

O 32: Poster Session - Organic Molecules on Inorganic Substrates: Adsorption and Growth

Time: Monday 18:15–20:00

Location: P1C

O 32.1 Mon 18:15 P1C

STM Investigations of Insulating Xenon Interfaces on Silver Surfaces as Low Interaction substrates for Advanced Carbene Studies — ●INGA LANGGUTH¹, MARVIN QUACK¹, IRIS TROSIEN², WOLFRAM SANDER², and KARINA MORGENSTERN¹ — ¹Chair of Physical Chemistry I, Ruhr-University of Bochum, Germany — ²Chair of Organic Chemistry II, Ruhr-University of Bochum, Germany

The outstanding high reactivity of carbene molecules is of central interest in catalysis and basic research. For the understanding of these reactive intermediates, scanning tunneling microscopy (STM) is a highly favorable technique to gain locally resolved insight into the electronic structure of carbenes and their precursors. For an unperturbed characterization of these molecules, advanced surface decoupling methods are needed, in order to exclude dominating surface influences. Hence, the strategy of this work is to mimic the low interaction conditions between carbenes and their chemical environment as present in rare gas matrices by preparation of an ultra-thin non-conducting rare gas interface. Thus, the consecutive adsorption of xenon (Xe) followed by fluorene based carbene precursors on silver single crystals is investigated by low-temperature STM in ultra-high vacuum. Kinetically restricted precursor molecules are found to dictate the rotational orientation of Xe domains.

O 32.2 Mon 18:15 P1C

Comparison of Donor-Acceptor Coupling Strength with Chemisorption on Different Metal Substrates — ●QI WANG, ANTONI FRANCO-CAÑELLAS, ALEXANDER GERLACH, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany

As crucial element in opto-electronic devices heterostructures are of pivotal importance. Here, we present a comprehensive study on the properties of a donor-acceptor (D-A) bilayer structure using X-ray photoelectron spectroscopy (XPS) and normal-incidence X-ray standing wave (NIXSW) measurements. Accordingly, an acceptor material-pentacene (PEN) and a donor material-perfluoropentacene (PFP) are chosen to build bilayer structures. PFP/PEN bilayers have been grown on Au(111) and Cu(111) substrates, i.e., coinage metal surfaces with different reactivity. By comparing the adsorption behavior of pentacene and its perfluorinated partner, we found that: i) on Au(111), the first layer (PEN) is physisorbed, whereas on Cu(111) the molecule-substrate interaction is much stronger, ii) the D-A bonding distances indicate that within the bilayer van-der-Waals interactions dominate.

O 32.3 Mon 18:15 P1C

The adsorption structure of acetophenone on Si(100) — ●PAULA L. LALAGUNA^{1,2}, PAUL T. P. RYAN^{1,3}, PROCOPI C. CONSTANTINOU⁴, MATTHIAS MUNTWILER⁵, HOLLY HEDGELAND⁶, STEVEN R. SCHOFIELD⁴, and DAVID A. DUNCAN¹ — ¹Diamond Light Source, Didcot, OX11 0QX, UK — ²University of Glasgow, G12 8QQ, UK — ³Imperial College London, SW7 2AZ, UK — ⁴University College London, WC1H 0AH, UK — ⁵Paul Scherrer Institute, 5232 Villigen, Switzerland — ⁶The Open University, Milton Keynes, MK7 6AA, UK

Over the last decade, Moore's law has begun to slow as fundamental length scale limits are being reached in the utilization of Si for transistors (~14 nm)[1]. One potential method for delaying the end of Moore's law is to pattern Si surfaces with organic molecules, providing an accessible length scale in the order of a few ångströms. However, in order to understand how these molecules interact and alter the Si substrate, high quality and high precision measurements are required. Here we will present one such study of Si(100) patterned with acetophenone by energy scanned photoelectron diffraction (PhD). Acetophenone is believed to anchor to the Si substrate via a strong covalent bond[2]. Utilizing PhD, we provide an insight into this anchoring, specifically measuring the Si-O bond length of the adsorbed molecule to a precision of a few hundredths of an ångström. [1] Nature 530, 144 (2016); [2] J. Phys. Condens. Matter 27, 054002 (2015).

O 32.4 Mon 18:15 P1C

Structure of tetracene films on hydrogen-passivated Si(111) and amorphous Si — ●HAZEM ALDAHAK¹, JENS NIEDERHAUSEN², ROWAN W. MACQUEEN², WOLF GERO SCHMIDT¹, KLAUS LIPS², and

UWE GERSTMANN¹ — ¹Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany — ²Institute for Nanospectroscopy, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

The properties of the Tetracene (Tc)-Silicon (Si) interfaces are of particular interest when trying to augment the Si solar cells by singlet fission in Tc. Here, we combine Near-edge X-ray absorption fine structure (NEXAFS), x-ray photoelectron spectroscopy (XPS) as well as density functional theory (DFT) calculations to elucidate the structure of the first Tc monolayer on hydrogen-passivated Si(111) and amorphous Si (H:a-Si). Typically, the first monolayer is hampered by the significant dewetting tendency of Tc at room temperature. Here, we present a selective study using cooling to limit the thermal energy of the Tc molecules during growth and measurements. We find that the first Tc monolayer on cooled substrates exhibits a mixture of the bulk-like Tc (Tc I) and the surface-induced thin film (Tc II) phases. The DFT calculated total-energies and angle-dependent NEXAFS fingerprints support the measurements. Further heating of the cool Tc/H:Si(111) film to room temperature indicates structural changes towards lower Tc inclination, rendering the appearance of this phase to rely on sufficient amount of thermal energy being available.

O 32.5 Mon 18:15 P1C

Adsorption of miRNA molecules on metal surfaces studied by STM — ●MIRIAM MEYER^{1,2}, CHRISTOPHE NACCI¹, GRANT J. SIMPSON¹, OLIVER WERZER², ANDREAS ZIMMER², and LEONHARD GRILL¹ — ¹Institute of Chemistry, University of Graz, Austria — ²Institute of Pharmaceutical Sciences, University of Graz, Austria

In solution, microRNAs and protamine spontaneously form nanoparticles, which are auspicious candidates for the treatment of various diseases [1]. This self-assembly process is induced by strong electrostatic interactions. To deliberately modify this interplay, accurate knowledge of the molecular interactions at the single molecule level is desired. The deposition of microRNA molecules onto a metallic surface is done via electrospray ion beam deposition (ES-IBD). This method allows for the clean and intact transfer of large molecules onto a surface in ultrahigh vacuum (UHV) [2]. The adsorption geometry of microRNA is dependent on the kinetic energy with which it impinges on the surface. We have then investigated the adsorption of these molecules on metallic substrates by scanning tunneling microscopy (STM). The adsorption is compared for different preparation techniques, ES-IBD and drop-casting.

Acknowledgements: The financial support from the Doctoral Academy NanoGraz is highly acknowledged by the Grill and the Zimmer group.

[1] M. Junghans, J. Kreuter, and A. Zimmer, Nucleic Acids Res 28, 10 (2000). [2] Z. Deng, N. Thontasen, N. Malinowski, G. Rinke, L. Harnau, S. Rauschenbach, and K. Kern, Nano Lett 12, 5 (2012)

O 32.6 Mon 18:15 P1C

Investigation of the formation of densely packed caffeine monolayers on Au(111) — MALTE G.H. SCHULTE^{1,2}, ANDREAS JEINDL³, ●JULIAN A. HOCHHAUS¹, ISMAIL BALTACI^{1,2}, MARIE SCHMITZ^{1,2}, ULF BERGES^{1,2}, OLIVER T. HOFMANN³, and CARSTEN WESTPHAL^{1,2} — ¹Experimentelle Physik 1, TU Dortmund, Otto-Hahn-Str. 4, D-44221, Dortmund, Germany — ²DELTA, TU Dortmund, Maria-Goeppert-Mayer-Str. 2, D-44221, Dortmund, Germany — ³Institut für Festkörperphysik, NAWI Graz, Technische Universität Graz, Petersgasse 16, A-8010 Graz

In this study, we investigate caffeine monolayers on Au(111). Caffeine is well known for influencing the human central nervous system, therefore knowledge of the structural behaviour of caffeine is essential.

Low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and x-ray photoelectron spectroscopy (XPD) have been used to examine the formation of caffeine on Au(111). In addition, density functional theory (DFT) calculations were carried out which allow conclusive interpretation as well as a comparison with the measured data.

We observed the caffeine molecules to be adsorbed in a quasi-hexagonal formation similar to the high-temperature α -phase, comprising two domains. The DFT calculations suggested a unit cell containing three molecules, the theoretically calculated structure is in excellent agree-

ment to the experimental measured LEED and STM pattern, as well as to the measured XP-spectra. Furthermore, within the XPS measurements, no strong adsorbate-surface interaction was found.

O 32.7 Mon 18:15 P1C

Atomistic Modeling of the Synthesis of New Carbon Structures by Surface-Assisted Cyclodehydrogenation — ●FLORIAN WULLSCHLÄGER, ROBERT MAIDL, SEBASTIAN GSÄNGER, and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

A new synthesis route for chirality-pure single-walled carbon nanotubes (SWCNTs) has been proposed, which relies on the surface-catalyzed cyclodehydrogenation (CDH) of appropriately designed precursor molecules on Au(111) [1] followed by a new roll-up synthesis technique. Using a hierarchy of methods, from atomistic force-fields to quantum-chemical density-functional theory (DFT) calculations and combining them in QM/MM approaches, we studied the SWCNT formation process in the gas phase and on the Au(111) surface. We were able to identify the crucial reaction step and we could show that structural hindrance leads to an interruption of the current CDH process. The same approach of on-surface cyclodehydrogenation can be used for the synthesis of new forms of carbon allotropes like nanocones, bowls or spoons. First insights into the formation process of nanocones with a porphyrin unit at the tip on Pt(111) surfaces will be shown.

[1] J.R. Sanchez-Valencia, T. Dienel, O. Gröning, I. Shorubalko, A. Mueller, M. Jansen, K. Amsharov, P. Ruffieux, R. Fasel, *Nature* **512** (2014) 61–64.

O 32.8 Mon 18:15 P1C

STM study of CuPc molecules codeposited with C60 on a Au(110) surface — ●HÜSEYİN AZAZOĞLU, PHILIP KAPITZA, and ROLF MÖLLER — Fakultät für Physik/Cenide, Universität Duisburg-Essen, Germany

Here, we show an STM study of CuPc molecules codeposited with C60 on a Au(110) surface at room temperature. It turns out that C60 molecules form close packed islands. In between the CuPc molecules form ordered rows along the rows of the Au(110) surface. The results are compared to previous for C60 on Au(110) [1], [2] and the codeposition of CuPc and C60 on Au(111) [3], [4].

- [1] J. K. Gimzewski et al. *J. Vac. Sci. Technol.*, B, 12, 2153 (1994).
 [2] J. K. Gimzewski et al. *Phys. Rev. Lett.*, 72, 1036 (1994).
 [3] M. Stöhr et al. *Adv. Funct. Mater.*, 11, 175 (2001).
 [4] M. Fendrich et al. *Phys. Rev. B*, 73, 115433 (2006).

O 32.9 Mon 18:15 P1C

A highly ordered commensurate structure of merocyanine tetramers on Ag(100): STM- and SPA-LEED-investigations — ●ANNA J. KNY¹, NIKLAS HUMBERG¹, DIRK HERTEL², KLAUS MEERHOLZ², and MORITZ SOKOLOWSKI¹ — ¹Institut für Physikalische und Theoretische Chemie der Universität Bonn, Germany — ²Department Chemie, Universität zu Köln, Germany

Vacuum deposited films of the merocyanine molecule 2-[5-(5-dibutylamino-thiophen-2-yl-methylene)-4-*tert*-butyl-5*H*-thiazol-2-ylidene]-malononitrile (HB238) have been investigated in the context of organic solar cells [1]. Although the specific structural order in these films is important for photovoltaic properties, only very little is known about the adsorption, ordering and film growth of this molecule on surfaces. Therefore, we investigated monolayers of HB238 on a Ag(100) surface by SPA-LEED and STM.

When HB238 is deposited onto the Ag(100) at room temperature and then cooled down immediately to 34 K, the formation of two different phases can be observed. Directly after growth, a phase with chain-like aggregates and only short-range order prevails. Upon annealing at 68 K, it transforms into a second highly ordered phase with a commensurate superstructure. This phase is composed of homochiral tetramers of HB238 molecules. The thiophene and thiazole units are bonded to the Ag(100) surface yielding a flat lying molecular orientation. Upon further annealing dewetting and cluster formation occurs. [1] *JACS* 137 (2015) 13524.

O 32.10 Mon 18:15 P1C

On-surface synthesis of BN-doped carbon nanostructures — ●TOBIAS WEISS¹, ALEKSANDR BAKLANOV¹, KNUD SEUFERT¹, JOHANNES KÜCHLE¹, MARC GONZALEZ CUXART¹, FRANCESCO ALLEGRETTI¹, JACOPO DOSSO³, DAVIDE BONIFAZI³, NICOLAS BACHELLIER², MATTHIAS MUNTWILER², and WILLI AUWÄRTER¹ —

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Hybrid hexagonal boron nitride - carbon (BNC) layers provide promising properties for potential applications in electronics and gas adsorption [1]. Recently, BNC-based tectons were introduced to assemble covalent networks and supramolecular arrays on metal surfaces [1-3].

Here, we report the formation of BNC nanostructures on Ag(111) and Au(111) via bottom-up synthesis from borazine derivatives in UHV. We employed both a dehydrogenation approach using a BN-doped coronene derivative and an Ullmann-type coupling approach using a chlorine- and bromine-functionalized hexaphenylborazine. The resulting 2D structures, the sequential dehalogenation steps, and the Ullmann coupling are investigated with (fast) XPS and STM. Additionally, we probed the CO, CO₂, and borazine adsorption on the BNC structures, revealing the inertness of the borazine core.

- [1] M. M. Lorenzo-García et al., *Chimia*, 2017 **71**, 9, 550-557.
 [2] C. Sánchez-Sánchez et al., *ACS Nano*, 2015 **9**, 9, 922.
 [3] M. Schwarz et al., *Chem. Eur. J.*, 2018 **24**, 9565.

O 32.11 Mon 18:15 P1C

Influence of polarity on adsorption and growth of conjugated organic molecules on inorganic substrates — ●MILA MILETIC¹, KAROL PALCZYŃSKI^{1,2}, and JOACHIM DZUBIELLA^{1,2} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — ²Physikalisches Institut, Albert-Ludwigs-Universität, Freiburg, Germany

We present atomistically resolved computer simulations of the vapor-phase deposition and layer-by-layer growth of organic molecules on inorganic substrates. We study the effects of chemical tuning of the organic para-sexiphenyl (p-6P) molecule on the nucleation and growth on amorphous silicon dioxide: We characterize surface diffusion barriers and the growth of layers of upright standing molecules once a critical coverage is achieved.

Crystalline islands of standing molecules form as a result of a collective reorientation of clusters of flat-lying molecules. The growth proceeds by molecules attaching to the clusters and ascending over the terraces to integrate into the existing cluster units. We describe the crossing mechanisms and quantify the barriers for descending over the terraces. Our simulations reveal some of the interesting features of molecular surface kinetics and binding. The results shall be useful to control thin film growth in order to obtain desired structures and properties in experiments.

O 32.12 Mon 18:15 P1C

Explaining surface polymorphism of acenequinones on Ag(111) with SAMPLE — ●ANDREAS JEINDL¹, LUKAS HÖRMANN¹, JARI DOMKE², ALEXANDER T. EGGER¹, FALKO SOJKA², and OLIVER T. HOFMANN¹ — ¹Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria — ²Institute of Solid State Physics, Friedrich Schiller University Jena, Germany

Understanding (and modifying) the formation of surface polymorphs is still not straightforward as it is hardly known why specific structures form. Normally, the exponential growth of possible polymorphs with system size prohibits rigorous computational studies, that could explore the full configurational and thermodynamic search space. The peculiar physics that govern the interface formation, however, allow to reduce the search space and make the problem tractable.

In this contribution we use SAMPLE, a program package developed to efficiently predict energies for commensurate surface layers. It employs machine learning to suitably fit a physical energy model which consists only of molecule-substrate and molecule-molecule interactions. We perform a comprehensive structure search for a homologous series of acenequinones on Ag(111) to explain the mechanisms driving the formation of surface polymorphs and compare some of our results to experimental observations. Our research shows that the structures differ fundamentally. Insights from our model suggest that this originates mostly from the van-der-Waals interaction of the substrate with the backbone as well as the fact that upon increasing the backbone length, vdW interactions between the molecules become more important.

O 32.13 Mon 18:15 P1C

The Effect of Plasma Treatment of Gold Electrodes on the Molecular Orientation of CuPc films — ●FELIX WIDDASCHECK, MICHAEL KOTHE, ALRUN A. HAUKE, and GREGOR WITTE — Philipps Universität Marburg

Gold is a commonly used material for many organic electronic device electrodes due to its chemical stability and high work function, which is required for p-type semiconductors. The orientation and morphology of organic semiconductors deposited on such electrodes often depends crucially on the cleanliness of the Au surface. In this study, we examine the effect of a common cleaning method, namely oxygen plasma cleaning, on sputter-deposited polycrystalline Au electrodes and subsequently deposited copper-(II)-phthalocyanine (CuPc) films. Using X-ray diffraction (XRD), atomic force microscopy (AFM) and near-

edge X-ray absorption fine structure (NEXAFS) measurements, we show that the metastable Au oxide typically formed during an oxygen plasma cleaning process significantly impacts the molecular orientation and morphology in CuPc thin films, forcing molecules to adopt an upright orientation. We further demonstrate that the typical recumbent orientation of CuPc adopted on clean polycrystalline Au can be achieved by an additional annealing step after oxygen plasma treatment of the Au electrode that causes a decomposition of the gold oxide.