O 64: Solid/liquid interfaces I (focussed session)

Time: Thursday 10:30–13:00   Location: H33

Invited Talk   O 64.1   Thu 10:30   H33
Metal/Electrolyte interfaces under atmospheric corrosion conditions — •Michael Rohwerder — Max-Planck-Institut für Eisenforschung, Max-Planck-Str.1, D-40237 Düsseldorf, Germany

Atmospheric corrosion conditions are characterized by ultra-thin electrolyte layers covering the metal surface. As will be shown, although in not too diluted electrolytes the electrochemical double layer extends only about a nanometre from the metal surface, the corrosion behaviour of metals covered by an electrolyte layer of a few hundred nanometres is different from the one of an immersed metal. This can not easily be studied with standard electrochemical set-ups. An indispensable method for electrochemical investigations in ultra-thin electrolyte layers is the Kelvin probe. Indeed, the Kelvin probe technique can be considered as a natural reference electrode that is applicable to immersed electrodes, metals covered by ultra-thin electrolyte layers and even "dry" surfaces alike. It will also be shown that the potentials measured on "dry" surfaces are of real physical importance as they have a direct impact on corrosion mechanisms.

Invited Talk   O 64.2   Thu 11:00   H33
Copper Damascene Process: From the wafer to the atomic scale — •Alexander Flügel[1], Dieter Mayer[1], Werner Reckien[3], Thomas Bredow[3], N.T.M. Hai[2], and Peter Broekmann[2] — [1]BASF SE, Ludwigshafen — [2]University of Bern — [3]University of Bonn

Copper plating is one of the key processing steps in the state-of-the-art fabrication of high-end microprocessors. The internal wiring of highly integrated circuits is achieved by an electrochemical copper deposition route also known as Copper (Dual) Damascene Process. Trenches and vias in the dielectric are filled defect-free with the copper material due to an enhanced deposition rate at the feature bottom with respect to a suppressed deposition rate at the wafer surface. This non-uniform deposition rate is triggered by the time-dependent interplay of various inorganic and organic additives at the copper surface or the near-surface regime upon electrodeposition. This presentation comprises a surface science approach providing an atomistic understanding of the additive action at the interface under reactive conditions with an electrochemical engineering approach providing a phenomenological characterization of the synergistic and antagonistic additive action at the interface. Our results are discussed in the light of successful fill experiments of sub-50nm Damascene structures relevant for the forthcoming 32-nm technology node.

Invited Talk   O 64.3   Thu 11:30   H33
Atomic-scale dynamics and interactions at solid-liquid interfaces — •Olaf Magnussen — Institut für experimentelle und angewandte Physik, Universität Kiel, Kiel, Germany

A wide variety of interface reactions, such as dissolution and growth, self-assembly, or catalytic reactions, are crucially affected by the surface transport and the interactions of species at solid-liquid interfaces. Understanding how the presence of the liquid phase and the precise interface structure influence these atomic-scale dynamic processes is hence of great interest. Using well-controlled electrochemical model systems and scanning tunnelling microscopy at video-frequency image acquisition rates, direct in-situ observations of such dynamic events are possible, providing quantitative data on surface diffusion barriers and interaction energies in these complex systems. As examples, the diffusion and interaction of different types of adsorbates as well as the collective dynamics of nanostructures are discussed for the case of Cu(100) electrode surfaces in aqueous solution.

O 64.4   Thu 12:00   H33
Computation of the interfacial excess free energies of solid-liquid interfaces by molecular dynamics simulation and thermodynamic integration — •Frédéric Leroy and Florian Müller-Plathe — Eduard-Zintl-Institut für Physikalische und Anorganische Chemie, Technische Universität Darmstadt, Darmstadt, Germany

Solid-liquid interfacial tension is a key quantity in the thermodynamics of systems where a liquid is in the vicinity of a solid substrate. While fluid-fluid surface tensions have received a lot of attention, calculation of the solid-liquid interfacial tension is still an on-going task. We

present an algorithm[1] that allows the computation of that quantity.
Rather than trying to compute an absolute interfacial free energy, we intend to obtain the free energy difference between the system where the liquid is interacting with the structured solid surface of interest and a reference system where the liquid is in contact with a flat surface, by performing thermodynamic integration from one system to the other. For example, the algorithm is useful in determining the change in free energy with respect to a modification of the chemical composition of the solid or a change in its topography.

We discuss the applications of the method in the frame of wetting in nano-scale systems and present its advantages through results dealing with Lennard-Jones model systems and water in interaction with graphite-based surfaces.

[1] F. Leroy, D.J.V.A. dos Santos and F. Müller-Plathe, Macromolecular Rapid Communications 2009, vol. 30, pp 864-870.

O 64.5   Thu 12:15   H33
Temperature-dependence of molecular self-organization at solid-liquid interfaces — •Sissi de Beer, Peter Wennink, and Frieder Mugele — University of Twente, PCF, Enschede, the Netherlands

When a liquid is confined it behaves different from the bulk. A specifically interesting confinement-effect is called layering; close to the solid wall the liquid molecules structure and form layers. When the two surfaces are approached, this layering effect gives rise to an oscillatory disjoining pressure, which can be measured as the oscillatory forces. We present measurements of the effect of temperature on layering of an organic long-chained hydrocarbon (hexadecane) and a quasi-spherical liquid (octamethylcyclotetrasiloxane; OMCTS) confined upon approach of an atomic force microscope tip towards a solid Highly Ordered Pyrolytic Graphite (HOPG) surface. When the distance between the tip and the surface is reduced, both liquids rupture in discrete steps corresponding to the squeeze-out of individual liquid-layers. We measured the force required to squeeze-out the last liquid layers for various temperatures close to the melting-temperature. For OMCTS we found no change in the squeeze-out force. However, for hexadecane we found that the structuring at the wall strongly increases when the melting temperature is approached and surprisingly, the squeeze-out force is not maximum closest to the melting temperature, but around 3-5 degrees above. We argue that this is due to epitaxial effects between the alkanes and the HOPG surface; the hydrogen-atoms of hexadecane exactly occupy the centers of the graphite hexagons.

O 64.6   Thu 12:30   H33
Adsorption and Phase Transition of Heptylviologen on HOPG observed by EC-STM — •Knud Gentz and Klaus Wandelt — Institut für Physikalische und Theoretische Chemie der Uni Bonn, Wegelerstraße 12, 53115 Bonn

Heptyl Viologen (1,1'-diheptyl-4,4'-bipyridin, HV) has been the focus of several publications which derived possible structures of the adsorbate films and it's behavior during phase transitions by means of cyclic voltammetry and chronoreflectometry. The purpose of this contribution is to verify these proposed structures as well as the behavior upon adsorption and phase changes by scanning tunneling microscopy. We adsorbed Heptylviologen on an HOPG electrode surface from a supporting electrolyte of sulfuric acid and potassiumchloride (-bromide). In the CV the characteristic voltammetric spikes of the surface phase transition were observed both in the presence of chloride as well as bromide. The STM images clearly show a stripe structure on the surface in the regime negative of the spike voltammetric peaks indicating the presence of the radical cationic phase ($HV^{•+}$) stabilized by π-π-interaction of the individual molecules. A single row and a double row structure were found showing a herringbone-like arrangement of the molecules. Above the spike peak no ordered layer was observed. The proposed dimers of the radical cation were not found on the surface at any given potential, instead we observed long-chained oligomers. In the presence of bromide an insoluble viologen bromide is formed on the surface hampering the stabilization of the surface phase which causes the spike peak to fade with progressing voltammetric cycles.

O 64.7   Thu 12:45   H33
Preparation, characterization and reactivity of sub-monolayers of platinum on carbon based model surfaces

— •Tine Brülle[1] and Ulrich Stimming[1,2] — [1]Technische Universität München, Department of Physics E19, James-Franck-Str. 1, D-85748 Garching, Germany — [2]Bavarian Center for Applied Energy Research (ZAE Bayern) Division 1 Walther-Meißner-Strasse 6, D-85748, Germany

In connection with fuel cell related research, catalyst nanoparticles on porous carbon supports got into the focus of attention. However, the complex morphology of these technical catalysts makes a thorough understanding of the influence of parameters such as noble metal particle size and morphology as well as particle distance on reactivity rather difficult. Therefore, we aim at a better understanding of these effects by using nanostructured flat surfaces as model systems in our investigations. Platinum nanoparticles supported on HOPG (highly oriented pyrolytic graphite) were prepared. This crystalline form of carbon provides a well-defined support regarding geometric and electronic structure. The platinum nanostructured surfaces were used to investigate catalytic properties for hydrogen related reactions.

Another form of crystalline carbon is diamond. High doping rates cause a sufficient electronic conductivity that make electrochemical measurements possible, while the very flat surfaces diamond monocrystals make imaging of metal nanoparticles via SPM-methods possible. Preliminary results on platinum nanostructured diamond surfaces will be shown.