

O 60: Solid-Liquid Interfaces: Structure, Spectroscopy, Reactions and Electrochemistry

Time: Tuesday 18:30–20:30

Location: P2-OG2

O 60.1 Tue 18:30 P2-OG2

The spin-resolved electronic structure of Au(110) — ●KATHARINA T. RITTER, FABIAN SCHÖTTKE, and MARKUS DONATH — Physikalisches Institut, Westfälische Wilhelms-Universität Münster

Materials with strong spin-orbit coupling are known to exhibit Rashba-split electronic band structures. To understand the basic concepts, Au(111) is a widely used prototypical system for a spin-split surface state around the $\bar{\Gamma}$ point. As on Au(111), the surface state on Au(110) originates from the L-gap, but exists at the \bar{Y} point.

It is predicted that the Au(110) surface state around the \bar{Y} point shows a spin-dependent splitting in energy and momentum. Only the spin-integrated dispersion of the electronic states has been experimentally investigated so far. Here, we present spin-resolved data using spin- and angle-resolved (inverse) photoemission for the $\bar{\Gamma}\bar{Y}$ direction to reveal the spin texture of the Au(110) surface state.

O 60.2 Tue 18:30 P2-OG2

Overcharging and charge reversal of surface charge in high electrolyte concentrations — ●CHRISTINE KLINGER, MARKUS VALTNER, and CHRISTIAN WEBER — Institut für physikalische Chemie, Fakultät für Chemie und Physik, Technische Universität Bergakademie, Freiberg, Deutschland

The structure of water and ions in the electric double layer influences adhesion and reactivity at solid/liquid interfaces. Previous investigation showed the suitability of atomic force microscopy (AFM) for the investigation of electric double layer structures, based on molecularly resolved force spectroscopy and imaging with atomic resolution. Using the AFM, we quantitatively measure the effect of overcharging and charge reversal of surface charge on mica due to the condensation of Cs-ions into the mica lattice. We examine the surface charge at mica applying different concentrations of aqueous CsCl solution with ionic strengths ranging from 10 mM to 100 mM. Thereby we can show that mica surfaces overcharging leading to a charge reversal in high electrolyte concentrations. In detail, our results provide an insight into the interaction forces and electric double layer structures depending on different environmental conditions.

O 60.3 Tue 18:30 P2-OG2

How accurate is the PBE functional for describing the properties of liquid sulfuric acid in ab-initio molecular dynamics simulations? — ●FLORIAN WULLSCHLÄGER, STEFFEN SEILER, and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

The structural properties of liquid sulfuric acid were investigated using the PBE functional in Car-Parrinello molecular dynamics (CPMD) simulations. The temperature and concentration dependency of the degree of H₂SO₄ dissociation was determined to gain insights into the accuracy of this common generalized-gradient functional in reproducing experimental data derived from Raman spectroscopy [1,2]. Furthermore, the structural features of the liquid were characterized by calculation of pair distribution functions and diffusion coefficients. Overall, we observed an overestimation of the degree of dissociation at low sulfuric acid concentrations, whereas in the high concentration limit the results of the PBE calculations are in good agreement with the experimental data.

[1] C.E. Lund Myhre, et al., *J. Phys. Chem. A* **107**, 1979 (2003).

[2] D.A. Knopf, et al., *J. Phys. Chem. A* **107**, 4322 (2003).

O 60.4 Tue 18:30 P2-OG2

Tuning oxygen reduction through interface engineering — ●PATRICK ALEXA¹, DORIS GRUMELLI¹, DIANA HÖTGER¹, SVETLANA KLAYATSKAYA², MARIO RUBEN², RICO GUTZLER¹, and KLAUS KERN^{1,3} — ¹) Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany — ²Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany — ³Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Electrocatalytic reactions, especially the oxygen reduction reaction (ORR) in alkaline media, are widely examined. They are of interest for the development of efficient fuel cells and metal-air batteries. Functionally designed catalysts at interfaces are crucial for the improvement of such reactions. The catalytic reactive sites can be metal centers (e.g. Co) incorporated within organic molecules, e.g. phthalocyanines (Pcs).

Here, we study the effect of side groups in Co-phthalocyanines (CoPcs) deposited on Au(111). Deposition of the CoPcs was followed by STM and XPS prior to oxygen reduction in 0.1M NaOH. By increasing the distance between Co atom and Au(111) surface through Pc functionalization with triisopropyl protection groups, the ORR activity is significantly diminished. Thus, a small distance between gold electrode and metal active site is essential for efficient ORR. The results highlight the importance of chemical tailoring of the catalyst interface for the rational design of efficient catalysts.

O 60.5 Tue 18:30 P2-OG2

First-Principles Studies of the Structural Properties of Nickel (Oxy)hydroxide as Oxygen Evolution Reaction Electrocatalysts — ●MOHAMMAD JAVAD ESLAMIBIDGOLI¹, MICHAEL H. EIKERLING¹, and AXEL GROSS² — ¹Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, V5A 1S6, BC, Canada — ²Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Nickel oxide (NiO_x)-based electrocatalysts are among the most promising materials for oxygen/hydrogen evolution reactions in alkaline conditions. In the late 1960s, X-ray diffraction studies revealed four main phases for Ni (oxy)hydroxide electrodes [1]: It involves two phases of nickel hydroxide, α - and β -Ni(OH)₂, and two phases for the oxidized materials, β - and γ -NiOOH. In this contribution, we report first-principles calculations of bulk properties, surface configuration, electronic structure, charging effects and catalytic properties of various phases and surface terminations of Ni (oxy)hydroxide. Using a spin polarized DFT-D + U approach, we first focus on understanding the structure and orientational order of interfacial water on the (001) surfaces. This is followed by investigations of the mechanisms of the oxygen evolution reaction at the surface accounting for implicit and explicit solvent.

[1] H. Bode *et al.*, *Electrochim. Acta* **11**, 1079 (1966).

O 60.6 Tue 18:30 P2-OG2

Electrochemical etching of GaAs, InP and InSb after ion irradiation — ●ALRIK STEGMAIER, ULRICH VETTER, and HANS HOF-SÄSS — 2. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen

Microelectromechanical systems (MEMS) combine electrical and mechanical features on the micrometer scale and are used for an increasing number of applications, including energy harvesters, accelerometers and pressure sensors [1]. With Proton Beam writing (PBW) it is possible to produce these three dimensional MEMS structures by varying only the fluence of the proton irradiation on a III-V semiconductor sample, followed by electrochemical etching [2,3].

As such, the electrochemical etching of the sample is of large importance for producing high quality final structures. Here we extend the reported electrochemical models [4] to both InSb and the highly irradiated case, typically encountered during PBW. With this, we can show significant improvements of both the etching time and quality over our previous findings [5].

[1] V. Cimalla et al., *J. Phys. D: Appl. Phys.*, **40**(20), 6386, 2007

[2] J.A. van Kan et al., *Appl. Phys. Lett.*, **83**(8), 1629, 2003

[3] P. Mistry et al., *Nucl. Instr. Meth. Phys. Res. B*, **237**, 188, 2005

[4] P. Allongue et al., *J. Electroanal. Chem.*, **317**, 77-99, 1991

[5] M. Schulte-Borchers et al., *J. Micromech. Microeng.*, **22**, 025011, 2012

O 60.7 Tue 18:30 P2-OG2

In situ X-ray reflectivity studies of electrochemical Cu deposition on industrial Ru covered Si wafers — ●TIMO FUCHS, JONATHAN LAUFER, FINN REIKOWSKI, JOCHIM STETTNER, and OLAF MAGNUSSEN — Institut für Experimentelle und Angewandte Physik, Universität Kiel, Olshausenstr. 40, 24098 Kiel, Germany

Further decrease in size of Cu semiconductor interconnects is of special interest for the ongoing improvements in computing capacity. An interconnect consist of trenches and vias, which are typically coated with a Cu seed layer on top of a Ta/TaN diffusion barrier layer, that allows homoepitaxial growth of the electrochemically applied Cu. However, the fabrication of reliable devices on the base of Cu seed layers becomes increasingly difficult, when typical feature sizes are below 20 nanome-

ters and the homogeneity and roughness of the layers become crucial. Consequently, current efforts focus on the development of substrates for seedless Cu electroplating, using ultrathin Ru adhesion layers of high conductivity on a TaN diffusion barrier.

For the successful control of structural properties of the Cu layer, an in-deep understanding of early Cu growth processes on an atomic level, i.e. nucleation and coalescence of Cu islands on Ru, is indispensable. We are presenting first structural data, gained by *in situ* X-ray reflectivity measurements at a lab source of the bare Ru/TaN/SiO₂/Si substrate as well as *in operando* studies of the growing Cu layer. The results of this investigation will serve as a base for future grazing incidence small angle x-ray scattering (GISAXS) studies using synchrotron radiation.

O 60.8 Tue 18:30 P2-OG2

DFT study of the diffusion of S on a Br-precovered Cu(100) surface — •LUKAS DEUCHLER¹, ECKHARD PEHLKE¹, BJÖRN RAHN², and OLAF MAGNUSSEN² — ¹Institut für Theoretische Physik und Astrophysik, CAU Kiel, Germany — ²Institut für Experimentelle und Angewandte Physik, CAU Kiel, Germany.

Diffusion at electrochemical interfaces is a decisive factor for, e.g., metal electrodeposition using halide ion containing electrolytes [1]. The modification of surface diffusion energy barriers due to an applied sample potential has been ascribed to the interaction of the electric dipole moment of the system with the electric field at the surface [1,2]. The diffusion of Sulfuric tracer adatoms on Cu(100) surfaces has been investigated using video-STM. On the c(2x2)Cl/Cu(100) [3] and on the c(2x2)Br/Cu(100) surface, S-adatoms respond qualitatively differently to the applied sample potential, i.e. by a decrease or an increase of the hopping rate of the S adatom. Density-functional total-energy calculations with VASP [4] for the diffusion path suggest a possible explanation to this unexpected experimental observation. We note that our theoretical analysis is based on former theoretical research on S/c(2x2)Cl/Cu(100) diffusion by J. Stremme and A. Franke [5,6].

- [1] M. Ruge *et al.*, Phys. Rev. Lett. 112, 055503 (2014).
- [2] M. Giesen *et al.*, Surf. Sci. 595, 127 (2005).
- [3] T. Tansel, O. Magnussen, Phys. Rev. Lett. 96, 026101 (2006).
- [4] See //www.vasp.at.
- [5] J. Stremme, A. Franke, private communication.
- [6] J. Stremme, Diplomarbeit 2009, Universität Kiel.

O 60.9 Tue 18:30 P2-OG2

DFT-study of adsorption and diffusion including electric field effect for halogen atoms on the (001) surfaces of Cu, Ag, Au and an AgAu-alloy — •ALEXANDRA DAVILA, JAN THIEL, NICO REIMANN, and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, CAU Kiel, Germany

The growth dynamics in metal electrodeposition experiments depend on the electric potential of the sample electrode [1]. This has been ascribed to the dependence of the activation energy for surface diffusion of the metal adatoms on the sample potential. The composition of the electrolyte, especially halides, e.g. Cl⁻ ions, will also play an important role on the surface mobility [1]. Motivated by these results, we present a DFT based analysis [2,3] of activation energies under homogeneous electric field, which simulates the effect of the sample potential, for halogen (Cl, Br, I) adatoms on the (001) surfaces of Cu, Ag, and Au. The effect of electric field on the energy differences between hollow and bridge sites follow the linear relation derived by Giesen *et al.* [4], with deviations from linearity less than 10 meV for

electric field ranging from -0.6 V/Å to 0.6 V/Å. In case of I/Au(001) we observe a qualitative change of the PES as a function of electric field. Furthermore, we show changes of the topology of the PES for the case of an adsorbed Cl-atom on an AgAu alloy.

- [1] T. Tansel and O. Magnussen, Phys. Rev. Lett. 96 (2006).
- [2] //www.vasp.at.
- [3] P. Giannozzi *et al.*, J. Phys. Condens. Matter 21, 395502 (2009).
- [4] M. Giesen *et al.*, Surf. Sci. 595, 127 (2005).

O 60.10 Tue 18:30 P2-OG2

The Ag_xPt_{1-x}/Pt(111) surface alloy system as model catalyst for the ORR - Studies on the effect of structure and corrosion on the electrocatalytic activity — •STEPHAN BECKORD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, 89069 Ulm, Germany

Bimetallic surface alloys often exhibit catalytic and electrochemical properties which significantly differ from those of the respective pure metals. AgPt electrode surfaces were predicted to exceed the activity of Pt on the oxygen reduction reaction [1], where the latter is known to be the best mono metallic catalyst for this reaction. The increased activity of AgPt was also confirmed by experimental studies in our institute. In this work we present results on the effect of restructuring and corrosion of the model electrode surfaces under reaction conditions on the electrocatalytic characteristics and activity of well-defined Ag_xPt_{1-x}/Pt(111) surface alloys. The surface alloys were prepared and structurally characterized by scanning tunneling microscopy (STM) under ultra high vacuum (UHV) conditions before and after electrochemical investigation. The electrochemical behavior of the model electrodes was studied before and after electrochemical dissolution of Ag atoms in a flow-cell setup by cyclic voltammetry (CV), the activity by measurements on the ORR, respectively. Correlation between structural changes in the corroded surfaces and the oxygen reduction reaction activity are discussed. [1] J. Greeley and J.K. Norskov, J. Phys. Chem. 113 (2009) 4932.

O 60.11 Tue 18:30 P2-OG2

Influence of Mg²⁺ und Li⁺ Ions on the electrochemical decomposition of BMP TFSI on Au electrodes — •GÜLSAH YETIS¹, DOROTHEA ALWAST¹, JOHANNES SCHNAIDT², and R. JÜRGEN BEHM^{1,2} — ¹Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

Many ionic liquids (ILs) are known for their high electrochemical stabilities and therefore, in combination with Li⁺ and Mg²⁺ salts, are regarded as promising electrolytes for lithium-ion or magnesium batteries, respectively. In order to improve these batteries, a fundamental understanding of the interaction between the IL and said metal salts is necessary which determines the stability of the electrolyte. The influence of Li⁺ and Mg²⁺ cations on the decomposition of the IL N-butyl-N-methylpyrrolidinium-bis(trifluoromethanesulfonyl)imide (BMP TFSI) is studied by differential electrochemical mass spectrometry (DEMS). Thus, volatile decomposition products can be detected during cyclovoltammetric measurements. We show that the addition of LiTFSI and MgTFSI₂ diminishes the stability window of the IL at both positive and negative potentials. In the presence of the metal cations, products of the TFSI anion decomposition are detected during the negative potential scan, whereas no BMP reduction is observed. Further effects of the metal salts on the IL degradation in comparison to the behavior of the pure IL will be discussed.