O 58: Organic molecules on inorganic substrates: Adsorption and growth III

Time: Wednesday 10:30–12:30 Location: TRE/PHYS

O 58.1 Wed 10:30 TRE/PHYS

Probing weak chemical interactions of metal surface atoms with CO-terminated AFM tips identifies molecular adsorption sites — Jalmar Tschakert[1], Qigang Zhong[1], Alexander Sekels[1], Pascal Henkel[2], Jannis Jung[2], K. Linus H. Pohl[2], Hermann A. Wegner[3], Doreen Mollenhauer[4], André Schirmeisen[1], and •Daniel Ebeling[1] — [1]Inst. of Applied Physics, Justus Liebig University Giessen — [2]Inst. of Physical Chemistry, Justus Liebig University Giessen — [3]Inst. of Organic Chemistry, Justus Liebig University Giessen — [4]Inst. for Technical and Environmental Chemistry, Friedrich Schiller University Jena

Understanding reaction mechanisms of adsorbed organic molecules is key to neat on-surface synthesis of functional nanomaterials. Low temperature atomic force microscopy has become an invaluable tool for studying on-surface reaction mechanisms as it allows to visualize the chemical structure of the reactants and products. However, directly accessing the molecule-surface interactions that are responsible for the pathway of on-surface reactions is difficult. Here, we measure chemical interactions between CO-terminated tips and coinage metal surface atoms in all spatial directions with picometer resolution. Identifying the small covalent bonding contributions in the background of the dispersion-dominated interaction enables revealing insights into the nature of chemical bond formation with metal surface atoms and a reliable determination of molecular adsorption sites. The latter can serve as a starting point and for a comparison with theoretical studies.

[1] Tschakert et al., *Nature Communications* **16**, 7874 (2025)

O 58.2 Wed 10:45 TRE/PHYS

Rare earth modified silicon surfaces: A promising template for ordered organic growth — •Milan Kubicki, Philipp Gruber, Marie-Louise Fraser, Mario Dähne, and Martin Franz — Technische Universität Berlin, Institut für Physik und Astronomie, Berlin, Germany

The formation of self-assembled layers of organic molecules on solid surfaces is an important research field because of their possible application in advanced (opto)electronic devices. While the formation of self-assembled layers is well established on metal surfaces, the growth on silicon surfaces, which are still the material of choice in present semiconductor technology, is much less studied. On pure silicon, however, the formation of ordered organic films is usually hindered by its high dangling bond density, so that an appropriate surface modification is required.

Here we demonstrate the high potential of a rare-earth modification of the Si(111) surface for promoting ordered growth. Using scanning tunneling microscopy, the adsorption of different organic molecules on rare-earth modified silicon surfaces was examined, exemplarily for highly reactive N-heterocyclic carbenes and less reactive transition metal phthalocyanines. Our data demonstrate that single molecules remain mobile on the surface at room temperature. At a coverage of one full monolayer highly ordered films can be formed, demonstrating the great potential of rare-earth modified silicon surfaces as template for organic film growth.

[1] M. Kubicki *et al.*, J. Phys. Chem. C **128**, 13347 (2024).

O 58.3 Wed 11:00 TRE/PHYS

N-Heterocyclic Carbenes on GaAs: From Chain Formation to Ordered Monolayers — •Martin Franz[1], Ankita Das[2], Sandhya Chandola[3], Milan Kubicki[1], Mowpriya Das[2], Andrea Sette[4], Domenico Corona[4], Maurizia Palummo[4,5], Letizia Chiodo[6], René Schöder[1], Preeti Chahar[2], Benjamin Fuhrmann[1], Jonathan Engelhardt[1], Oskar Düren[1], Mario Dähne[1], Conor Hogan[4,7], Norbert Esser[1,3], and Frank Glorius[2] — [1]Technische Universität Berlin, Institut für Physik und Astronomie, 10623 Berlin, Germany — [2]Organisch-Chemisches Institut, Universität Münster, 48149 Münster, Germany — [3]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany — [4]Dipartimento di Fisica, Università di Roma ”Tor Vergata”, Rome 00133, Italy — [5]CNR Centro S3, CNR-Istituto Nanoscienze, Modena 41125, Italy — [6]Department of Engineering, Università Campus Bio-Medico, Rome 00128, Italy — [7]CNR-Istituto di Struttura della Materia (CNR-ISM), Rome 00133, Italy

N-Heterocyclic carbenes (NHCs) have emerged as well-established ligands for metal surfaces. First studies on silicon exist as well, while III-V compound semiconductors are the materials of choice for optoelectronic devices. Here, the adsorption behavior of NHCs on GaAs is studied in detail [1]. A covalent binding to the surface and a formation of well-ordered monolayers is found, accompanied by exceptionally large work function reductions. The monolayers consist of NHC chains being the result of an attractive interaction between the molecules.

[1] M. Franz et al., Angew. Chem. Int. Ed., 64, e202511094 (2025).

O 58.4 Wed 11:15 TRE/PHYS

Tuning the adsorption of Subphthalocyanine molecules on Au(111) by peripheral and axial functionalization — •Franz Plate[1], Soyoung Park[2,3], Ebru Cihan[1], Natasha Khera[1], Ningwei Sun[2,3], Dmitry A. Ryndyk[1], Franziska Lissel[2,3], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Institute of Macromolecular Chemistry Leibniz Institute of Polymer Research, Hohe Strasse 6, Dresden, Germany — [3]Institute for Applied Polymer Physics, TU Hamburg, 21073 Hamburg, Germany

Subphthalocyanine (SubPc)-based molecules have been shown to be chemically versatile and tunable molecules, which can be functionalized with a variety of different chemical groups. This makes them promising candidates for designing single molecule machines to store and convert energy. Examples include vertical molecular rotors on surface. Although SubPc is nonplanar, SubPc-based molecules have been shown to form well-ordered molecular assemblies on surfaces, enabling them to function as modular rotor bases. Their chemically stable and rigid core, allows for a functionalization with different axial ligands as well as extensions at the peripheral positions of the π-conjugated base, which leads to different orderings on the surface. We have studied different SubPc based molecules with different axial and peripheral functionalizations on Au(111) using low-temperature scanning tunneling microscopy, supported by simulations. Depending on the peripheral functionalization with methoxy and thiophene groups, we found different adsorption behaviors, ordering, and intermolecular interactions.

O 58.5 Wed 11:30 TRE/PHYS

From Inert Nitrogen to Reactive Metal Nitrene: An On-Surface Route to N-Heterocycles — •Marco Thaler[1], Ricardo Ruvalcaba Briones[2], Shadi Fatayer[2], and Laerte Patera[1] — [1]Department of Physical Chemistry, University of Innsbruck, Innsbruck, Austria — [2]Applied Physics Program, Division of Physical Science and Engineering (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

Nitrenes are highly reactive intermediates in organic chemistry and play a key role in the synthesis of nitrogen containing compounds. In solution, nitrenes are typically generated from chemically activated precursors (e.g., azides), whereas direct conversion of primary amines remains challenging due to the inherent strength of N-H bonds. On surfaces, reactive nitrenes have likewise been formed from organic azides [1]; however, azides are thermally and photochemically labile and can decompose violently upon exposure to heat, light, or mechanical shock, posing safety risks. Here, using combined scanning tunneling microscopy (STM), non contact atomic force microscopy (nc AFM), and density functional theory (DFT), we demonstrate the thermally activated formation of a surface stabilized metal-nitrene intermediate from a chemically inert amine, which mediates the on-surface formation of a nitrogen-containing heterocycle. Our findings establish non activated nitrogen functionalities as viable nitrene precursors and reveal new mechanistic pathways for on-surface synthesis of N-heterocyclic compounds.

[1] Hellerstedt et al., Angew. Chem. 131, 2288-2293 (2019).

O 58.6 Wed 11:45 TRE/PHYS

Mirror domains and adsorption induced dipoles in organic semiconductor films revealed by LEEM and μLEED — •Franz Niklas Knoop, Klaus Stallberg, and Winfried Daum — Institute of Energy Research and Physical Technologies, TU Clausthal, Germany

We apply low-energy electron microscopy (LEEM) and microspot low-energy electron diffraction (μLEED) to study the film growth of nonpolar para-sexiphenyl (p-6P) molecules on natively oxidized silicon.

In their second monolayer, the molecules form μm-sized, 2D-crystals with a bulk-like unit cell. LEEM reveals dark lines that split individual islands along their long axis into two domains of roughly equal size. The corresponding diffraction patterns are laterally shifted relative to each other, allowing for dark-field imaging of each domain. We attribute this apparent shift in k-space to the presence of lateral electric fields pointing in opposite directions on either side of an island. Given *p*-6P's large polarizability, we ascribe these fields to induced electric dipole moments in the tilted molecules. Thus, the observed dark lines represent boundaries between adjacent domains of mirrored tilt. Since the shift in k-space is independent of the LEEM extractor field, the dipoles must be inherent to the adsorbed molecules on the Si substrate. We observe an increased work function for the second-layer islands compared to the substrate. This and temperature-dependent measurements support our conclusion that adsorption-induced charge transfer causes the polarization of the molecules.

O 58.7 Wed 12:00 TRE/PHYS

The Role of Metal Ions in Metal-Phthalocyanine Adsorption on Oxide Surfaces — Matthias Blatnik[1], Fabio Calcinelli[2], Andreas Jeindl[2], Michael Schmid[1], Ulrike Diebold[1], Peter Jacobson[3], Oliver T. Hofmann[2], and •Margareta Wagner[1] — [1]TU Wien, Austria — [2]TU Graz, Austria — [3]University of Queensland, Australia

The interaction of conjugated organic molecules with surfaces is of fundamental interest and also important in many applied areas. Surface science investigations have advanced understanding of organic/metal interfaces, but the second electrode in organic optoelectronic devices – typically the transparent conductive oxide In_2O_3 – remains largely unexplored. Our work aims at closing this gap by examining the model system phthalocyanines on indium oxide surfaces.

Phthalocyanines adsorbed on the $In_2O_3(111)$ surface were studied experimentally with low temperature STM and AFM, combined with DFT calculations. A key aspect is the comparable size of the molecules and the surface unit cell, which allows a (1×1) arrangement despite the differing symmetries. Various metal phthalocyanines (MPc: CuPc, CoPc, etc.) are investigated to reveal the influence of the metal ion in the selection of adsorption sites, 2D condensation, and the formation of the first layer. We identify a common, robust adsorption site for different MPc that forces the molecules to overlap in the (1×1) structure of the first layer, and a less common site, where a (1×1) packing without overlap is realized.

O 58.8 Wed 12:15 TRE/PHYS

***In Situ* Field-Induced Switching of Global Chirality in Halogen-Bonded Kagomé Networks** — •Nico Kubetschek, Jana Dietrich, and René Matzdorf — Institute of Physics, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

We used small organic molecules to construct a chiral Kagomé lattice on the Ag(111) and Au(111) surfaces. The chirality arises from triple halogen bonds that form windmill-like structures. Under certain conditions, we observe a switching in the rotational sense of whole terraces while scanning with STM. The total molecular coverage was used to tune the switching probability between the two chiral states. We demonstrate a bias-dependent attraction or repulsion of the molecules relative to the STM tip position, explaining the observed perturbation leading to the switching events.