in possible candidates for shuttle molecules. Besides, we try to understand the impact of various rest groups on the binding properties.

[1] M. A. Reddy and M. Fichtner, *J. Mater. Chem.* **21**, 17059 (2011).

O 45.4 Wed 11:15 H42

**Kinetics of Single D<sub>2</sub>O Molecules and Dimers on Cu(111)** — •CORD BERTRAM and KARINA MÖRGENSTERN — Lehrstuhl für Physikalische Chemie 1, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum

Water is well-known to form hydrogen-bonded networks on metal surfaces with a high structure variety, even at low temperature. Previous work on Cu(111) explored this variety by observing different amorphous and crystalline phases (Mehlhorn et al., *Phys. Rev. Lett.* **99** (2007), 246101). For further understanding of these networks, it is useful to analyse the kinetics of single molecules and the formation of nanoclusters. In this talk, we will discuss the diffusion of single D<sub>2</sub>O molecules and dimers on Cu(111) measured by low temperature time-lapsed scanning tunneling microscopy. We deposit D<sub>2</sub>O onto the surface below a temperature of 15 K with fluxes below  $1.54 \cdot 10^{-4} \frac{\text{molecules}}{\text{nm}^2 \text{s}}$ . The diffusion of monomers, the formation of dimers, and the subsequent diffusion of dimers is recorded between 19 K and 29 K. The height of the diffusion barrier and the prefactors are determined via the Arrhenius law. Surprisingly both species show similarities to the diffusion via tunneling of hydrogen. The results will be compared to previous works on e.g. Pd(111), Pt(111), and Ag(111) (Mitsui et al., *Science* **297** (2002) 1850; Motobayashi et al., *Surf. Sci.* **602** (2008) 3136).

O 45.5 Wed 11:30 H42

**Study of Alloyed Gold Surfaces by Photon Emission STM** — BIRSEN KESİK, ELIF PEKSU, SELMAN TAMER, DILEK YILDIZ, and •OĞUZHAN GÜRLÜ — Istanbul Technical University, Department of Physics, Maslak, 34469, Istanbul, Turkey

Photon emission from surfaces, simultaneously with the surface topography measurements with Scanning Tunneling Microscopy was observed on various surface systems. Several types of photon detection mechanisms were developed. Regardless of the surfaces under consideration or the set up used, it is well known that the photon emission spectrum and intensity heavily depends on both the tip material and the tip geometry. We modified a commercial STM and implemented our photon collection setup; also a modified tip preparation procedure was employed. Using this setup we studied the photons emitted from different gold surfaces with various surface morphologies. Contrary to common knowledge, the intensity of the photon emission from similar regions of a rough Au surface was observed to be different. The local surface morphology was correlated to the photon emission intensity, as well as to the spectrum of the emitted photons. Here we suggest the possible dependence of the intensity and spectra of the emitted photons on the local alloying of the gold surfaces (Supported by TUBITAK 109T687).

O 45.6 Wed 11:45 H42

**Surface structure of ultrathin Fe films on Ag(001) post-deposition annealed in O<sub>2</sub> atmosphere** — •DANIEL BRUNS, STEFFEN JENTSCH, SÖREN LINDEMANN, and JOACHIM WOLLSCHLÄGER — Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49076 Osnabrück

Iron oxides are used in different applications as spintronics or heterogeneous catalysis. In this work, ultrathin Fe films grown at room temperature on Ag(001) were post-deposition annealed in  $10^{-5}$  mbar O<sub>2</sub> atmosphere at 300°C for 50 minutes. Since the surface has a strong influence on the properties of ultrathin films, the surface structure was investigated by LOW ENERGY ELECTRON DIFFRACTION (LEED) and SCANNING TUNNELING MICROSCOPY (STM). Submonolayer Fe films wet the Ag(001) substrate due to annealing in oxygen forming at least partial FeO, as concluded from LEED. Straight trenches aligned either in Ag[110] or Ag[1 $\bar{1}$ 0] direction separate different FeO domains. On the other hand, with increasing Fe coverage the films show a three dimensional behavior upon annealing forming several exposed layers. In this case, LEED suggests two hexagonal structures as well as two low ordered rectangular structures rotated by 90° against each other,

respectively. These structures were found to be located on different exposed layers at the surface via STM. The topmost layer of the oxidized films revealed a poorly ordered ( $2 \times 3$ ) superstructure, while the hexagonal surface structure was only found on deeper exposed layers. We created models to describe the observed surface structures suggesting partial formation of FeO as well as  $\text{Fe}_3\text{O}_{4-\delta}$  at the surface.

O 45.7 Wed 12:00 H42

**Kinetic vs. thermodynamic limitations of the formation of PtCu submonolayer alloys on Ru(0001) single crystals.** —

•ALBERT K. ENGSTFELD, CHRISTOPH K. JUNG, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Core shell particles consisting of a metal A rich shell and a bi- or multialloy core, show a catalytic activity which may strongly differ from that of the pure metal particles. An interesting example are Pt enclosed alloy particles containing Cu, Co and Pt, which were found to be much more active towards  $\text{O}_2$  electroreduction than pure Pt. In this work we focus on the formation of Pt and Cu submonolayer alloys on Ru(0001), which represents the core for a core shell model catalyst. The surfaces have been investigated under ultra high vacuum conditions, using scanning tunneling microscopy (STM), to reveal the surface morphology as well as the atom distribution within the surface alloy. The limitation in the preparation of the surface alloy is the temperature, since at 750 K Pt starts intermixing with the Ru(0001) substrate. Just below this temperature, the intermixing of Cu and Pt on the surface is however kinetically hindered, which leads to coexistent mixed and unmixed 2D phases of both metals. Optimizing the experimental conditions (e.g. evaporation sequence, temperature ...), we are able to prepare short-range ordered monolayer surface alloys covering the entire surface over the full concentration regime (0-100%). The distribution of surface atoms in the monolayer surface alloys will be discussed based on the Warren Cowley short-range order parameters.

O 45.8 Wed 12:15 H42

**The study of Pb self-diffusion from first principles** —

•XIAOHANG LIN and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

With the single-atom transistor [1], the first actively switchable electronic device on the atomic scale was demonstrated. By the controlled relocation of one individual atom within an electrochemically fabricated metallic quantum point contact, an electrical current could be

switched on and off. Changes in the atomic-scale structure within the contact area controlled by the electrode potential in an electrochemical set-up result in conductance changes of the atomic-scale contact.

Here, we study atomic-scale relocation processes in contacts from at Pb electrodes with periodic density functional theory (DFT) calculations. It is known that diffusion processes play a crucial role during the atomic-scale deposition and structure formation. For this reason, as a first step barriers for self-diffusion processes have been calculated using automatic transition state search routines. In order to address structured surfaces more realistically, an emphasis has been put on processes near step edges. It turned out that at such edges, two-particle exchange processes are very important for the diffusion in contrast to the “naive” direct single-particle hopping mechanism.

[1] F.-Q. Xie, L. Nittler, Ch. Obermair, Th. Schimmel, Phys. Rev. Lett. **93**, 128303 (2004).

O 45.9 Wed 12:30 H42

**Mechanism of anisotropic crystal growth of gold nanorods** —

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Anisotropic noble metal nanostructures are of general interest due to their optical and physical properties. Specifically, Au nanorods can be grown by immersing nanoparticles in supersaturated solution and addition of specific surfactants, which induce a strong anisotropy in the growth of (100) and (111) facets. While it is known that aspect ratio and quality of the final nanorods are affected by the choice of surfactant, a qualitative understanding of surface-surfactant interaction and growth mechanism are lacking.

In the present work we address these points by a combination of density functional theory (DFT) calculations and kinetic Monte Carlo (kMC) simulations. The most common surfactant is cetyl trimethyl ammonium bromide (CTAB), which interacts with the surface via a Br atom. This allows us to focus our attention on the behavior of Br on Au surfaces. We systematically determined adsorption and migration energies for both Br and Au adatoms and small clusters on flat (100) and (111) surfaces as well as surface steps. We find a strong asymmetry in the migration of both species between (100) and (111) surfaces. More importantly we identified a pathway for growth of (111) facets that does not require desorption of Br (or CTAB molecules). Using the DFT data we then parametrized a kMC model to study the dynamics of the growth process taking into account surface coverage and temperature.