

O 32.11 Tue 15:30 MA 042

Structural arrangement of room temperature ionic liquids at a hard wall — ●HEIKO SCHRÖDER, MARKUS MEZGER, SEBASTIAN SCHRAMM, HARALD REICHERT, JOHN OKASINSKI, and HELMUT DOSCH — Max-Planck-Institut für Metallforschung, Stuttgart

Interfacial phenomena in physical, chemical, and biological systems are of increasing relevance in many of today's technological applications. In order to access solid-liquid interfaces and extract microscopic details of their local structure with high resolution, we have employed high energy x-ray microbeam reflectivity. Here, we discuss the analysis and interpretation of reflectivity data recorded at the interface between different room temperature ionic liquids (RTIL) and a hard wall (sapphire). Real space structures could be resolved with Å-resolution. Although crucial for the understanding of solvent properties, only little is known about the structural arrangement of anions and cations in RTILs at solid interfaces. We systematically examined different parameters altering the interfacial properties. By choosing different combinations of anions and cations, the ion-ion and ion-substrate interaction as well as the size ratio of the involved ions could be varied. By modifying the temperature, the ratio between entropy and interfacial energy can be tuned as well, favoring a disordered liquid or interfacial layering, respectively. This results in different structural arrangements at the molecular level.

O 32.12 Tue 15:45 MA 042

The Au(111) Electrolyte Interface: A DFT Investigation — SUDHA VENKATACHALAM¹, FELICE C. SIMEONE¹, DIETER M. KOLB¹, and ●TIMO JACOB^{1,2} — ¹Institut für Elektrochemie, Universität Ulm, D-89081 Ulm — ²Fritz-Haber-Institut der MPG, D-14195 Berlin

Density functional theory calculations have been performed to derive a detailed model of the electric double layer for Au(111) in contact with an aqueous H₂SO₄ electrolyte. At potentials of $E \geq +0.8$ V vs. SCE various surface sensitive techniques found evidence for a ($\sqrt{3} \times \sqrt{7}$)R19.1° (bi)sulfate structure, but the nature of coadsorbates remains still unclear. Focusing on a sulfate adlayer, the coadsorption of H₃O⁺ and/or H₂O has been studied [1]. The calculated binding energies show that the coadsorption of a single H₃O⁺ per sulfate (stabilizing the adlayer by hydrogen bonds) is the most stable configuration. In addition, the charge density distribution within the adlayer well agrees with effective barrier heights deduced from recent distance tunnelling spectroscopy measurements [2].

Afterwards we studied the interfacial structure that forms at negative electrode potentials and found that water arranges near the electrode in an ice-like hexagonal structure with hydronium ions being located in the second water layer and non-specifically adsorbed. Again the calculated charge density distribution shows a perfect correspondence to distance tunnelling spectroscopy measurements.

[1] S. Venkatchalam, T. Jacob, *Z. Phys. Chem.*, **221**, 1393 (2007).

[2] S. Venkatchalam *et al.*, *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200702868.

O 32.13 Tue 16:00 MA 042

Surface Stress Variation as a Function of Charge for the Metal at Metal - Electrolyte Interface — ●MAXIM SMETANIN¹, RAGHAVAN N VISWANATH¹, DOMINIK KRAMER¹, and JOERG WEISSMUELLER^{1,2} — ¹Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany — ²Universität des Saarlandes, Saarbruecken, Germany

During the last decade, there has been considerable progress in measuring and understanding the capillary forces on metal surfaces. The present work revisits the question, what is the magnitude of the surface stress charge coefficient (SSCC) for the gold in an electrolyte near the potential of zero charge, in particular in respect to comparison to

numerical computation. We report in-situ measurements of $f(q)$ for planar gold electrodes in weakly adsorbing electrolytes, using a cantilever bending technique with optical detection. We used 40 nm thick, (111)-textured gold films on 100 μ m thick (100)-oriented silicon wafers in aqueous NaF and HClO₄. The films were characterized in respect to roughness (using a scanning probe microscopy) and to contamination (using Auger microscopy). Their pzc value was determined in 7 mM NaF using the minimum of the differential capacitance, it is ca. 0.20 V vs. SCE. The wafer bending results testify to an essentially linear $f(q)$ near the pzc and electrode charging occurs mainly within the diffuse double layer at minimum influence of specific ions adsorption. SSCC was found to be of the order of -1.95 V for 7 mM NaF and -2.02 V for 10 mM HClO₄.

O 32.14 Tue 16:15 MA 042

STM of superstructures and surface transformations on Pt(111) in a sulfuric acid electrolyte — ●BJÖRN BRAUNSCHWEIG and WINFRIED DAUM — Institut für Physik und Physikalische Technologien, TU-Clausthal, Leibnizstrasse 4, D-38678 Clausthal-Zellerfeld

Imaging of weakly chemisorbed species on Pt surfaces with the STM in electrochemical environments and with molecular resolution is a challenge to the experimenter as these electrode surfaces are very susceptible to contaminations at a level well below the sensitivity of cyclic voltammetry. We have investigated the surface structure of Pt(111) in a 0.1 M H₂SO₄ electrolyte in the potential range of sulfate adsorption. In agreement with a previous study [1] we observe a disorder-order transitions at a potential of 0.5 V versus the reversible hydrogen electrode (RHE). For potentials between 0.5 and 0.8 V RHE we identified two distinctly different sulfate superstructures: the well-known ($\sqrt{3} \times \sqrt{7}$)R19.1° superstructure and a new (3x1) superstructure. We were able to simultaneously image the sulfate and the Pt surface lattice and to determine the registry of the sulfate anions with the substrate. The structure in the unit cell of the (3x1) superstructure indicates the presence of an additional molecular component, possibly hydronium or water molecules. For potential sweeps to 0.8 V RHE and above the ordered sulfate overlayer changes instantaneously to a more disordered structure presumably due to adsorption of OH⁻ ions.

[1] A.M. Funtikov, U. Linke, U. Stimming and R. Vogel; *Surf.Sci.* **324**, L343 (1995) and *J. Electroanal. Chem.* **428**, 147 (1997)

O 32.15 Tue 16:30 MA 042

The quest for ZnO(11 $\bar{2}$ 0) surface states – an ARPES study — ●CHRISTIAN PETTENKOFER and STEFAN ANDRES — Hahn-Meitner-Institut, Glienicker Str. 100, D-14109 Berlin

We present angle resolved photoemission data from differently prepared ZnO(11 $\bar{2}$ 0) single crystals and epitaxially grown thin films. ZnO(11 $\bar{2}$ 0) single crystal surfaces were prepared by both cleaving in vacuum and sputtering-annealing cycles of pre-polished crystals. ZnO(11 $\bar{2}$ 0) thin films were grown heteroepitaxially on the r-face of sapphire by MOMBE using diethylzinc and water as precursor molecules. The ARUPS-spectra were recorded at the TGM7 beamline at BESSY-II synchrotron light facility in Berlin.

The band dispersion along k_{\parallel} and k_{\perp} is discussed in accordance with theoretical band structure calculations of the bulk electronic states within the GGA-DFT framework. An excellent agreement between the theoretically and experimentally determined band structure is achieved for the upper valence bands. Furthermore the surface electronic structure of both the epitaxially grown thin films and the single crystals coincide very well with each other.

It is shown, that despite the very different nature of the surface preparation methods no surface states could be observed. Therefore different effects such as hydrogen adsorption, surface defects and lattice relaxation will be discussed with regard to the specific surface preparation method.

O 33: Symposium: Frontiers of Surface Sensitive Electron Microscopy I (Invited Speakers: James Hannon, Raoul van Gastel, Thomas Schmidt)

Time: Tuesday 13:45–16:15

Location: MA 005

Invited Talk

O 33.1 Tue 13:45 MA 005

Dynamics at Strained Surfaces — ●JAMES B. HANNON — IBM T.J. Watson Research Center, Yorktown Heights, NY 10598, USA

It has long been recognized that surface stress influences surface mor-

phology and kinetics. For example, stress can drive the spontaneous formation of periodic patterns. Analysis of the equilibrium configuration of stress domains can be used to determine surface thermodynamic parameters [1]. However, in many (if not most) systems, reaching equi-