

O 68: Metal Substrates: Solid-Liquid Interfaces

Time: Thursday 13:15–14:45

Location: MA 043

O 68.1 Thu 13:15 MA 043

In situ STM characterisation of electrochemically prepared ultrathin copper sulfide films on Au(100) — ●CHRISTIAN SCHLAUP, PETER BROEKMANN, and KLAUS WANDELT — Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn

An ultrathin copper sulfide compound film was prepared on a Au(100) electrode using the technique of electrochemical atomic layer epitaxy (ECALE). In a first step, a copper monolayer was deposited on a Au(100) electrode by Cu underpotential deposition from a sulfuric acid solution. By subsequential electrolyte exchanges this copper film was subjected to a sulfide containing sodium hydroxide solution. In situ STM measurements revealed a close packed commensurate $c(2 \times 2)$ adlayer structure indicating a sulfur layer with a significantly increased coverage ($\Theta_S = 0.5$ ML) with respect to a sulfur adlayer on a blank Au(100) surface at the same potential. The relative copper to sulfur ratio of 2:1 within the assumed Cu-S bilayer structure supports an interpretation of this structure as a Cu_2S species, which was already supposed for similar Cu-S compound films on a Au(111) electrode. These compound films are rather stable in a wide potential range, neither sulfur desorption at lower potentials nor a structural transition pointing to the formation of CuS at higher potentials can be observed. Instead the film dissolves completely at anodic potentials, probably due to the formation of soluble copper-thio-oxo species.

O 68.2 Thu 13:30 MA 043

Electrochemical oxygen reduction at pseudomorphic Pt thin films on Ru(0001) — ●OTÁVIO B. ALVES, HARRY E. HOSTER, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

We report on the electrochemical properties of model surfaces consisting of 1-5 pseudomorphic Pt layers on Ru(0001), which are fabricated by vapor deposition under ultrahigh vacuum conditions. Due to electronic ligand and strain effects, the interaction of these surfaces with H_{ad} , OH_{ad} , and O_{ad} is weakened compared to Pt(111). According to theoretical predictions,[1,2] this can lead to a higher activity for the electrochemical reduction of oxygen, similar to the behavior previously reported for Pt_3Ni model electrodes.[3] By changing the layer thickness, it is possible to tune the adsorption properties within a certain range.[4] We investigated the oxygen reduction current as a function of potential under well-defined mass transport conditions for all model surfaces in an electrochemical flow cell coupled to a UHV system. The electrochemical behaviour of the pseudomorphic Pt films was found to be clearly different from that of Pt(111). The results are discussed in comparison to the behavior of other model electrodes and to theoretical predictions.

[1] M. Mavrikakis *et al.*, Phys. Rev. Lett. 1998, 81, 2819.[2] J. R. Kitchin *et al.*, J. Chem. Phys. 2004, 120, 10240.[3] V. R. Stamenkovic *et al.*, Science 2007, 315, 493.[4] A. Schlapka *et al.*, Phys. Rev. Lett. 2003, 91, 016101.

O 68.3 Thu 13:45 MA 043

Additives for the copper damascene process - in-situ EC-STM and XPS studies — ●KNUD GENTZ¹, SASCHA HÜMMANN¹, STEFAN BREUER¹, RALF HUNGER², KLAUS WANDELT¹, and PETER BROEKMANN¹ — ¹Institute of Physical and Theoretical Chemistry, Bonn University — ²Institute of Material Research, Technical University of Darmstadt

Copper has become a focus of research activities over the last two decades due to its use as interconnect material in microchip design. Presently the dimensions of circuit layout is dependent on the wavelength of the applied light. To continue the ongoing process of miniaturization, cationic organic molecules have been studied as additives in the copper damascene process. In the present investigation the influence of various halides on structure and reactivity of a Diphenylviologen (DPV) layer adsorbed on a Cu(100) surface have been studied by in-situ electrochemical STM and high-resolution XPS, conducted at the synchrotron source BESSY2.

N,N' -diphenyl-4,4'-bipyridinium (Diphenylviologen, DPV) spontaneously adsorbs on a halide-modified Cu(100)-surface, forming a striped pattern, which has been characterized by in-situ Scanning Tunneling Microscopy. Cyclic Voltammetry indicates that the build-

ing block is the radical cation of the viologen. These results have been confirmed by ex-situ high resolution XPS after transfer into UHV in a process allowing conservation of the surface redox-states upon emersion. A careful analysis of the N1s and C1s core level shifts then allows the determination of the redox-state of the adsorbed viologens.

O 68.4 Thu 14:00 MA 043

Electrochemical Faceting of Ir(210) — PAYAM KAGHAZCHI¹, KHALED A. SOLIMAN², FELICE C. SIMEONE², LUDWIG A. KIBLER², and ●TIMO JACOB^{1,2} — ¹Fritz-Haber-Institut der MPG, D-14195 Berlin — ²Institut für Elektrochemie, Universität Ulm, D-89081 Ulm

Highly-disperse nanoparticles are often used to catalyze (electro)-chemical reactions. Unfortunately not all nanoparticles have the same size and shape, but rather show a relatively large distribution, limiting our understanding of the ongoing processes.

Focusing on Ir(210), which experimentally was found to form pyramidal-like nano-facets in presence of oxygen [1], we used density functional theory and the extended *ab initio* atomistic thermodynamics approach [2] to study the adsorption of oxygen on these surfaces being involved in the nanostructures on Ir(210). Constructing the corresponding (p,T,ϕ) -phase diagram for Ir(210) in contact with an aqueous electrolyte, we found that the same nano-facets should be stable under electrochemical conditions. Recently we were able to confirm this theoretical prediction by cyclic voltammetry and *in-situ* scanning tunneling microscopy. The presence of nanofacets for Ir(210) gives rise to a characteristic current-peak in the hydrogen adsorption region for sulfuric acid solution. Regarding the electrocatalytic behavior of the nano-facets we found a considerably lower activity compared to planar Ir(210).

[1] I. Ermanoski, C. Kim, S. P. Kelty, T. E. Madey, Surf. Sci. 2005, 596, 89.

[2] T. Jacob, J. Electroanal. Chem., **607**, 158–166 (2007).

O 68.5 Thu 14:15 MA 043

A new approach to obtain electrochemical E/pH diagrams derived from the viewpoint of semiconductor defects — ●MIRA TODOROVA and JÖRG NEUGEBAUER — Max-Planck Institut für Eisenforschung, Düsseldorf

We present a novel approach for obtaining Pourbaix diagrams, which depict possible thermodynamically stable phases of an aqueous electrochemical system under given environmental conditions as a function of potential and pH. Such diagrams play a crucial role in corrosion science and various areas of chemistry.

Being similar to the approach used in defect chemistry [1] the new method is safely based on the formation energy of ions in the host matrix. Within the new approach the electrode potential and the pH-scale can be easily understood. We obtain an astonishingly good agreement with the standard electrochemical potential series. The construction of E/pH diagrams for any given environmental conditions and without *a priori* assumptions about ion concentrations is possible and will be demonstrated by the example of zinc and iron.

[1] C.G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).

O 68.6 Thu 14:30 MA 043

A Quantum Chemistry Roadmap Towards Highly Accurate Adsorption Energies at Ionic Surfaces — ●BO LI¹, ANGELOS MICHAELIDES^{1,2}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Materials Simulation Laboratory, London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, U.K.

A roadmap is established to compute adsorption energies of molecules at ionic surfaces with an accuracy approaching chemical accuracy (a precision of 1 kcal/mol or ~ 43 meV). The approach relies on established quantum chemistry methodologies and involves a separation of the total adsorption energy into contributions from Hartree-Fock and electron correlation, the use of embedded cluster models of the substrate, and extrapolations to the complete basis set limit. Application of the procedure to the example of water on salt, with electron correlation treated at the CCSD(T) level, yields an adsorption energy for a water monomer on NaCl(001) of 480 ± 20 meV.