

DS 24: Metal substrates: Structure, epitaxy and growth (joint session with O)

Time: Wednesday 10:30–12:45

Location: MA 042

DS 24.1 Wed 10:30 MA 042

Investigation of nanocluster formation far from equilibrium in heteroepitaxial system: Co/Cu(111) — •QUANG HUY VU, SEBASTIAN KUNZE, and KARINA MORGENSTERN — Physical Chemistry I, Ruhr-Universität Bochum, Universitätsstr. 150,44801 Bochum, Germany

Lattice mismatch plays an important role in heteroepitaxial systems. Here we present such a system, Co adsorbed on Cu(111). Why is so important to study this system? The small lattice mismatch between cobalt and copper of 1.9% makes it attractive to investigate its structural characteristics and study its effect onto submonolayer adsorption. The growth mechanism of cobalt was measured by means of fast-scanning tunneling microscopy within the range of surface temperatures from 100 K to 300 K and for different deposition rates. At very low coverage, cobalt forms nanoclusters on Cu(111). These clusters adsorb favorably at step edges on Cu(111) at 115 K. In contrast at higher coverage, cobalt forms islands of fractal shapes with 1 ML height at 165K. Furthermore, the nucleation of 2 ML island height is studied at 165 K not only on the terraces but also on the step edges. Finally, the etching of Cu is observed at room temperature indicates growth of intermixed nanoclusters. In this presentation the atomic processes of the island formation will be discussed

DS 24.2 Wed 10:45 MA 042

Surface induced stabilization of the metallic Sn phases in Sn nanoparticles. — •NICOLAS G. HÖRMANN¹ and AXEL GROSS^{1,2} — ¹Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstr. 11, 89069 Ulm — ²Universität Ulm, Institut für Theoretische Chemie, Albert-Einstein-Allee 11, 89069 Ulm

Sn is a widely used element and besides new applications in optoelectronics [1] it is also a promising electrode material for established and future battery systems (Li⁺, Na⁺ and F⁻ batteries [2,3]). Yet, not many detailed ab-initio studies have been reported so far.

In the presentation we will report results of DFT calculations of bulk and surface structures and energies of elemental Sn. By combining this with vibrational free energy data we derive the Gibbs free energy of Sn nanostructures and show that the phase stability diagram of Sn is significantly altered, which has significant impact on the expected performance of Sn nanostructures in real-world application. Furthermore we discuss briefly the initial steps of battery charging which occurs via atomic adsorption processes.

[1] S. Kufner et al., *Nanotechnology* **24**, 405702 (2013). [2] H. Zhu et al., *Nano Lett.* **13**, 3093–3100 (2013). [3] M. Anji Reddy et al. *J. Mater. Chem.* **21**, 17059–17062 (2011).

DS 24.3 Wed 11:00 MA 042

Intermixing of Pt and Cu atoms in PtCu/Ru(0001) surface alloys — •LUIS MANCERA¹, AXEL GROSS¹, ALBERT ENGSTFELD², ANDREAS BENSCH², and R. JÜRGEN BEHM² — ¹Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany — ²Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

In this contribution, we report on a joint theoretical and experimental study addressing model surface catalysts consisting of bimetallic PtCu surface alloys formed on a Ru(0001) substrate. The PtCu/Ru(0001) surface is obtained by deposition of Pt onto a previously prepared monolayer of Cu on Ru(0001) surface. In spite of the high stability of Ru(0001) that prevents exchange of Cu or Pt atoms with the substrate, Ru(0001) can still induce strain on the deposited Cu layer, due to the different lattice parameter, and thus modulate the formation of the PtCu alloy. Using STM imaging, it has been observed that the surface alloy is formed following a specific nucleation behavior that shows an atypical island density increase with growing Pt coverage. Here we apply periodic density functional theory (DFT) calculations to study various situations for atom diffusion on different surface alloy configurations in order to elucidate the origin of those nucleation patterns. We determine the stability of PtCu surface alloys and address the diffusion of Pt and Cu atoms on PtCu/Ru(0001) as well as Pt-Cu atom-exchange processes that lead to the formation of these alloys. Based on these findings, the effect of Pt substitutional atoms in the nucleation is discussed.

DS 24.4 Wed 11:15 MA 042

Alloying and dealloying of Mg on the Ag(100) surface — •MARINA SCHULER, PASCAL FERSTL, LUTZ HAMMER, and M.ALEXANDER SCHNEIDER — Lst. für Festkörperphysik, FAU Erlangen-Nürnberg

Ultrathin oxide films on metal substrates play an important role in basic surface research and technological applications. Since these oxide films are often prepared via postoxidation of pre-deposited metal films, their structural properties may strongly influence the quality of the growing oxide. In this study we investigate the structures developing during Mg deposition on Ag(100) prior to oxidation to MgO by means of quantitative LEED and STM.

Submonolayers of Magnesium adsorbed at 90 K on top of the plain Ag(100) surface form an ordered ($\sqrt{5} \times \sqrt{5}$)R arctan 0.5 phase. Annealing to 150 K leads to an atomic reorganisation at the surface and a c(2×2) phase appears, which has been reported already [1]. The crystallographic structure of this c(2×2) phase is shown to be a bimetallic surface alloy by means of a quantitative LEED analysis: every second Ag atom of the top layer is substituted by Mg, which relaxes outward by 0.13 Å. The Mg/Ag-c(2×2) structure persists further Mg deposition at elevated temperatures dissolving surplus Mg atoms into the underlying substrate layers. By offering 1·10⁻⁷ mbar oxygen at 400 K the dissolved Mg is driven at the surface of the crystal again, forming MgO films of the corresponding thickness.

[1] C. Tegenkamp *Appl. Surf. Sci.* 151 40 (1999)

DS 24.5 Wed 11:30 MA 042

Comparative study of the carbide-modified surfaces C/Mo(110) and C/Mo(100) using high resolution x-ray photoelectron spectroscopy — •CHRISTOPH GLEICHWEIT, UDO BAUER, MAX AMENDE, STEFAN SCHERNICH, OLIVER HÖFERT, JÖRG LIBUDA, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Lehrstuhl f. Physikal. Chemie II

We present a comparative study of the carbide-modified surfaces C/Mo(100) and C/Mo(110) using synchrotron-based high-resolution x-ray photoelectron spectroscopy (HR-XPS), with the objective of elucidating the differences and similarities of the two crystal facets depending on the C/Mo ratio. We are interested in changes at the surface due to exposure to carbon and oxygen right at the temperature sufficient to drive carbon into the interstitial sites of the Mo lattice. Carburization by dosing ethylene, i.e. carbide preparation, and subsequent oxidative carbon removal by dosing O₂ at 1200 K is followed in great detail through careful analysis of the C 1s, Mo 3d and O 1s core levels. We show that the thin carbide overlayers show spectroscopic differences compared to the thick carbides obtained at high carbon dose. Furthermore we show that the carbide thickness on Mo(110) influences the adsorption properties towards H₂ and CO, pointing towards the importance of the surface structure for reactivity.

DS 24.6 Wed 11:45 MA 042

Surface self-diffusion of the battery anode materials lithium, sodium and magnesium studied using DFT — •MARKUS JÄCKLE^{1,2} and AXEL GROSS^{1,2} — ¹Helmholtz Institut Ulm - Elektrochemische Energiespeicherung, 89069 Ulm, Germany — ²Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

Lithium, sodium and magnesium represent rather interesting anode materials for next-generation batteries. These metals vary in their tendency to form dendrites which represent a hazard as their formation can lead to short-circuits during battery operation. As metal growth processes are intimately linked to diffusion, we have studied the self-diffusion properties of the metals in order to understand the differences in their tendency towards dendrite formation.

According to our calculations, self-diffusion of Mg is much faster than the one of Li or Na on the energetically most stable surface terminations [1]. These results can be connected to the fact that Mg is an hcp metal, whereas Li and Na are bcc metals. In addition, we have determined the interaction between adatoms of these metals. We will discuss the relevance of our findings for the understanding of the dendrite growth on battery anodes. Furthermore, we will address first attempts to assess the influence of the electrochemical environment on metal diffusion properties.

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

DS 24.7 Wed 12:00 MA 042

Ultra-thin stepped iron oxide films on high index Pt surfaces

— •ELIN GRÄNÄS^{1,2}, NICLAS JOHANSSON¹, MOHAMMAD A. ARMAN¹, JACEK OSIECKI³, KARINA THÄNEL³, JESPER N. ANDERSEN^{1,3}, JOACHIM SCHNADT¹, and JAN KNUDSEN^{1,3} — ¹Division of Synchrotron Radiation Research, Lund University, Sweden — ²Deutsches Elektron Synchrotron (DESY), Hamburg, Germany — ³MAX IV Laboratory, Lund University, Sweden

Iron oxide films grown on metal surfaces show high catalytic activity for reactions such as CO oxidation and the water-gas shift, and it has been suggested that the high activity is due to under-coordinated Fe atoms at the edge of FeO islands[1]. Whether the metal substrate is essential for the activity of the edge sites remain an open question and the few and heterogeneous edge sites present on FeO islands make it difficult to characterize them with chemically sensitive techniques like X-ray photoelectron spectroscopy (XPS).

We have grown FeO films on Pt(322), producing films with a very high density of homogenous FeO-FeO edge sites. Scanning tunneling microscopy show that approx. 20 % of the sites are edge sites. In water adsorption studies on the stepped FeO film we observe an enhanced ability to split water compared to planar FeO. As the Pt(322) substrate is fully covered by stepped FeO we assign the high water splitting ability to the pure FeO-FeO step site.

[1] L. Xu, Z. Wu *et al.*, *J. Phys. Chem. C* **115**, 14290 (2011)

DS 24.8 Wed 12:15 MA 042

MD study of gold growth on MnAs — •ANDREAS RÜHL and CHRISTIAN HEILIGER — I. Physikalisches Institut, Justus Liebig Universität Giessen, D-35392 Giessen, Germany

We present the results of our Molecular Dynamics (MD) study concerning the atomic deposition of gold atoms on different MnAs surfaces. Those growth simulations show a 'layer-plus-island growth', also known as the Stranski-Krastanov (SK) growth. Our research is motivated by the experimental work on ferromagnetic MnAs nanoclusters, which can be easily tuned in different shapes and sizes. Taking two of

those clusters and connect them via a non-magnetic metal, for example gold, leads to a GMR-like structure (Giant magnetoresistance).

In order to analyze the structure of the deposited gold atoms, needed for later calculation of the electric transport, we created an EAM potential for the MnAsAu system in the scope of Force Matching by fitting the potential model to ab initio data. The resulting potential is validated by different tests, including the comparison of bulk and surface energies to the corresponding ab initio data. We then carried out growth simulations for different MnAs surfaces and different substrate temperatures. The observed SK-growth exhibits a critical layer thickness at which the island growth starts and by using Bond-Angle analysis we see the gold atoms mainly relaxing to fcc phases.

DS 24.9 Wed 12:30 MA 042

Development and testing of a plasma coating apparatus —

•CORNELIA KUNZ¹, SEBASTIAN DAHLE^{1,2}, and WOLFGANG MAUS-FRIEDRICH^{1,2} — ¹Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstraße 4, D-38678 Clausthal-Zellerfeld, Germany — ²Clausthaler Zentrum für Materialtechnik, Technische Universität Clausthal, Agricolastraße 2, D-38678 Clausthal-Zellerfeld, Germany

Thin coatings on metal surfaces have known advantages in many applications, e.g. passivation or corrosion protection. In this work, a plasma coating apparatus was constructed and tested to develop uniform, particle-free coatings on titanium surfaces. A primary Si₃N-coating was achieved via plasma ignition in nitrogen diluted silane at atmospheric pressure. A procedure was devised to control the growth mechanisms yielding particle-free coatings. In order to minimize particle formation, nucleation and agglomeration of radicals formed in the plasma have to be inhibited. The critical parameter leading to a silicon radical controlled growth mode and thus to minimized nucleation was found to be the excitation frequency. In a secondary step, these Si₃N-coatings were treated with air plasma, leading to oxidation and clean silicon dioxide coatings. Surface topography was analysed using atomic force microscopy (AFM) in order to determine a growth mode suppressing particle formation mode. In a following step, surface stoichiometry was determined via X-ray photoelectron spectroscopy (XPS).