O 39: Poster: Metal Substrates

Time: Tuesday 18:00–20:00 Location: Poster D

O 39.1 Tue 18:00 Poster D

Chemisorption and diffusion of fluorocarbon compounds on Ag(110) — •Shilpa Panchami Raj, Matthew Timm, and Leonhard Grill — University of Graz

The chemisorption and diffusion of molecules adsorbing at metal surfaces are key processes in heterogeneous catalysis [1]. In this work, we present a scanning tunnelling microscopy (STM) study under ultrahigh vacuum (UHV) of the deposition of CF3I on the anisotropic Ag(110) surface. Experiments were done at cryogenic temperatures of 5 K, which allows imaging single molecules in a stable fashion and also to manipulate them with the tip of the microscope in a controlled way. Dissociative chemisorption of CF3I on Ag (110) was observed and studied in dependence on the sample temperature. Moreover, first attempts will be presented of how diffusion of individual molecules can be induced in a controlled way.

[1] G. Ertl, Angew. Chem. Int. Ed. 47, 3524 (2008)

O 39.2 Tue 18:00 Poster D

S on Ir(111): transition between two superstructures observed by LEED and Auger electron spectroscopy — •Alice Bremerich, Paulus Aleksa, Robin Ohmann, and Carsten Busse — Department Physik, Universität Siegen, Deutschland

Detailed knowledge of the adsorption of chalcogens on metal surfaces is of high interest to control the preparation of complex atomically thin materials like transition metal dichalcogenides (TMDC) or even their heterostructures. Furthermore, chalcogens are also useful intercalants, which can modify the interaction of 2D materials with their substrates. We investigated the adsorption of elemental sulfur on pristine Ir(111), which was proven to be an excellent substrate for TMDCs on a graphene buffer layer. The resulting superstructures are determined by low energy electron diffraction (LEED), and with Auger electron spectroscopy (AES) we could quantify the S coverage Θ_S for each deposition to calibrate the sulfur source in terms of sulfur pressure and deposition time.

For S coverages $\Theta_\mathrm{S} < 0.3$ ML we observe the well-defined superstructure $\left(\sqrt{3}\times\sqrt{3}\right)R30^\circ$. For $0.3\ \mathrm{ML} < \Theta_\mathrm{S} < 0.5$ ML we found a transition between this and the $c\,(4\times 2)$ superstructure by the formation of domain walls. Here the LEED spots of the $\left(\sqrt{3}\times\sqrt{3}\right)R30^\circ$ structure split into three spots where the distance between them increases with increasing coverage until it forms the $c\,(4\times 2)$ structure for $\Theta_\mathrm{S} > 0.5$ ML.

O 39.3 Tue 18:00 Poster D

Optimizing a Surfactant-Free Silver Substrate for Surface-Enhanced Raman Spectroscopy — •Georgiana Ion, Stefania D Iancu, and Nicolae Leopold — Faculty of Physics, Babes-Bolyai University, 400084, Cluj-Napoca, Romania

Surface-Enhanced Raman Spectroscopy (SERS) relies on the adsorption of analytes to metallic nanoparticles, such as silver, a process often impeded by surfactants. This study introduces a straightforward and efficient method to obtain a surfactant-free SERS-active substrate, facilitating prompt analyte adsorption.

Citrate-capped silver nanoparticles (AgNPs) were concentrated, dried on a glass slide, and exposed to an ozone-rich environment (UV Ozone Cleaner) to eliminate the citrate surfactant. However, exposure of AgNPs to O_3 resulted in metal oxidation, rendering the substrate SERS inactive. To remove AgO from the surface, we tested various pH and time combinations and found that the most effective method involved immersing the glass slide with the silver substrate in a pH 4-5 H_2O_2 solution for 70 seconds. After removing the AgO, SERS analysis revealed the disappearance of citrate from the AgNPs surface present before the cleaning process. Subsequently, immersion in a fumaric acid solution ($5\mathrm{x}10^{-5}$M) was employed to assess SERS enhancement. The SERS signal suggested spontaneous adsorption to the metallic surface, affirming the creation of a SERS-active substrate.

In conclusion, a rapid method for producing a surfactant-free SERS substrate was developed and tested, based on surface O_3 cleaning followed by H_2O_2 reduction.

O 39.4 Tue 18:00 Poster D

Probing the chemical bond between Ni and a CO-terminated AFM tip — •Maximilian Krüger, Fabian Stilp, Marco Weiss, and Franz J. Giessibl — Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany

AFM with a CO-terminated tip usually images the total charge density of atoms in a sample. Huber *et al.* [1] discovered exceptions to the chemically inert behaviour of the CO tip. For single Fe adatoms on Cu(111) a subatomic toroidal configuration was found, which maxima are aligned with the threefold symmetry of the underlying Cu lattice. This is resulting from the hybridisation of electronic states of CO and the adatom.

DFT calculations [2] suggest a similar, by 60 degrees rotated signature for Ni adatoms on the Cu(111) surface. Motivated by this, the same AFM measurement processes are used to examine Ni.

It is revealed that the interaction between Ni and CO also transitions from physisorption to chemisorption when approaching. At small tip-sample distances Ni appears as an attractive center with a surrounding repulsive ring as it is the case for Fe, but with different ratios between attractive and repulsive forces. Ultimately the three maxima could not be detected.

[1]: F. Huber, et al. 'Chemical Bond Formation Showing a Transition from Physisorption to Chemisorption'. Science **366**, 6462 (2019): 235–238.

[2]: S. Polesya, S. Mankovsky, H. Ebert. unpublished calculations.

O 39.5 Tue 18:00 Poster D

On-top hydrogen adsorption on Pt(111): A complementary studies by LEED, TPD and sum-frequency generation spectroscopy — •Zhipeng Huang, Tobias Roos, Yujin Tong, and R. Kramer Campen — Faculty of Physics and Center of Nanointegration (CENIDE), University of Duisburg-Essen

Studying the hydrogen (H) adsorption on a metal surface is important for understanding the hydrogen evolution and oxidation reactions occurring at catalytic metal surfaces. However, there remain controversies on whether hydrogen can be adsorbed on-top sites stably even for the most-stable and close-packed (111) surface of platinum (Pt) under well-defined UHV conditions.

Here we present our studies on hydrogen adsorption on Pt(111) by the surface sensitive thermal desorption spectroscopy (TDS), low-energy electron diffraction (LEED) and vibrational-resonant sum-frequency generation spectroscopy (VSFG). We found that the stable adsorption sites of hydrogen on Pt(111) depend strongly on the substrate temperature when dosing hydrogen. The on-top adsorbed hydrogen is observed by both LEED and VSFG when dosing hydrogen with the substrate temperature at 210 K. We systematically studied the on-top adsorbed hydrogen on Pt(111) under different coverages using VSFG and revealed how the lateral interaction affects the on-top hydrogen-Pt vibrational frequency. Our results indicate that the prepared on-top adsorbed hydrogen might be accessed through a local equilibrium and different than that predicted by current generations of theory.

O 39.6 Tue 18:00 Poster D

***Ab initio*-based Chemisorption and Thermodynamic Stability of Atomic H and O on Pt-Ir Alloy Surfaces** — •Tobias Wittemann, Thorsten Klüner, and Halil Ibrahim Sözen — Institute of Chemistry, Carl-von-Ossietzky University of Oldenburg, 26129 Oldenburg, Germany

Fuel cell electric vehicles (FCEVs) powered by proton-exchange membrane fuel cells (PEMFCs) are a CO_2 emission-free alternative to conventional fossil fuel vehicles. By preventing the phenomenon of anodic carbon corrosion, bifunctional Pt-Ir anode catalysts could help enhancing the long-term durability of the PEMFCs applied in such vehicles.

In our study, we employed density functional theory (DFT) to investigate the chemisorption of atomic hydrogen (H) and oxygen (O) on bimetallic $Pt_3Ir(111)$ and PtIr(111) surfaces in comparison to the monometallic Pt(111) and Ir(111) surfaces. Our results show that the chemisorption on the alloys becomes more exothermic with increasing number of Ir atoms at the adsorption site. Using the *ab initio* thermodynamics approach, we calculated phase diagrams for the H and O adsorption to quantitatively describe the interplay of the pressure, temperature and surface coverage under typical operation conditions of PEMFCs.

Our findings provide a fundamental insight into the H and O adsorption on bimetallic Pt-Ir surfaces and can serve as a starting point for subsequent studies of the hydrogen oxidation reaction (HOR) and oxygen evolution reaction (OER), which are crucial for the rational design of novel anode catalyst materials.

O 39.7 Tue 18:00 Poster D

On-surface reactions of triazido-s-heptazine — •Ilias Gazizullin[1], Christophe Nacci[1], Friedrich Esch[2], and Leonhard Grill[1] — [1]Physical Chemistry Department, University of Graz, Austria — [2]Faculty of Chemistry, TU München, Germany

2,5,8-Triazido-s-heptazine is an aromatic molecule containing only carbon and nitrogen atoms. Heptazine core functionalized with reactive azido-groups makes it an interesting candidate as a precursor for on-surface synthesis of graphitic carbon nitride, an important 2D material [1]. The challenge in this approach is that there are several alternative reaction pathways, which are difficult to control, due to the high reactivity of the aromatic azides [2].

Here, we study these molecules by low temperature scanning tunneling microscopy (STM) under ultra-high vacuum conditions, which allows to study changes in single molecules induced by different impacts. Molecular transformations are induced either by voltage pulses from the STM tip or by illumination with UV light. In each case, we observe two types of processes. Short illumination or short voltage pulse induce dissociation of the azido-group into a molecular nitrogen and a nitrene molecule. On the other hand, longer illumination times lead to drastic increase of the apparent height, which will be discussed in view of other options, for instance the formation of another product or different adsorption configurations.

[1] Krinninger et al., Chem. Mater., 35, 17, 6762 (2023)
[2] Hellerstedt et al., Angewandte Chemie, 58, 2266 (2019)

O 39.8 Tue 18:00 Poster D

Design of a simple and highly reliable evaporator for rare-earth metals — •Tobias Edelmann, Patrick Härtl, Markus Leisegang, and Matthias Bode — Physikalisches Institut, Experimentelle Physik II, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Rare-earth metals exhibit versatile structural, electronic, optical, and magnetic properties. In our technology-based society, there is a significant demand for these metals in various applications, both in applied and basic research. Since the high chemical reactivity of rare-earth metals essentially impedes the preparation of clean surfaces from bulk crystals, their properties are usually studied as thin films which are epitaxially grown on highly pure mono-crystalline substrates. To guarantee the chemical purity of rare earth metal films, we have developed a simple and highly reliable evaporator design. Mounted on a DN35CF-sized electrical feedthrough, this home-built evaporator does not require any external cooling but still remains stable over extended periods of times, facilitating even the deposition of thick layers [1]. The design details will be presented in-depth in this poster, showcasing its application by the characterization of one specific evaporant by means of spin-polarized scanning tunneling microscopy.

[1] P. Härtl *et al.*, Phys. Rev. B **105**, 174431 (2022).

O 39.9 Tue 18:00 Poster D

P2O and P4O on Ag(111): Homogeneous layers, heterostructures, and mixed layers — Ravi Priya, Keda Jin, and •Peter Jakob — Department of Physics, Philipps-Universität Marburg, Germany

A refined structural analysis of 6,13-pentacenequinone (P2O) and 5,7,12,14-pentacenetetrone (P4O) phases on Ag(111) has been conducted using SPA-LEED. In addition, FT-IR absorption spectroscopy and TDS have been employed to characterize the various phases and associated phase transformations. For both species, lateral ordering is governed by orientation-dependent intermolecular interactions including steric hindrance and in particular hydrogen bonding. P2O as well as P4O display characteristic reflexes in LEED, signalling long-range ordering. These patterns are largely retained up to bilayer coverages. When heterolayers are grown, the reflexes of the ordered contact layers are preserved. Layer exchange is found to occur for the 'P4O on P2O' stacking at T > 200K; no such processes are found for the reversed stacking sequence up to the desorption temperatures of second layer P2O. Different ordered P2O-P4O mixed phases have been identified depending on their relative concentrations in the monolayer and their structure determined. In our study different initial layers have been used to create the various P2O-P4O mixed phases: (i) well-defined 'P4O on P2O' heterolayer stacks plus thermal annealing, (ii) co-deposition of P2O and P4O at 83K, followed by annealing, and (iii) incremental increase of P4O concentration within P2O/Ag(111) monolayer by stepwise addition of P4O followed by annealing.

O 39.10 Tue 18:00 Poster D

Structure of tellurium phases on Fe/Ir(111) — •Alexander Wegerich, Tilman Kisslinger, Lutz Hammer, and M. Alexander Schneider — Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

Within the group of transition metal chalcogenides (TMCs), iron tellurides hold great promise in terms of their magnetic and electronic properties [1-2]. A way to prepare such systems in a scalable way accessible for surface science methods is to induce reactions between Te and Fe at the surface of a chosen substrate in ultra-high vacuum. Ir(111) was chosen, since no (surface) telluride formation was observed on Ir(111) enhancing the chance of iron telluride growth upon deposition of Fe and Te.

By quantitative LEED-IV analyses, STM and DFT, we determine the occurring surface structures as function of Te and Fe content and preparation temperatures. No iron telluride phases but the formation of Te adphases on pseudomorphic Fe layers on Ir(111) were observed. At $\Theta_{\mathrm{Te}} = 0.25\,\mathrm{ML}$ a stable Fe/Ir(111)-(2×2)-Te occurs that has no counterpart on the bare Ir(111) surface, whereas increasing Θ_{Te} to 0.33 ML and beyond produces a $\left(\sqrt{3} \times \sqrt{3}\right)\mathrm{R}30^\circ$ adsorbate phase that can be further compressed to accommodate more Te, exactly as for Te on Ir(111).

[1] Z. Zhang et al., Phys. Rev. Mater. **4**, 125003 (2020)
[2] D. Fobes et al., Phys. Rev. Lett. **112**, 187202 (2014)

O 39.11 Tue 18:00 Poster D

Re-calibrating the experimentally derived structure of the metastable surface oxide on copper via machine learning-accelerated in silico global optimization — •Hyun Jun Kim[1], Giyeok Lee[1,2], Seung-Hyun Victor Oh[1], Catherine Stampfl[2,3], and Aloysius Soon[1,2] — [1]Department of Materials Science and Engineering, Yonsei University, Seoul, Republic of Korea — [2]School of Physics, The University of Sydney, NSW, Australia — [3]The University of Sydney Nano Institute, The University of Sydney, NSW, Australia

The oxidation of copper and its surface oxides are gaining increasing attention due to the enhanced CO_2 reduction reaction (CO2RR) activity exhibited by partially oxidized copper among the copper-based catalysts. The "8" surface oxide on Cu(111) is seen as a promising structure for further study due to its resemblance to the highly active $Cu_2O(110)$ in the C-C coupling of CO2RR, setting it apart from other O/Cu(111) surface oxides resembling $Cu_2O(111)$. However, recent X-ray photoelectron spectroscopy experiments analysis challenges the currently accepted atomic structure of the "8", prompting a need for reevaluation. In this study, we highlight the limitations of conventional methods when addressing such challenges, leading us to adopt global optimization search techniques. After a rigorous process to ensure robustness of our computational workflow, the unbiased global minimum of the "8" structure is identified. Interestingly, this new configuration differs significantly from other surface oxides and also from previous "8" models while retaining similarities with the $Cu_2O(110)$ surface.