

O 28: Organic Molecules on Inorganic Substrates III: Adsorption and Growth I

Time: Tuesday 10:30–13:00

Location: CHE 89

O 28.1 Tue 10:30 CHE 89

Tuning interfaces properties via deposition conditions: thermodynamic's deed and kinetic's contribution — ANNA WERKOVITS, JOHANNES J. CARTUS, LUKAS HÖRMANN, and •OLIVER T. HOFMANN — Institute of Solid State Physics, Tu Graz

The interface dipole of an inorganic-organic interface depends strongly on the structure, i.e. the polymorph, the organic molecules assume. This is not a subtle effect: In the past years, studies reported work functions differing between up to 3 eV between different polymorphs, illustrating how important it is to control the growth of these interfaces.

In this work, we discuss on the basis of first-principle calculations how the molecule-substrate, the intermolecular interaction and the size of the molecule affect the relative thermodynamic stability of different phases for different deposition conditions, and how this directly relates to observed work function changes. Based on this, we discuss two ways strategies to tune interface properties. Either, the relative stability can be modified, e.g. by growing the interface in an electric field. Alternatively, it is also possible to exploit kinetic effects during the growth and trap desired phases. Based on the example of TCNE on Cu(111) we discuss how a given phase can be kinetically trapped, and under which circumstances we expect thermodynamic equilibrium to prevail.

O 28.2 Tue 10:45 CHE 89

Homo- and Heterochiral Phases of Quinacridone Monolayers on Ag(110) and Ag(111) — •RAVI PRIYA, WEISHAN WU, KEDA JIN, and PETER JAKOB — Fachbereich Physik, Philipps-Universität Marburg, Germany

When adsorbed on a surface, parallel-oriented quinacridone (QA) transforms into a chiral species and lateral interaction between neighboring molecules will depend on the types of enantiomers facing each other. On Ag(111) a homochiral phase comprising rows of (identical) QA has been reported that, upon thermal annealing, converts to a heterochiral phase consisting of alternating pairs (dimers) of the two enantiomers [1]. In our study, we have refined the structural analysis of QA/Ag(111) phases and have extended the available database to QA on Ag(110). Besides SPA-LEED, IR-spectroscopy and TDS were employed to characterize the various phases and associated phase transformations in detail. From IRAS and TDS a stronger molecule-substrate interaction is deduced for Ag(110) as compared to Ag(111). In parallel, interfacial dynamical charge transfer (IDCT) is considerably enhanced for QA/Ag(110) which is ascribed to an extra downshift of the QA-LUMO, increasing its DOS at the fermi energy. Interestingly, IDCT vanishes completely upon the transition of the homochiral to the heterochiral arrangement, both on Ag(111) and Ag(110). This could be explained by a completely empty, or a fully occupied LUMO [2]. As this transition is accompanied by a notable increase in the work function, we conclude that the latter applies.

[1] <https://doi.org/10.1021/jp502148x>[2] <https://doi.org/10.1103/PhysRevLett.126.116801>

O 28.3 Tue 11:00 CHE 89

Morphology and luminescence of rubrene nanocrystals: a road to tailor nanoplatelets — •MOHA NAEIMI, KATHARINA ENGSTER, CHRISTIAN VÖLKNER, REGINA LANGE, SYLVIA SPELLER, and INGO BARKE — University of Rostock, Institute of physics, Rostock, Germany

Rubrene (C₄₂H₂₈ 5,6,11,12-tetraphenyltetracene) single crystals with a few monolayers had been reported to have high charge mobility of 43 cm²/Vs [1] and singlet-fission dynamics [2] which are promising properties for the application of excitons for energy transfer or information processing. We aim for the investigation of the spatial distribution of excitons in molecular assemblies on surfaces, requiring thin films or flat nanocrystals. In the present work, we report on the preparation of rubrene platelets by various methods from simple spin-coating to thermal evaporation and broad growth conditions, followed by a high-rate post-annealing temperature treatment on different types of substrates [3]. Ranging from 10 nm to 150 nm, we show that the thickness of rubrene platelets is widely dependent on the rate and time of temperature treatment as well as on the rubrene coverage on the surface. Moreover, we discuss thermal stability and photo-degradation

for different morphologies.

[1] A. Saeki. et al., *Adv. Mater.* 20, 2008, 920-923[2] Lin Ma. et al., *Phys. Chem. Chem. Phys.* 14, 2012, 8307-8312[3] Hyeok Moo Lee. et al., *Org. Electron.* 12, 2011, 1446-1453

O 28.4 Tue 11:15 CHE 89

Photoelectron Spectroscopy of N-heterocyclic carbenes on Si(111)(√3 × √3)R30°-B surface — •MIKE THOMAS NEHRING¹, ROBERT ZIELINSKI¹, MOWPRIYA DAS², HAZEM ALDAHAK³, CONOR HOGAN⁵, UWE GERSTMANN³, WOLF GERO SCHMIDT³, MARIO DÄHNE¹, MARTIN FRANZ¹, FRANK GLORIUS², and NORBERT ESSER⁴ — ¹Institut für Festkörperphysik, Technische Universität Berlin, Berlin, Deutschland — ²Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Münster, Deutschland — ³Institut für Theoretische Materialphysik, Universität Paderborn, Paderborn, Deutschland — ⁴Leibniz-Institut für Analytische Wissenschaften - ISAS e.V., Berlin, — ⁵Institute for Structure of Matter (ISM-CNR), Rome, Italy

Silicon is the most commonly used element in the industry for manufacturing semiconductor-based components. Semiconductor devices today represent a cornerstone of modern technology, with a multitude of possible applications in research and development. A relatively new area of research is the growth of organic films on modified silicon surfaces. In this work we investigate the adsorption behaviour of various N-heterocyclic carbenes (NHCs) on the Si(111)(√3 × √3)R30°-B surface. This research is conducted using X-ray photoelectron spectroscopy (XPS). By comparison of the experimental spectra with theoretical calculations it is found that all investigated NHCs bind to the Si adatoms of the Si(111)-B surface in an upright adsorption geometry. In addition, the monolayers show a high thermal stability and large work function reductions.

O 28.5 Tue 11:30 CHE 89

Adsorption and thermal stability of phenyl phosphonic acid on cerium oxide: effect of surface morphology, stoichiometry and composition. — •VIACHESLAV KALINOVYCH¹, LESIA PILIAT¹, YULIYA KOSTO¹, SASCHA L. MEHL², TOMÁŠ SKÁLA¹, IVA MATOLINOVÁ¹, VLADIMÍR MATOLÍN¹, KEVIN C. PRINCE², and NATALIYA TSUD¹ — ¹Charles University, Faculty of Mathematics and Physics, Department of Surface and Plasma Science, V Holešovičkách 2, Prague, 18000, Czech Republic — ² Elettra-Sincrotrone Trieste S.C.p.A., in Area Science Park, Strada Statale 14, km 163.5, Basovizza (Trieste), 34149, Italy

In the present work, the binding properties and thermal stability of the phosphonate group to several well-ordered cerium oxide systems: stoichiometric CeO₂(111), fully reduced Ce₂O₃(111), Ce₆WO₁₂(100) and polycrystalline RF CeO₂ were studied. Phenyl phosphonic acid (PPA) has been chosen as a molecule consisting of a phosphonate group and a benzene ring. PPA deposition was performed in UHV conditions. The binding properties and thermal stability has been investigated in the range of 25-450 °C by synchrotron radiation photoelectron spectroscopy, resonant photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. This work comprehensively describes the phosphonate group binding to cerium oxide as a function of substrate morphology, stoichiometry, composition and temperature.

O 28.6 Tue 11:45 CHE 89

Adsorption of a Cyclic (Alkyl)(Amino)Carbene on Si(111)(√3 × √3)R30°-B: Influence of the Defect Density — •ROBERT ZIELINSKI¹, MOWPRIYA DAS², CANAN KOSBAB¹, MIKE THOMAS NEHRING¹, MARIO DÄHNE¹, NORBERT ESSER^{1,3}, MARTIN FRANZ¹, and FRANK GLORIUS² — ¹Institut für Festkörperphysik, Technische Universität Berlin, Berlin, Deutschland — ²Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Münster, Deutschland — ³Leibniz-Institut für Analytische Wissenschaften - ISAS e.V., Berlin, Germany

N-Heterocyclic carbenes (NHCs) have been shown to be excellent modifiers and anchors for the functionalization of surfaces, but so far mostly on metals. Thus a controlled functionalization of semiconductor surfaces by ordered NHC layers is of great interest. In the present work we investigate the adsorption behavior of cyclohexyl cyclic (alkyl)(amino)carbene (cyCAAC) molecules on the Si(111)(√3 ×

$\sqrt{3}$)R30°-B surface using scanning tunneling microscopy and X-ray photoelectron spectroscopy. We find a self-limited, well-ordered growth of a stable monolayer with large domains characterized by a 3×3 periodicity and an upright adsorption geometry of the molecules. A strong correlation between the domain size and the substrate defect density is found, revealing that the initial molecular adsorption preferentially takes place on a particular type of surface defect. Work function measurements of the cyCAAC monolayer reveal a large reduction of work function.

O 28.7 Tue 12:00 CHE 89

Electronic properties of radical helicene molecules on metallic substrates — ●ALEŠ CAHLÍK¹, DANYANG LIU¹, CAROLINA A. MARQUES¹, YA-CHU HSIEH², YAO-TING WU², KARL-HEINZ ERNST³, and FABIAN D. NATTERER¹ — ¹Department of Physics, UZH, Zurich, Switzerland — ²Department of Chemistry, National Cheng Kung University, Tainan, Taiwan — ³Molecular Surface Science Group, EMPA, Zurich, Switzerland

Helicenes are π -conjugated aromatic compounds with helical shape arising from angularly fused aromatic rings. Radical helicenes combine unpaired electron spins with structural chirality and a π -conjugated framework that can offer intriguing prospects to study the synergy of electronic transport, magnetism and photoactivity. In our work, we employ STM and nc-AFM to investigate an open-shell biradical helicene that we adsorb onto metallic substrates, including magnetic nanoislands. Notably, we observe a Kondo resonance pointing towards the preservation of the open-shell character upon deposition onto Au(111).

O 28.8 Tue 12:15 CHE 89

STM growth studies of 5,14-ol-5,14-diborapentacyclo on low-index coinage metal surfaces — ●WUN-CHANG PAN¹, JING QI¹, CARINA MÜTZEL², PAULA WEBER¹, FRANK WÜRTHNER², and MATTHIAS BODE¹ — ¹Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Institut für Organische Chemie & Center for Nanosystems Chemistry (CNC), Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

In recent studies [1, 2], heteroatoms-doped precursors have frequently been used to polymerize graphene nanoribbons with a large variety of structures or dopant heteroatoms. Using cryogenic scanning tunneling microscopy, we investigated the structure of self-assembled 5,14-ol-5,14-diborapentacyclo (CM218) on low-index coinage metal surfaces. The main focus of our study is on CM218 on Ag(111), where we find that molecular clusters and chains coexist with molecular islands. At low annealing temperature $T_{\text{ann}} < 100^\circ\text{C}$, the islands exhibit a rail track-like structure with a rhomboid-shaped unit cell. Besides, we find irregular clusters and molecular chains. At higher $T_{\text{ann}} \geq 180^\circ\text{C}$, is-

lands with a honeycomb (HC) structure are observed. Topographic images of these HCs display a pronounced bias dependence. Molecule-functionalized tips allow for high-resolution images of these structures for which we suggest structural models.

[1] L. Grill and S. Hecht, *Nature Chemistry* **12**, 115 (2020)

[2] Q. Zhong *et al.*, *Nature Chemistry* **13**, 1133 (2021)

O 28.9 Tue 12:30 CHE 89

Variable Temperature Scanning Tunneling Microscopy Investigation on Pyrene Monolayers — ●PATRICK PENNER, XI-ANGHUI ZHANG, BERTHOLD VÖLKEL, and ARMIN GÖLZHÄUSER — Physik Supramolekularer Systeme und Oberflächen, Universität Bielefeld, Bielefeld, Germany

Pyrene (C₁₆H₁₀) monolayers were prepared by physical vapor deposition on Au(111). Afterwards they were investigated with a variable temperature scanning tunneling microscope with the capability to cool the surface down to -80°C . Without prior cooling, it was impossible to image any molecules at room temperature. After reaching a temperature of 10°C first images could be made. Independent of the temperature the molecules seem to be lying flat on the sample, with a next-neighbor distance of 1.05 nm. After cooling down it was possible to scan at room-temperature small domains of pyrenes near edges of gold terraces, as well as single mobile pyrene molecules.

O 28.10 Tue 12:45 CHE 89

Predicting optimal growth conditions for metastable interface structures — ●SIMON HOLLWEGER, ANNA WERKOVITS, RICHARD K. BERGER, LUKAS HÖRMANN, JOHANNES CARTUS, and OLIVER T. HOFMANN — Institute of Solid State Physics, University of Technology Graz, Austria

For tailoring organic-inorganic interfaces of organic electronic devices controlling the structure that forms during growth is of high importance. Indeed, interface properties often strongly vary for different interface structures. But growing the structure that has the optimal properties for a certain technical application is nothing but trivial, due to the subtle interplay of thermodynamics and kinetics that strongly depend on the growth conditions like temperature and pressure. Therefore, we study how to change temperature and pressure over time in an optimal way to maximize the concentration of a specific high-performance polymorph. The target structure must then be one that is either thermodynamically or kinetically accessible. Finding optimal processing parameters experimentally is a tedious trial and error task, which can be greatly simplified with theoretical guidance. Using the framework of Optimal Control theory, such optimal temperature and pressure protocols can be obtained. In this talk we will demonstrate how this method can be technically implemented, discuss first applications, and point out its possible pitfalls and limitations for the case of designing organic-inorganic interfaces.