O 118: Metal substrates: Structure, epitaxy and growth

Time: Friday 11:00–13:00 Location: MA 005

O 118.1 Fri 11:00 MA 005

Metal self-diffusion barriers on terraces and steps and their relation to dendrite growth in batteries — •Markus Jäckle[1,2] and Axel Gross[1,2] — [1]Helmholtz Institut Ulm - Elektrochemische Energiespeicherung, 89069 Ulm, Germany — [2]Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

The formation of dendrites poses a serious safety and efficiency problem in batteries and can lead to short-circuits during battery operation. As metal growth processes are intimately linked to diffusion behaviour, we initially studied the self-diffusion properties of lithium, sodium and magnesium on the most stable surface terminations by first-principles electronic structure calculations [1]. We have now extended this study to the diffusion properties along and across steps and to other metals that are also used as charge carriers in batteries such as Zn and Al. Additionally, we have investigated the effect of the presence of electric fields on the terrace diffusion behaviour.

We argue that particularly the Ehrlich-Schwoebel barrier is relevant for the three-dimensional growth of metals and thus also dendrite growth. We will show that the new results confirm our previous considerations for Li and Mg. However, no consistent picture arises across all considered metals. Possible reasons for the inconsistencies will be discussed.

[1] M. Jäckle and A. Groß, J. Chem. Phys. **141**, 174710 (2014).

O 118.2 Fri 11:15 MA 005

Surface segregation and electromechanical coupling at the Ag-Au (111) surface — •Sandra Hoppe and Stefan Müller — Institute of Advanced Ceramics, Hamburg University of Technology, Hamburg, Germany

Recently, the sponge-like nanoporous gold (npAu) has attracted the attention for heterogeneous catalysis due to its promising characteristics, such as high catalytic activity at ambient temperature and pressure and a high surface-to-volume ratio[1]. Residual silver that is left after the fabrication process has been found to influence the catalytic activity and selectivity of npAu[2]. In order to better understand this phenomenon, it is crucial to analyze the way silver is distributed in the Ag-Au alloy surface and how segregation affects the surface composition. For this purpose, we have employed a combination of first-principles calculations and statistical physics to investigate surface segregation at the Ag-Au (111) surface. Interestingly, we obtain Au enrichment in the topmost layer, which we explain with a charge transfer from Ag to Au, stabilizing Au in the surface layer. Furthermore, we analyzed the influence of the surface composition and Ag surface concentration on the electromechanical coupling behavior, which offers an opportunity to alter the catalytic activity by applying strain to a surface.

[1] B. Zielasek *et al. Angew. chem. Int. Ed.* **45** (2006) 8241.

[2] L.-C. Wang *et al. Beilstein J. Nanotechnol.* **4** (2013) 111.

O 118.3 Fri 11:30 MA 005

(Meta)-stability of bimetallic surfaces: A computational study — •David Mahlberg and Axel Gross — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

The catalytic properties of bimetallic surfaces sensitively depend on their composition and/or structural arrangement. However, it is often not clear how stable these structures are under reaction conditions such as high temperatures. Here we present first principles-based kinetic Monte-Carlo (kMC) simulations to analyze the (meta-)stability of PtRu/Ru(0001) surface alloys.

Typically structural changes in metals occur via vacancy diffusion. In a first step, the enthalpy of vacancy formation was determined by density functional theory calculations. There is a high energetic cost of their formation, resulting in a small concentration of vacancies on the surface, in agreement with scanning tunneling microscope (STM) results [1]. In a second step, barriers for vacancy diffusion were derived as a function of the surrounding composition of bimetallic surface alloy which then enter the kMC simulations as jump rates derived via transition state theory. We will present results of the time evolution of the structure of PtRu/Ru(0001) surface alloys and analyze them in terms of the interaction between the constituents of the bimetallic surface.

[1] H. E. Hoster, A. Bergbreiter, P. M. Erne, T. Hager, H. Rauscher and R. J. Behm, Phys. Chem. Chem. Phys. **10**, 3812 (2008).

O 118.4 Fri 11:45 MA 005

X-ray standing wave excited photoemission experiments on W/C multilayer mirrors — •Marie Schmitz[1], Martina Müller[2], Ronja Anika Heinen[2], Patrick Lömker[2], Andrei Gloskovskii[3], Martina Müller[2], and Carsten Westphal[1] — [1]Experimentelle Physik 1 - Technische Universität Dortmund, Otto-Hahn-Str. 4, D-44221 Dortmund, Germany — [2]Forschungszentrum Jülich GmbH, PGI-6, Jülich, Germany — [3]Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

We report on the measurements of x-ray standing waves (XSW) generated on a bilayer system of alternating Carbon and Tungsten (W/C). The method of photo electron spectroscopy provides a high chemical sensitivity thus being element sensitive, without giving a spacial resolution. In contrast, X-ray reflection methods can provide this depth-resolution, without being element specific. The stated disadvantages can be overcome by using XSW-measurements as they both provide the advantages of these methods. In order to this, a thin periodic layer system of alternating refractive index materials has to be used to generate a strong standing wave while rocking the sample around the bragg angle. The multilayer including Si and Mo is a widely used system to generate standing waves on a surface. We use a W/C multilayer system, as it provides better temperature-stabilities, while keeping a high reflectance. In this context the reflectivity is an important figure of merit. The smoothness of the interface is a key property leading to a perfect interface without boundary imperfections.

O 118.5 Fri 12:00 MA 005

X-ray standing wave excited photoemission experiments on W/C multilayer mirrors — •Marie Schmitz[1], Philipp Espeter[1], Ronja Anika Heinen[2], Patrick Lömker[2], Andrei Gloskovskii[3], Wolfgang Drube[3], Martina Müller[2], and Carsten Westphal[1] — [1]Experimentelle Physik 1 - Technische Universität Dortmund, Otto-Hahn-Str. 4, D-44221 Dortmund, Germany — [2]Forschungszentrum Jülich GmbH, PGI-6, Jülich, Germany — [3]Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

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O 118.6 Fri 12:15 MA 005

Temperature dependent growth of Zn and formation/decomposition of ZnO_x on Au(111) — •Konstantin M. Schüttler, Albert K. Engstfeld, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

Methanol is a promising molecule for chemical energy storage, e.g., when using H_2 from renewable sources for its synthesis. Au/ZnO was found to be a highly active catalyst for the synthesis of "Green Methanol" from CO_2/H_2 as a "Solar Fuel"[1]. Previously, CuZn alloys have been used as model systems for the industrially used Cu/ZnO catalysts, for which it has been found that under reaction conditions ZnO at the perimeter of the Cu nanoparticles is partly reduced forming bimetallic CuZn sites[2]. For Au/ZnO this approach is similarly plausible. In order to gain more insight into the formation and nature of active sites, the formation, structure, electronic and chemical properties of bimetallic Zn/Au(111) surfaces serving as structurally well-defined 2D model catalysts were studied under UHV conditions. The temperature dependence of the nucleation, growth and alloy formation processes of Zn on Au(111) is discussed, based on STM studies. In addition, the reactivity of Zn surface atoms in the Au/Zn/O system, which may be crucial for the catalytic performance of ZnO supported MeOH synthesis catalysts, was studied by exposing Zn/Au(111) surfaces to molecular and atomic oxygen. Furthermore the deposition of Zn in an oxygen atmosphere and the thermal decomposition of these ZnO_x/Au(111) ($0 \leq x \leq 1$) surfaces has been studied.

O 118.7 Fri 12:30 MA 005

Energetics and structure of FeO/Fe(001) interfaces — •Tomasz Ossowski and Adam Kiejna — Institute of Experimental Physics, University of Wrocław, Pl. M. Borna 9, 50-204 Wrocław, Poland

The metal-oxide interfaces are of great importance in many fields of science and technology, including corrosion, catalysis, magnetic devices and spintronics. FeO thin layers on iron surfaces play significant role in growth of iron-oxides on the surfaces and in early stages of iron surfaces oxidation. In this work, we have performed DFT calculations of interaction of thin oxide films of 1-5 FeO atomic layers with Fe(001) surface. It is found that adsorption of single FeO layer on the Fe(001) surface results in a surface covered by oxygen atoms and subsequent oxide layers grow at the surface precovered by oxygen atoms. For thicker films of 2-5 FeO adlayers on Fe(001) surface, the system with oxygen atoms at the oxide-substrate interface is energetically most stable. The iron-oxide adsorption affects weakly substrate geometry causing expansion of the first interlayer distance compared to the clean iron surface. The work function of FeO/Fe(001) system is larger by about 0.2 eV than for the clean Fe(001) surface. The calculated work of separation shows that the strongest FeO-Fe(001) interactions occur for double FeO layers thick which is by about 0.45 eV stronger bound to Fe(001) surface than monolayer of FeO. For thicker FeO adlayers interaction weakens, however remains stronger than for the monolayer film. It is also found that FeO on Fe(001) surface exhibits antiferromagnetic order, with the interface layer oriented ferromagnetically to the substrate surface.

O 118.8 Fri 12:45 MA 005

Surface crystallography of large organic molecules on metal and insulator surfaces by LEED-IV using Fourier coefficients — •Ina Krieger[1,3], Georg Held[2], Christian Kumpf[3], and Moritz Sokolowski[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Bonn, 53115 Bonn, Germany — [2]Department of Chemistry, University of Reading and Diamond Light Source, UK — [3]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52428 Jülich, Germany

We will report on LEED-IV analysis of the large organic molecules PTCDA and NTCDA on the metal and insulator surfaces Ag(100), Ag(111), and KCl(100). Using data from different angles of electron incidence and optimizing the LEED-IV program code we were able to extend the experimental data set and shorten the calculation times required for the complex and large unit cells. Furthermore, the distortion of the PTCDA molecule and the buckling of the Ag surface were described by Fourier coefficients taking into account the symmetry of the system [1]. The idea of this procedure is to suppress unphysical vertical displacements of atoms on a short-wave-length scale by restriction to lower order coefficients.

By this, we obtain good Pendry R-factors, for PTCDA/Ag100 of about 0.23. We were able to derive the vertical distortions of the oxygen atoms in the functional group and the buckling of the Ag surface in rather good agreement with earlier results from DFT and NIXSW studies.

[1] W. Moritz et al, Phys. Rev. Lett. 104, 136102 (2010).