O 11: Metal & Semiconductor substrates: Adsorption and reaction of small molecules II

Time: Monday 15:00–17:00 Location: HSZ/0401

O 11.1 Mon 15:00 HSZ/0401

Ethylene on Si(001) revisited: New insights from XPS, STM, and Monte Carlo Simulations — •Jannick A. Peters, Sophie Göbel, and Michael Dürr — Institut für Angewandte Physik and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany

The adsorption of ethylene - the smallest organic molecule with a C=C double bond - on Si(001) seems straightforward and is widely used as reference, e.g., for the determination of absolute surface coverage. On the other hand, there is ongoing discussion about adsorption configurations, coverage dependence, and in particular the site-selective adsorption based on strongly reduced reactivity on the partially covered surface, leading to two-step adsorption kinetics. In this study, the adsorption of ethylene on Si(001) was investigated at 300 K by means of XPS and STM with special focus on the coverage dependence, and was further modelled by means of Monte Carlo simulations. We can show that the first step of the two-step adsorption kinetics results in a saturation coverage of 0.7 ML, which is significantly higher than the commonly referenced coverage of 0.5 ML. STM measurements show that this behaviour is caused by a combination of adsorption statistics, nearest-neighbour interactions, and site-selective hindrance. Higher coverage up to 1 ML is then reached with a significantly higher dose due to the reduced reactivity of the remaining surface sites. Monte Carlo simulations taking into account a limited set of reaction channels accurately describe the complete coverage dependence as well as the local order of the adsorbates on the surface.

O 11.2 Mon 15:15 HSZ/0401

The Influence of Doping on Inelastic H Atom Scattering from Silicon — •Malte Opfermann, Kerstin Krüger, Sophia Tödter, and Oliver Bünermann — Institut für physikalische Chemie, Georg- August-Universität Göttingen, Tammannstraße 6, 37077 Göttingen

Inelastic H atom scattering experiments on the semiconducting Ge(111)c(2x8) surface have revealed a bimodal energy-loss distribution consisting of a narrow low energy-loss component and a broad high energy-loss component with an onset equal to the surface band gap. Theoretical calculations attribute the low energy-loss component to an adiabatic scattering mechanism at the adatom. The high energy-loss component is explained by a non-adiabatic scattering mechanism involving electron transfer across the surface band gap from the rest atom to the adatom.

Recently, we extended our studies to scattering experiments from the Si(100)2x1 surface. Although the experimental energy loss distributions resemble the bimodal behavior of Ge(111)c(2x8), the first component is broader, and the second exhibits a visible but less well-defined onset at the surface band gap. To gain further insight, we carried out scattering experiments from n-doped and p-doped surfaces. The first component shifts to lower energy losses for n-type doping and to higher energy losses for p-type doping, whereas the second component remains essentially unaffected. Based on the theoretical results for Ge(111)c(2x8), we propose a scattering mechanism for the Si(100)2x1 surface.

O 11.3 Mon 15:30 HSZ/0401

***Ab initio* insights into the OER activity of pristine and metal-supported Co$_3$O$_4$(111)** — •Muhammad Munawar[1,2] and Rossitza Pentcheva[1] — [1]Department of Physics and Center for Nanointegration (CENIDE), Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany — [2]IMPRS SusMet, Max Planck Institute for Sustainable Materials GmbH, Max Planck-Straße 1, 40237, Düsseldorf, Germany

Co$_3$O$_4$ is a promising anode material for the oxygen evolution reaction (OER), yet the role of metallic supports on its electronic properties and performance remains elusive. Here, we employ density functional theory with a Hubbard U term (DFT+U) to investigate the structural, electronic, and catalytic properties of pristine Co$_3$O$_4$(111) and Co$_3$O$_4$(111) grown on Pt(111). Using *ab-initio* thermodynamics, we determine that the Co tetrahedral termination is the most stable Co$_3$O$_4$(111) surface across a broad range of oxygen chemical potentials. Our results reveal that a built-in electric field emerges when Co$_3$O$_4$(111) is grown on a metallic substrate like Pt(111), that shifts the valence band maximum in the surface layer toward the Fermi level. Moreover, the work function increases monotonically with applied strain. Furthermore, we compare the OER activity of the pristine Co$_3$O$_4$(111) and Co$_3$O$_4$(111)/Pt(111) surface. These results provide atomic scale insight into structure-property relationships at oxide and oxide/metal interface, offering guidance for the rational design of next generation oxide-based electrocatalysts.

O 11.4 Mon 15:45 HSZ/0401

Through Stronger Hinderance to Higher Reactivity: Influence of the Alkyl Chains on the Activation Energy of Ether Cleavage on Silicon — Timo Glaser[1], Gustav F. Nolte[1], Tamam Bohamud[1], Philip Keller[1], Mathieu G. Silly[2], Hendrik Weiske[3], Ralf Tonner-Zech[3], and •Michael Dürr[1] — [1]Institut für Angewandte Physik and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany — [2]Synchrotron SOLEIL, Gif sur Yvette, France — [3]Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Germany

Reactivity in surface chemistry is often discussed in terms of the interaction between surface states and the functional groups of the reacting molecule. Herein we demonstrate that for finite submonolayer coverage, i.e., surface coverage at which the molecular adsorbates cannot be treated as isolated molecules anymore, the seemingly innocent side chains of the adsorbate can also play a decisive role. For the example of ether cleavage on Si(001), which represents the surface analogue of an S$_N$2-type reaction, we show both experimentally by means of real-time XPS as well as based on ab-initio calculations that steric hindrance by the side chains determines the activation energy for C-O dissociation into the final state. In contrast to a simple expectation, the *stronger* steric hindrance of the butyl group in butyl methyl ether leads to a *lower* activation energy for ether cleavage on Si(001) when compared to diethyl ether. This effect was traced back to different degrees of destabilization of the precursor and the transition state [1].

[1] T. Glaser, et al., Angew. Chem. Int. Ed. e19990 (2025).

O 11.5 Mon 16:00 HSZ/0401

Frontier Orbitals Control Adsorbate Bonding to Stepped Transition Metal Surfaces — •Florian Nitz[1], Stefan Hörandl[1], Dmitriy Borodin[2], and Alec Wodtke[1] — [1]Institute for Physical Chemistry, Georg-August University of Goettingen, Tammannstraße 6, 37077 Goettingen, Germany — [2]Center for Quantum Nanoscience (QNS), Institute for Basic Science (IBS), Seoul 03760, South Korea

Developing intuitive models of bonding and reactivity lies at the heart of physical chemistry. While such models have been developed for atoms and molecules, we still lack concepts to explain bonding and reactivity in the solid state, including surface chemistry and catalysis. Here, we address this gap and present a model of covalent bonding between molecular orbitals of an adsorbate and symmetry-specific bands on a metal surface atom, analogous to frontier orbital theory in molecular chemistry. We apply the model to the adsorption of three molecules–CO, NO, and NH$_3$–on stepped platinum surfaces of varying step density and compare its predictions to experimental adsorption energies. The experiment reveals that the adsorption energies vary systematically with step density, an unexpected phenomenon that can only be explained by the frontier orbital model. Correlations of the adsorbate bond strength with the mean energy of the metal d-electrons or with surface strain fail to describe the experimental observations. This highlights frontier orbitals as a powerful concept to rationalize bonding and reactivity in condensed-phase systems.

O 11.6 Mon 16:15 HSZ/0401

Memory friction and zero-point motion in hydrogen surface diffusion — •George Trenins and Mariana Rossi — MPI for the Structure and Dynamics of Matter, Hamburg, Germany

By virtue of their small mass, hydrogen atoms readily manifest quantum dynamical effects under typical experimental conditions. In particular, hydrogen diffusion on metal surfaces is strongly influenced by nonadiabatic interactions with the conduction electrons. Such “electronic friction” is incorporated into numerical simulations via the generalized Langevin equation (GLE). Additionally, hydrogen possesses substantial zero-point energy and can undergo quantum tunnelling.

This is accurately described by "ring-polymer molecular dynamics" (RPMD), an atomistic simulation approach rooted in the path-integral formulation of quantum mechanics. Using a rigorous combination of the GLE and RPMD frameworks, we show that a combination of zero-point motion and non-Markovian (memory) friction are key to the temperature dependence of H-atom diffusion on copper surfaces [1]. In a limited temperature range, the two effects happen to mask each other almost perfectly, creating the appearance of classical, memoryless dynamics. Outside this range, the experiment displays non-Arrhenius behaviour that is not captured by classical dynamics but is readily explained when quantum effects are taken into account. [1] G. Trenins, M. Rossi, Phys. Rev. Lett. **134**, 226201 (2025).

O 11.7 Mon 16:30 HSZ/0401

When plasma meets surfaces - Nitrogen plasma-induced surface transformations on copper — •Ester Perez Penco and Roland Bliem — ARCNL, Amsterdam , The Netherlands

Inside EUVL setups, materials are exposed to challenging conditions, most importantly a plasma generated by the interaction of EUV radiation with the main background gas, hydrogen, and trace elements such as nitrogen. The reactive nature of plasma environments causes even trace gases to significantly influence material properties and affect the condition of surfaces. Copper is widely used in semiconductor technology, including applications as functional parts of the latest generation of chip manufacturing tools using extreme ultraviolet lithography (EUVL), therefore, it is relevant to study its behaviour in such reactive environment.

In this surface science study, we investigate the interaction of plasma-activated nitrogen with Cu(111) surfaces using in situ X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED). By systematically comparing the effects of molecular nitrogen, neutral atoms, ions, and nitrogen plasma, we provide detailed insights into how individual plasma species modify the copper surface. Our findings reveal that while radicals modify the very surface layer, higher energy species are required to induce structural disorder and incorporate into deeper layers. The results presented in this study aid in the prediction of plasma-induced changes and the role of trace elements in the EUVL environment.

O 11.8 Mon 16:45 HSZ/0401

From Gold to Copper: N-heterocyclic Carbene Self-Assembly for Area-Selective Deposition — •Franz Thiemann[1], Patrick Melix[1], Emmett Desroche[2], Francesco Tumino[2], Cathleen Crudden[2], and Ralf Tonner-Zech[1] — [1]Wilhelm-Ostwald Institute, Universität Leipzig, Germany — [2]Carbon to Metal Coating Institute, Queen's University, Kingston, Canada

N-heterocyclic carbenes (NHCs) are promising small-molecule inhibitors for area-selective atomic layer deposition (ASD) due to their strong, selective binding to metal surfaces. Using density functional theory with PBE-D4 functionals and periodic surface slabs, this study investigates NHC adsorption on a Cu(111) surface and compares it with previously studied Au(111) systems. In both cases, experimentally observed overlayer formation could be reproduced by DFT calculations and verified using STM images, revealing a distinctive dimer pattern in which NHCs bind to extracted copper adatoms at high density (1.8 NHC/nm^2) with a tilted molecular orientation. Energy decomposition analysis for extended systems revealed the origin of the stable overlayer: strong σ-donation to the surface and π-backdonation, combined with dispersion interactions between the NHC backbones, result in a highly stable blocking layer. [1] Furlan et al. Chem. Mater., 5753, 37 (2025). [2] DesRoche et al., in Preparation. [3] Raupach et al. J. Chem. Phys., 194105, 142 (2015).