

O 20: Inorganic/Organic Interfaces: Growth III

Time: Tuesday 10:30–13:15

Location: MA 005

O 20.1 Tue 10:30 MA 005

Tetrahydrofuran adsorption mechanism on Si(001)-c(4x2): A systematic density functional study. — ●SLIMANE LAREF RALF TONNER — Fachbereich Chemie, Hans Meerwein Straße, 35032 Marburg, Germany

The silicon surface plays a decisive role for semiconductor devices. Thereby, the adsorption of organic molecules on silicon can play a major role in increasing functionalizing these semiconductors and even improve device properties in the long term [1]. Small organic molecules preferably react with one dimer on the clean surface which is related to the unique reconstruction of the clean silicon (001) surface [2-5]. Recently, experimental results [6] showed that tetrahydrofuran (THF) molecules exhibited a two-step reactivity on the silicon surface. Starting from these findings, we carried out a systematic density functional theory study to elucidate the main chemical processes of THF on Si(001)-c(4x2). All computational investigations were carried out within Vienna ab initio simulation package [7]. However, for treating electron interactions all calculations were established by mean of Perdew, Burke and Ernzerhof (PBE) for the exchange-correlation function [8]. In addition, for weak interaction we used semi-empirical dispersion correction terms (DF-T-D3) with an advanced damping function [9]. We calculate the adsorption energies and the kinetic barriers as well as the key structures that characterize the chemical reactions on the surface. A notable conclusion of this study is that the dissociation of THF molecules is dominated by kinetic effects in terms of a barrierless dissociation across the dimer trough.

O 20.2 Tue 10:45 MA 005

In-situ reflection anisotropy spectroscopy study of the MOCVD prepared Si(111) surface — ●AGNIESZKA PASZUK, WEIHONG ZHAO, MATTHIAS STEIDL, SEBASTIAN BRÜCKNER, OLIVER SUPPLIE, ANJA DOBRICH, PETER KLEINSCHMIDT, and THOMAS HANNAPPEL — Technische Universität Ilmenau, FG Photovoltaik, Gustav-Kirchhoff-Str. 5, 98693 Ilmenau

Integrating III-V materials with Si substrates could combine the superior optoelectronic properties of the III-V compounds with the low-cost silicon technology. Further benefits may arise from applying nanowires which require less material than planar devices and might achieve efficiencies similar to today's best solar cells. By forming a p-n junction within Si substrates we could create a tandem solar cell exceeding the Shockley-Queisser limit associated with a single junction. Our approach is to grow a thin GaP buffer layer as a transition between silicon and the active III-V material. In dependence on the pre-growth Si(111) surfaces preparation, we are able to control the polarity of the GaP buffer. GaP films grown on the H-terminated Si(111) have A-type polarity, while GaP grown on Si(111) surface terminated with arsenic have B-type polarity. Here, we studied the preparation of the clean Si(111) or arsenic terminated surfaces in hydrogen ambient. By XPS we confirm complete oxide removal after high temperature annealing. Moreover, we can observe a change in the reflectance anisotropy (RA) spectrum after the deoxidation process, which depends on the Si surface termination and Si offset direction. FTIR confirms Si surface termination by monohydride or arsenic.

O 20.3 Tue 11:00 MA 005

Growth of α -sexithiophene (α -6T) on a textured rutile TiO₂(110) surface — ●THORSTEN WAGNER, MICHAEL MÜHLEGGGER, EBRAHIM GHANBARI, and PETER ZEPPEFELD — Johannes Kepler University Linz, Austria

Titanium dioxide (TiO₂) is a wide band gap semiconductor with applications as photocatalyst, in solar energy converters, and in electronic devices based on organic thin films. In this work, we studied the growth of the prototype organic semiconductor α -sexithiophene (α -6T, C₂₄H₁₄S₆) on the (110) surface of rutile TiO₂ single crystals. In particular, we used the real-time imaging capabilities of Photoelectron Emission Microscopy (PEEM) to study side-by-side the growth of α -6T on a well prepared part of the surface and on a part of the surface which was modified by ion bombardment. To texture the surface, first several cycles of oxygen exposure, annealing, and sputtering were carried out. Finally, one part of the sample was sputtered with Ar⁺ ions for 5 min while the other part was protected by an aperture. The ion bombardment of the TiO₂ surface introduces oxygen vacan-

cies. Morphological changes of the surface and these oxygen vacancies can modify the growth of the organic dye molecules α -6T as demonstrated by Ivanco *et al.* By imaging spectroscopy we can confirm the local modification of the TiO₂ surface upon sputtering. Local transients of the PEEM intensity were obtained during deposition of the organic material. Finally, the individual crystallites were probed by imaging spectroscopy to study their electronic properties.

O 20.4 Tue 11:15 MA 005

Tuning the self-assembly of triarylamine derivatives on KBr(001) — ●CHRISTIAN STEINER¹, TIM SANDER¹, MAXIMILIAN AMMON¹, NATALIE HAMMER², BETTINA GLIEMANN², UTE MEINHARDT², MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, FAU Erlangen-Nürnberg, Germany — ²Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany

Electrically insulating surfaces generally have a lower surface energy than their metallic counterparts. As a consequence organic molecules without a specific bonding motif often lack sufficient interactions with the insulating surface, and tend to dewet or form unordered clusters along step edges.

Here, we present a low temperature non-contact AFM study on the adsorption geometry of hydrogen-bonding and halogen functionalized triarylaminos on KBr(001). Dimethyl bridged triarylaminos adopt a flat-lying adsorption geometry. The structure of the hydrogen-bonding networks is influenced by the underlying lattice geometry. In contrast, the more compact carbonyl bridged triarylaminos favour an intermolecular π - π interaction, which leads to a nearly upright adsorption geometry. The nearly upright molecules form linear aggregates along the [110]-direction. These results show that the adsorption geometry of triarylaminos can be tuned by a suitable choice of functional groups, and that the molecule-surface interaction is not neglectable on KBr(001).

O 20.5 Tue 11:30 MA 005

Self assembly of amino substituted carbonyl bridged triarylaminos — ●MAXIMILIAN AMMON¹, TIM SANDER¹, PATRICK SEITZ¹, CHRISTIAN STEINER¹, MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, FAU Erlangen-Nürnberg, Germany — ²Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany

Triarylamine derivatives are versatile building blocks for a variety of application-oriented molecular structures including organic field effect transistors [1] and optoelectronic devices [2]. Here we present a scanning tunneling and non-contact atomic force microscopy study at low temperatures on the self-assembly of triarylaminos with amino and carbonyl functional groups. Self-assembled porous networks are expected to form due to the hydrogen-bonding motif, which we observe on Au(111). Its structure will be discussed based on scanning tunneling hydrogen microscopy [3] measurements. The self-assembly strongly depends on the surface reactivity and the molecule-surface interaction. Scanning tunneling microscopy measurements on Cu(111) also show a porous network, but indicate a binding motif based on metal ligand interaction. In contrast, the molecules adopt a nearly upright adsorption geometry, stabilized by intermolecular π - π -interactions, on KBr(001).

[1] K. Schmoltner *et al.*, *Polym. Chem.* 4, 5337-5344 (2013).[2] C. Liu *et al.*, *Chem. Eur. J.* 18, 6928-6934 (2012).[3] Weiss, C. *et al.*, *PRL* 105, 086103 (2010).

O 20.6 Tue 11:45 MA 005

Steering molecular self-assembly of biphenyl-dicarboxylic acid on Cu(111) by tuning the carboxylic hydrogen content — ●TOBIAS SCHMITT, LUTZ HAMMER, and M.ALEXANDER SCHNEIDER — Solid State Physics, Univ. Erlangen-Nürnberg, 91058 Erlangen, Germany

Molecular self-assembly is mainly controlled by a complex interplay between molecule-substrate interaction and intermolecular interactions such as hydrogen bonding. We report on the ordered phases of 4,4'-biphenyl-dicarboxylic acid (BDA) on Cu(111) using low temperature scanning tunneling microscopy in ultra-high vacuum. We deposit the molecules at various temperatures to introduce different degrees of thermally activated deprotonation. This leads to different (locally) ordered supramolecular structures. In the case of non-deprotonated BDA head-to-tail coupling between carboxylic groups dominates due

to H-bond formation. This mechanism is observed also in semi-deprotonated structures. Fully deprotonated carboxylic groups, in contrast, form chevron-like structures by the interplay of intermolecular carboxylate-aromatic ring hydrogen bonds and carboxylate-copper interaction.

O 20.7 Tue 12:00 MA 005

Adsorption Phenomena of Thioether-functionalized $\{\text{Ni}^{\text{II}}_4\}$ Coordination Complexes on Au(111) — •VOLKMAR HESS¹, FRANK MATTHES¹, DANIEL E. BÜRGLER¹, CLAUS M. SCHNEIDER¹, KIRILL YU. MONAKHOV², CLAIRE BESSON², PAUL KÖGERLER², ALESSIO GHISOLFI³, and PIERRE BRAUNSTEIN³ — ¹Peter Grünberg Institute, Electronic Properties (PGI-6), Forschungszentrum Jülich, 52425 Jülich, Germany — ²Institut für Anorganische Chemie, RWTH Aachen University, 52074 Aachen, Germany — ³Laboratoire de Chimie de Coordination, Université de Strasbourg, 67081 Strasbourg, France

The anchoring and organization of sulfur-containing heterocyclic groups on metallic substrates is still barely explored. The chemical deposition of a cubane-type $\{\text{Ni}^{\text{II}}_4\}$ ($=[\text{Ni}_4(\mu_3\text{-Cl})_4\text{Cl}_4(\text{HL-S})_4]$) coordination complex terminated by cyclic thioether functional groups from a dichloromethane solution on the Au(111) surface is investigated by STM imaging and surface chemical characterization via XPS, AES, and LEED, both immediately after deposition and after subsequent post-annealing steps. The results provide strong evidence for a partial decomposition of the complex upon deposition on the Au(111) surface that however leaves the magnetic cubane-like $\{\text{Ni}^{\text{II}}_4\text{Cl}_{4n}\}$ ($n = 1$ or 2) core of the complex intact. Only post-annealing above 500 K induces further decomposition and fragmentation of the $\{\text{Ni}^{\text{II}}_4\text{Cl}_{4n}\}$ core. The detailed insight into the chemisorption-induced decomposition pathway provides guidelines for realizing the deposition of thioether-functionalized molecules on metal surfaces.

O 20.8 Tue 12:15 MA 005

Peptides as bio-organic building blocks for self-assembly on surfaces — •SABINE ABB¹, LUDGER HARNAU^{2,3}, STEPHAN RAUSCHENBACH¹, and KLAUS KERN^{1,4} — ¹Max-Planck-Institute for Solid State Research, Heisenbergstr. 1, Stuttgart — ²Max-Planck-Institute for Intelligent Systems, Heisenbergstr. 3, Stuttgart — ³IV. Institute for Theoretical Physics, University Stuttgart, Pfaffenwaldring 57, Stuttgart — ⁴Ecole Polytechnique Fédérale de Lausanne, Switzerland

In the past decade, the self-assembly of molecules on surfaces via hydrogen bonding and metal coordination has been studied extensively with small, specifically designed organic molecules, yielding a huge variety self-assembled structures. Peptides and proteins are the building blocks of biological self-assembly employing the same bonding motifs. Electro-spray ion beam deposition (ES-IBD) enables us to deposit these non-volatile molecules intact in ultra-high vacuum (UHV) where they can be investigated with high precision by STM.

Here, we report the self-assembly of angiotensin II, an 8 amino acid peptide, on metal surfaces. We deposited submonolayer coverage in vacuum by ES-IBD and subsequently investigated the assemblies by STM. While the peptide forms regular yet isolated trimer assemblies on Cu(111) surfaces, long range ordering into a chiral honeycomb network can be observed on Au(111). By a combination of high resolution STM and atomistic MD simulation, we are able to provide an atomistic model and highlight important aspects of peptides as bio-organic building blocks.

O 20.9 Tue 12:30 MA 005

Racemate versus conglomerate: Chiral pentahelicene on Cu(111) — •ANAÍS MAIRENA¹, JOHANNES SEIBEL¹, LIYING MA¹, ALIX F. TRÖSTER², KONSTANTIN GRENADER², ANDREAS TERFORT², and KARL-HEINZ ERNST^{1,3} — ¹Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland — ²Goethe Universität Frankfurt am Main, Germany — ³University of Zurich, Switzerland

We studied the 2D self-assembly of racemic pentahelicene ([5]H, C₂₂H₁₄) on Cu(111) with STM. Adsorption of [5]H leads to formation of homochiral pairs already at very low coverages, as observed with STM at 7 K. After deposition at room temperature and cooling to 50 K, two distinct long-range ordered structures have been observed at higher coverages (0,97% of ML). Both structures still have the homochiral pairs as building blocks. While one structure is racemic, i.e., it is composed of homochiral pairs with opposite handedness, the second structure consists of homochiral domains. At monolayer saturation coverage, only a conglomerate of homochiral domains prevails. The two types of homochiral domains are respectively tilted by +15° and -15° compared to the Cu substrate. A surface-mediated selection mechanism is presented and discussed.

O 20.10 Tue 12:45 MA 005

Pyrene derivatives on Au(111): the role of halogen substituents in self-assembled network formation — •VAN BAY TRAN¹, TUAN ANH PHAM¹, FEI SONG¹, MANH THUONG NGUYEN², and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, the Netherlands — ²The Abdus Salam International Center for Theoretical Physics, Strada Costiera 11, I-34151 Trieste, Italy

Halogen bonding is nowadays considered as an important tool for steering intermolecular interactions in supramolecular chemistry as well as crystal engineering. The formation of two dimensional (2D) molecular networks based on halogen bonding interactions has recently been reported at the solid-vacuum interface as well as at the solid-liquid interface. This is expected to open up new opportunities for the construction of organic thin film-based devices for future applications. However, the exact role of the halogen substituents in the structural formation of such networks attracts less attention and therefore, asks for more studies. In this work, we present the self-assembly of two bromine-functionalized pyrene derivatives on a Au(111) substrate by using scanning tunneling microscopy and low energy electron diffraction under ultrahigh vacuum conditions combined with density functional theory calculations. The study focuses on the influence of the halogen substituents on the resulting 2D molecular networks. Based on the theoretical calculations, the obtained self-assembled patterns are explained via optimizing the intermolecular interactions.

O 20.11 Tue 13:00 MA 005

Covalently bonded networks by surface-confined coupling of copper-octabromotetraphenylporphyrin — •LARS SMYKALLA¹, PAVEL SHUKRYNAU¹, MARCUS KORB², RASHA K. AL-SHEWIKI², HEINRICH LANG², and MICHAEL HIETSCHOLD¹ — ¹Technische Universität Chemnitz, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany — ²Technische Universität Chemnitz, Inorganic Chemistry, D-09107 Chemnitz, Germany

We demonstrate the on-surface synthesis of a two-dimensional covalent organic network starting from copper-2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin molecules. Results of this molecule on Au(111) [1] are compared to its adsorption on the more reactive and anisotropic Ag(110) surface. Splitting-off of bromine atoms bonded at the macrocyclic core of the porphyrin is monitored by X-ray photoelectron spectroscopy for different annealing steps. Upon annealing to high temperatures depending on the substrate, direct coupling between the reactive carbon sites of the molecules occurs which links the molecular macrocycles with phenyl groups of adjacent molecules. Thus, the initial, ordered, non-covalently interconnected supramolecular structure is completely transformed into a close-packed covalently bonded network of overall good quality. The structures are characterized using scanning tunneling microscopy. Lattice defects and the change of the electronic structure are discussed.

[1] L. Smykalla, P. Shukrynau, M. Korb, H. Lang, M. Hietschold: "Surface-confined 2D polymerization of a brominated copper-tetraphenylporphyrin on Au(111)", under review