

## O 2: Metal substrates: Solid-liquid interfaces

Time: Monday 11:15–13:00

Location: H31

O 2.1 Mon 11:15 H31

**Self-organized Porphyrin monolayers on iodine-modified noble metal surfaces** — ●MICHAEL SCHNEIDER, CHRISTIAN SCHLAUP, and KLAUS WANDEL — Inst. f. Phys. u. Theo. Chem., Universität Bonn, Wegelerstr. 12 D-53115, Bonn, Germany

In the field of template chemistry, new and interesting phenomena can be discovered at gold /electrolyte interfaces in the presence of anions and supramolecules as function of electrode potentials. The spontaneous self-assembly of organic molecules is considered a promising bottom-up technique in nanotechnology to create surface patterns and electronic devices. Porphyrins are important organic compounds in the fields of biology and technology. They open a series of potential applications in cancer therapy, or as catalysts and sensors. Halide-modified Au(111)-surfaces are desirable substrates due to their long range order. Iodide-modified Au(111)-surfaces show electrocompression and phase transitions dependent on the electrode potential, as shown in previous works. Our studies with STM and cyclic voltammetry not only reproduce previous works about Tetra (N-methyl-4-pyridyl)-porphyrin molecules (TMPyP) on iodide-modified Au(111)-surfaces, but provide an even more precise understanding. Namely, it is found that the TMPyP layer exhibits a long-range periodic superstructure beyond the molecular arrangement. This research complements one of our previous studies regarding adsorption of the same molecule on halide-modified copper-surfaces, allowing comparisons between systems with the same molecules but different substrates.

O 2.2 Mon 11:30 H31

**Effect of additives on Cu electrodeposition: an in-situ STM study** — ●YURIY YANSON, GEERT WIJTS, FRED SCHENKEL, and MARCEL J. ROST — Kamerlingh Onnes Laboratory, Leiden University, The Netherlands

Small amounts of specific substances, known as additives, can dramatically influence the growth of electrodeposited thin films. Although additives are often applied in the industry not only to change the film properties but also to enable a specific deposition, the microscopic (atomic) understanding of the additive influence on the growth is usually still lacking. We present an in-situ STM studies of Cu electrodeposition on the Au(111) substrate, in which we clearly show the atomic scale effect of industrially relevant additives on the growth. In particular, we discuss the influence of the accelerator bis-(3-sodiumsulfopropyl) disulfide (SPS) and the inhibitor polyethylene glycol (PEG) on Cu plating. We expect that our newly developed video-rate EC-STM will provide access to even shorter time scales enabling the study of growth dynamics.

O 2.3 Mon 11:45 H31

**Pb adsorption on Cu(100) studied in situ by electrochemical video STM** — ●OTAVIO ALVES<sup>1</sup>, HISAYOSHI MATSUSHIMA<sup>2</sup>, HARRY E. HOSTER<sup>1</sup>, R. JÜRGEN BEHM<sup>1</sup>, and OLAF MAGNUSSEN<sup>2</sup> — <sup>1</sup>Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — <sup>2</sup>Institute of Experimental and Applied Physics, Christian-Albrechts University, D-24118 Kiel, Germany

As a prototype for a lattice-mismatched system, the growth of Pb on Cu(100) was subject of various studies under ultrahigh vacuum conditions (UHV) [1-4]. It has been established that Pb grows on Cu(100) in a Stranski-Krastanov mode, with three well-defined ordered structures appearing in the submonolayer regime up to 0.6 monolayers. In this contribution, we will report on the growth of Pb on Cu(100) at the solid/liquid interface, which we observed in situ by electrochemical video scanning tunnelling microscopy (STM). At low Pb surface concentration, spontaneous formation of a surface alloy takes place on a reconstructed Cu(100). Increasing the Pb surface content leads to dealloying, finally resulting in a saturated Pb overlayer. Our in situ STM atomic-scale pictures are comparable to those obtained in UHV. Atomic Pb diffusion, dynamic structural fluctuation and coexistence of different Pb phases will be discussed.

[1] J. Henrion et al., *Surf. Sci.* 29, **1972**, 20.

[2] C. Nagl et al., *Surf. Sci.* 331, **1995**, 831.

[3] Y. Gauthier et al., *Surf. Sci.* 345, **1996**, 53.

[4] S. Robert et al., *Surf. Sci.* 350, **1996**, 136.

O 2.4 Mon 12:00 H31

**Formation of Ultrathin Copper Sulfide Semiconductor Films under Electrochemical Conditions** — ●CHRISTIAN SCHLAUP and KLAUS WANDEL — Institute for Physical and Theoretical Chemistry, Wegelerstr. 12, D-53115 Bonn, Germany

Ultrathin copper sulfide semiconductor films were prepared in an electrochemical environment using subsequential steps of copper deposition on an inert Au(100) electrode surface and reaction with bisulfide anions. The thickness of thus prepared copper sulfide films depends only on the initially deposited amount of copper and can be easily tuned within a range of a single monolayer to several layers. Structural characterization using in situ STM reveals commensurate  $c(2 \times 2)$  structure for an only one monolayer thick copper sulfide film, which remains stable over a wide potential range. In addition, these films could also be stabilized in a bisulfide free solution resulting in an even higher stability against anodic potentials. Preparing thicker copper sulfide films yields a mixed phase regime consisting of a bulk-like copper sulfide phase with a granular appearance and a metastable bilayer phase which can be completely converted into the bulky phase by initial oxidation.

O 2.5 Mon 12:15 H31

**About the Orientation of Viologen Monolayers on a Cu [1 0 0] Electrode Surface** — ●MELANIE RÖEFZAAD<sup>1</sup>, VLAD ZAMLYNNY<sup>2</sup>, and KLAUS WANDEL<sup>1</sup> — <sup>1</sup>Institute for Physical and Theoretical Chemistry, University of Bonn — <sup>2</sup>Chemistry Department, Acadia University, Canada

Detailed investigations of the metal/electrolyte interface in presence of the redox active 4,4'-Bipyridin with different substituents at 1,1'-position have been done combining Infrared Reflection Absorption Spectroscopy (IRRAS) and Cyclic Voltammetry (CV). To reveal indications about the orientation of certain parts of the molecule in the adsorbed monolayer and their changes, the Polarization Modulated IRRAS was applied.[1,2] Calculations showed that in general all viologen species adsorb with the longer molecular axis parallel to the surface. In contrast the orientation of the ring planes of the bipyridine moiety changes after the reduction process. For Dibenzylviologen (DBV) the angles with respect to the surface normal have been calculated to  $\sim 20^\circ$  for the dication and to  $\sim 70^\circ$  for the radical-cation. In the same way orientations of alkyl substituents were investigated. For example Heptylviologen shows a straightening up of the long alkyl chains, from  $50^\circ$  to  $24^\circ$  with respect to the surface normal, while lowering the potential. This orientation change is mainly caused by decreasing the area per molecule (ApM) with a closer packing of the stacking rows.

[1] H. Seki, K. Kunitatsu, W. G. Golden, *Appl. Spectroscopy* 1985, 39, 437.

[2] A. N. Parikh, D. L. Allara, *J. Chem. Phys.* 1992, 96, 927.

O 2.6 Mon 12:30 H31

**X-ray reflectivity studies at the mercury/electrolyte interface** — ●ANNIKA ELSSEN<sup>1</sup>, BRIDGET M. MURPHY<sup>1</sup>, BEN M. OCKO<sup>2</sup>, LILACH TAMAM<sup>3</sup>, MOSHE DEUTSCH<sup>3</sup>, IVAN KUZMENKO<sup>4</sup>, and OLAF M. MAGNUSSEN<sup>1</sup> — <sup>1</sup>Institut für Experimentelle und Angewandte Physik, CAU, D-24105 Kiel, Germany — <sup>2</sup>Department of Physics, BNL, Upton, New York 11973, USA — <sup>3</sup>Department of Physics, Bar-Ilan University, Ramat Gan 52900, Israel — <sup>4</sup>CMC-CAT, APS, ANL, Argonne, Illinois 60439, USA

The interface between the liquid mercury electrode and an electrolyte solution is one of the most extensively studied electrochemical systems. It was fundamental for verifying traditional and modern theories of the electrochemical double layer. Although the metal contributes significant to the double layer capacity, with its interface structure playing an important role, up to now there is almost no knowledge about this structure. Here we present the first X-ray reflectivity studies at the liquid mercury electrode in electrolyte solution (0.01M NaF), allowing to clarify the interface structure. The experiments exhibited atomic layering of the mercury perpendicular to the surface similar to that found for the mercury vapour interface. We found a significant influence on the width of the interface electron density profile which can be referred to two effects: first of all the potential dependent change in the surface tension causes a change in the capillary wave induced interface roughness. Secondly another potential controlled effect was found due to the intrinsic change in the electron density distribution

because of interface polarisation.

O 2.7 Mon 12:45 H31

**Simulating cyclic voltammograms of bimetallic model surfaces** — •HARRY E. HOSTER, OTAVIO B. ALVES, ALBERT K. ENGSTFELD, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Cyclic voltammograms recorded at bimetallic surfaces reflect the superposition of current contributions from adsorption, desorption, and reaction processes at surface regions with laterally varying chem-

ical properties. As will be demonstrated for some selected well-defined single crystalline model systems including Pt films on Ru(0001) and PtAu/Pt(111) surface alloys, voltammetric features at bimetallic surfaces can be simulated using the corresponding features for the monometallic surfaces in combination with information on the adsorption properties and abundance of the dominating sites at the bimetallic surfaces. Trends in the local adsorption properties can be predicted based on density functional theory calculations, whereas the necessary information about the local vertical and lateral metal distribution is obtained from scanning tunnelling microscopy imaging.