

O 12: Morphology Prediction at Interfaces

Time: Monday 15:00–18:30

Location: S051

O 12.1 Mon 15:00 S051

Flexible 2D crystals of polycyclic aromatics stabilized by static distortion waves — MATTHIAS MEISSNER¹, FALKO SOJKA¹, LARS MATTHES², FRIEDHELM BECHSTEDT², XINLIANG FENG³, KLAUS MÜLLEN³, STEFAN C. B. MANNSFELD⁴, ●ROMAN FORKER¹, and TORSTEN FRITZ¹ — ¹Institute of Solid State Physics, Friedrich Schiller University Jena, Germany — ²Institute of Condensed Matter Theory and Solid State Optics, Friedrich Schiller University Jena, Germany — ³Max Planck Institute for Polymer Research, Mainz, Germany — ⁴Center for Advancing Electronics, TU Dresden, Germany

The epitaxy of many organic films on inorganic substrates can be classified by established lattice match conditions. Yet, there are material-substrate combinations for which this classification fails and cannot be exploited to understand reproducible azimuthal alignments between adsorbate and substrate lattices. For decades it has been hypothesized in the literature that so-called static distortion waves (SDWs) could be responsible for the observed orientational epitaxy in such cases. By means of STM and LEED experiments we demonstrate unequivocally SDWs in films of hexa-*peri*-hexabenzocoronene on graphite, which manifest as sub-Ångström local molecular displacements from an ideal rigid adsorbate lattice, being itself *incommensurate* with graphite in contrast to previous reports. We present a model that consistently explains these displacements in both size and direction. Based on DFT we calculate for realistically large domains the energy gain due to the SDWs, thereby proving their crucial role for the observed epitaxy, and we successfully reproduce the measured domain angle.

O 12.2 Mon 15:15 S051

Structural properties of picene-perfluoropentacene and picene-pentacene blends: Superlattice formation versus limited intermixing — J. DIETERLE¹, K. BROCH^{1,2}, A. HINDERHOFER¹, H. FRANK¹, J. NOVÁK³, ●A. GERLACH¹, T. BREUER⁴, R. BANERJEE¹, G. WITTE⁴, and F. SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, Germany — ²Cavendish Laboratory, University of Cambridge, UK — ³Central European Institute of Technology, Masaryk University, Czech Republic — ⁴Fachbereich Physik, Philipps-Universität Marburg, Germany

The structure and morphology of mixed thin films of picene (C₂₂H₁₄, PIC) and perfluoropentacene (C₂₂F₁₄, PFP) as well as mixed thin films of PIC and pentacene (C₂₂H₁₄, PEN) grown by simultaneous coevaporation is investigated using X-ray diffraction, atomic force microscopy, and near-edge X-ray absorption spectroscopy. For both systems we find mixing on the molecular level and the formation of mixed structures. However, due to the strongly different interactions in both mixtures the ordering is fundamentally different [1]. The results are discussed in the context of other organic semiconductor binary mixtures [2] showing that besides chemical composition and steric compatibility the intramolecular arrangement of the atoms important for intermolecular interactions significantly influences the structure formation in organic semiconductor blends.

[1] J. Dieterle et al., *J. Phys. Chem. C* **119** (2015) 23211.[2] C. Lorch et al., *Appl. Phys. Lett.* **107** (2015) 201903.

O 12.3 Mon 15:30 S051

Exploring the Electronic and Vibrational Properties of Disordered TCNE on Cu(111) Using a Basin Hopping Algorithm — ●VERONIKA OBERSTEINER, EGBERT ZOJER, and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

While to date most first-principle studies focus on highly ordered crystalline materials, in this work we concentrate on the theoretical investigation of amorphous or disordered materials that are commonly used in experimental applications. To sample the complex potential energy surface (PES) of disordered organic/inorganic interfaces we develop a three-step geometry search algorithm based on Basin Hopping (BH) in conjunction with dispersion-corrected Density Functional Theory. First, we determine the local adsorption structures, then we coarse-grain the PES as a superposition of these local adsorption structures to finally efficiently jump between the locally optimized configurations using the BH algorithm.

Applying this approach to TCNE (tetracyanoethene) on Cu(111) we evaluate a set of energetically lowest lying structures, reflecting

the distribution of local conformations and their environment. Our investigations reveal that at finite temperature a noticeable amount of TCNE molecules are bound in an upright standing manner to the Cu(111) surface, although this is not the global minimum. The different adsorption conformations exhibit very different electronic properties characterized by the charge states of the TCNE molecules and their vibrational spectra.

O 12.4 Mon 15:45 S051

Machine learning of surface adsorbate structure — ●MILICA TODOROVIĆ¹, MICHAEL GUTMANN², JUKKA CORANDER², and PATRICK RINKE¹ — ¹Aalto University, Espoo, Finland — ²University of Helsinki, Helsinki, Finland

To efficiently search many atomistic configurations on large length scales, we developed a parameter-free machine learning tool for studying organic/inorganic interfaces. Our preferred Bayesian optimisation approach relies on probabilities to construct model functions, which are then iteratively refined by input of real data points balancing exploitation with exploration. A Bayesian optimisation algorithm was interfaced with both classical potential and density-functional theory codes to enable iterative learning (on-the-fly) of potential energy surfaces (PES) on large supercomputers without human input. For additional efficiency, the method exploits structural rigidity of molecular groups, reducing the degrees of freedom and making the learning process analogous to “molecular LEGO”. We present a proof-of-concept test based on the alanine molecule and an application featuring electron donor C₆₀ molecules on the (101) surface of TiO₂ anatase. The Bayesian optimisation structure search (BOSS) acquires PES information fast and is particularly efficient in pinpointing the global minimum structure. This versatile scheme for global minimum search could be extended beyond interface packing considerations to address complex configurational problems across scientific disciplines.

O 12.5 Mon 16:00 S051

Substrate-Induced Phases: Polymorphism of Organic Materials on Surfaces — ●ANDREW O. F. JONES¹, BASAB CHATTOPADHYAY², YVES H. GEERTS², and ROLAND RESEL¹ — ¹Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria — ²Laboratoire de Chimie des Polymères, Faculté des Sciences, Université Libre de Bruxelles CP206/01, Campus de la Plaine, 1050 Brussels, Belgium

An increase or change of structural order in the vicinity of a solid substrate is known for a wide variety of materials. For molecular materials crystallizing on a solid surface, it has been observed that new polymorphic forms may exist near the interface with the substrate which have structures markedly different to those observed in the bulk material; such phases are termed Substrate-Induced Phases (SIPs). [1] The presence of a SIP in a compound or a class of materials can be of crucial significance in terms of its physical properties. However, the factors that drive such a process are not clearly understood or studied in depth. With the ultimate aim of controlling material properties by controlling structure, it is essential to take account of changes in the structure brought about by SIPs and to work towards controlling polymorphism in organic thin films. Several examples, with a particular focus on organic semiconducting materials, will be discussed to highlight the types of materials that can display SIPs and the current understanding of their origins.

[1] A. O. F. Jones, B. Chattopadhyay, Y. H. Geerts, R. Resel, *Adv. Funct. Mater.*, 2015, Accepted for Publication.

O 12.6 Mon 16:15 S051

In-situ LEEM study of the growth of NTCDA on Cu(001) — ●JANA WOLTERS, JANINA FELTER, MARKUS FRANKE, CAROLINE HENNEKE, and CHRISTIAN KUMPF — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany and Jülich Aachen Research Alliance (JARA)-Fundamentals of Future Information Technology, Germany

A good understanding of the interactions between organic molecules and metal surfaces is essential for improving the performance of organic (opto-) electronic devices as well as for fundamental studies of thin organic films and metal-organic interfaces. In this context the first organic layer adsorbed on the metal substrate is of special impor-

tance since it is serving as a template for further growth and directly influences the physical properties of the interface.

As a model system, we investigated the growth of 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA) on the Cu(001)-surface in-situ and in real-time with LEEM, and correlated the results with structural information obtained by μ LEED. We identified several different phases occurring at different temperatures. For one of them, we observed an unexpected behavior that resembles dendritic growth.

O 12.7 Mon 16:30 S051

Long-Range Order Induced by Intrinsic Repulsion on an Insulating Substrate — JULIA L. NEFF¹, HAGEN SÖNGEN¹, ●RALF BECHSTEIN¹, PHILIPP MAASS², and ANGELIKA KÜHNLE¹ — ¹Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55099 Mainz, Germany — ²Fachbereich Physik, Universität Osnabrück, 49076 Osnabrück, Germany

Creating complex functional structures on surfaces requires tools like molecular self-assembly. Here, adjusting the balance between intermolecular and molecule-surface interactions is a versatile strategy for tailoring molecular structure formation. Short-ranged attractive forces have often been in the focus while long-ranged repulsive interactions have been explored only rarely, despite their potential for steering molecular order formation. We report an ordered arrangement of molecular stripes with equidistant appearance that is formed upon the adsorption of 3-hydroxybenzoic acid onto calcite (10.4) at room temperature. The observed next-neighbor stripe distance distributions deviate substantially from random distributions of non-interacting stripes, verifying the existence of a repulsive interaction between the stripes. Even at low molecular coverage, where the average stripe distance is as large as 16 nm, the stripes are significantly ordered, demonstrating the long-range nature of the involved repulsive interaction. We show, it is plausible that adsorption-induced charge redistribution alone is responsible for the observed long-range repulsion. This generic repulsion mechanism is expected to play an important role in molecular self-assembly on insulators.

O 12.8 Mon 16:45 S051

Interface formation of aromatic molecules on a metal/metal-oxide nano-template mediated by lateral and vertical interactions — ●ALEXANDER TIMMER, HARRY MÖNIG, OSCAR DÍAZ ARADO, SAEED AMIRJALAYER, MARTIN UPHOFF, and HARALD FUCHS — Physikalisches Institut, Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

The self-assembly of organic molecules on pre-structured surfaces is a promising approach to steer precise arrangement of molecular nanostructures. The Cu(110)-(2x1)-O added row reconstruction of a partially oxidized Cu(110) surface, where added Cu and O atoms are arranged in a striped super-grating along the [100] direction, forms an interesting nano-template exhibiting a well-defined lateral metal/metal-oxide phase boundary. Previous studies showed that various organic compounds exclusively adsorb on the pure metal domains. By STM imaging we confirm this finding for different polycyclic aromatic hydrocarbons. For low coverages, these molecules predominantly decorate the metal/metal-oxide boundaries of the (2x1)-O strings in a specific geometry. By constant height NC-AFM imaging with an O-terminated Cu tip we achieve both sub-molecular resolution and chemical identification within the oxide reconstruction allowing a precise adsorption site determination. Supported by DFT calculations the adsorption behavior adjacent to the Cu(110)-(2x1)O reconstruction is compared to the adsorption on the Cu(110) surface, providing a conclusive picture of the fine interplay between the involved lateral and vertical interaction.

O 12.9 Mon 17:00 S051

Interaction of free-base tetraphenyl porphyrin with MgO(001) surface — ●OSMAN BARIŞ MALCIOĞLU¹ and MICHEL BOCKSTEDTE^{1,2} — ¹Lehrstuhl f. Theoretische Festkörperphysik, FAU Erlangen-Nürnberg, Erlangen, Germany — ²Chemie und Physik der Materialien, Universität Salzburg, Salzburg, Austria

MgO(001) as a pristine surface is chemically rather inert. Under experimental conditions, step edges, kink-sites and other low coordinated sites are present. Such sites may chemically interact with adsorbates and hence play a role in structure formation. Recently, the metalation of H2TPP with Mg via low coordinated sites on MgO(001) has been demonstrated [1]. The mechanisms underlying this process, however, remain unclear. We employ ab-initio molecular dynamics simulations to study how H2TPP may interact with MgO(001) and common low

coordinated sites. We find that H2TPP is mobile on the pristine surface since the phenyl rings sterically hinder physisorption at a specific surface site. In the presence of a step or kink site, however, phenyl rings help form a rather stable complex. The molecule aligns at the step or kink such that spontaneous deprotonation of the macrocycle occurs. We present the electronic and structural properties of the adsorbate complex and investigate the photophysical fingerprint of intermediates and the metallized porphyrins using (hybrid) TDDFT, self consistent GW and BSE.

[1] J. Schneider *et al.*, ACS Appl. Mater. Interfaces 7, 22962 (2015).

O 12.10 Mon 17:15 S051

Temperature dependence of ethanol water nanophase separation in soft graphene mica slitpore — ●ABDUL RAUF¹, JONAS GIENGER², NIKOLAI SEVERIN¹, IGOR M. SOKOLOV¹, and JÜRGEN P. RABE^{1,3} — ¹Humboldt Universität zu Berlin — ²Physikalisch-Technische Bundesanstalt, Berlin — ³IRIS Adlershof, Berlin

Real space imaging with Scanning Force Microscopy (SFM) revealed nanophase separation in a fluid monolayer of ethanol and water confined in a soft graphene-mica slitpore. The interactions which determine the irregular equilibrium patterns had been attributed qualitatively to the interplay of short-range attractive, and long-range electrostatic repulsive interactions. However, determining strength and range of these interactions quantitatively presented a challenge due to the complex screened dipole-dipole interactions, the bending energy of the graphene sheet, and intermolecular interactions. The interaction potential, however, has been reconstructed applying an Inverse Monte Carlo approach on SFM micrographs of the system. The reconstructed potential was then used to predict the behavior of the system outside the experimentally accessible range of parameters such as temperature and vapor pressure, including critical demixing temperature. [1]

To validate this approach experimentally, its predictions regarding the response of the system to temperature changes were tested by imaging the nanophase-separated patterns at various temperatures using an SFM equipped with heating/cooling elements. [1] J. Gienger, N. Severin, J. P. Rabe, I. M. Sokolov 2015, arXiv:1505.03011 [cond-mat.stat-mech]

O 12.11 Mon 17:30 S051

An Interfacial Bridge from a Perovskite to a Fluorite — MARITA O'SULLIVAN¹, JOKE HADERMANN², ●MATTHEW S DYER¹, STUART TURNER², JONATHAN ALARIA¹, TROY MANNING¹, ARTEM M ABAKUMOV², JOHN B CLARIDGE¹, and MATTHEW J ROSSEINSKY¹ — ¹University of Liverpool, Liverpool, UK — ²EMAT, University of Antwerp, Antwerp, Belgium

Coherent interfaces between materials are essential for many technological processes, and can give rise to novel physical properties. Such interfaces can be obtained by controlled 2D layer-by-layer growth of one material on another. Dimensional matching on the unit cell length scale can usually be used to determine whether 2D layer-by-layer growth is possible when both materials have the same or similar structures, but not when the materials have very different structures. For example, perovskite / fluorite interfaces can be engineered with less than 1 % strain, but 2D layer-by-layer growth still cannot be achieved. Using pulsed laser deposition, we demonstrate 2D layer-by-layer growth of the lattice matched disordered fluorites La_{0.5}Zr_{0.5}O_{1.75} and Nd_{0.5}Zr_{0.5}O_{1.75} on the perovskite LaAlO₃. A joint DFT and STEM investigation of the interface shows that local restructuring occurs forming a bridge between the perovskite and fluorite, satisfying the local bonding of both structures. The restructuring is made possible by the chemical flexibility of the chosen fluorites. This suggests both dimensional and chemical matching are important for the creation of coherent interfaces between materials with significantly differing structures, and that chemical mismatches can be overcome by a careful choice of materials.

O 12.12 Mon 17:45 S051

Hydroxylation and segregation induced morphology changes of MgO cube based nanostructures — DANIEL THOMELE¹, ANDREAS STERNIG², JOHANNES BERNARDI³, SIMON KLACAR⁴, HENRIK GRÖNBECK⁴, and ●OLIVER DIWALD¹ — ¹Department of Chemistry and Physics of Materials, University of Salzburg, Salzburg, Austria — ²Institute of Particle Technology, University of Erlangen-Nürnberg, Erlangen, Germany — ³University Service Center of Transmission Electron Microscopy, TU Vienna, Austria — ⁴Department of Applied Physics and Competence Centre for Catalysis, Chalmers University of Technology, Göteborg, Sweden

Vapor phase grown MgO cubes have turned out to be extremely valuable probes for the investigation of interface chemistry and particle morphology evolution inside powders. Comparative annealing experiments on these materials in dynamic high vacuum and in different gas atmospheres revealed the dramatic impact of residual water and surface hydroxylation on particle morphology and sintering properties. Moreover, we investigated the structural and energetic properties of Barium oxide (BaO) units dissolved inside the MgO host and adsorbed on MgO particle surfaces with HR Transmission Electron Microscopy and Density Functional Theory (DFT) calculations. The shape of BaO and MgO particles in a water environment were investigated as a function of temperature. The calculations suggest that the spherical shapes of the segregates result from the growth process and become thermodynamically stabilized by surface hydroxylation.

O 12.13 Mon 18:00 S051

Probing the interface between semiconducting nanocrystals and molecular metal chalcogenide surface ligands: insights from *first principles*. — EMILIO SCALISE¹, STEFAN WIPPERMANN¹, GIULIA GALLI², and ●DMITRI TALAPIN² — ¹Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany — ²University of Chicago, Chicago, United States

Colloidal nanocrystals (NCs) are emerging as cost-effective materials offering exciting prospects for solar energy conversion, light emission and electronic applications. Recent experimental advances demonstrate the synthesis of fully inorganic nanocrystal solids from chemical solution processing. The properties of the NC-solids are heavily determined by the NCs surface and their interactions with the host matrix, due to the high surface-to-volume ratio. However, information on the atomistic structure of such composites is hard to obtain, due to the complexity of the synthesis conditions and the unavailability of robust experimental techniques to probe nanointerfaces at the microscopic level. Here we present a systematic theoretical study of the interaction between InAs and InP NCs with $\text{Sn}_2\text{S}_6^{4-}$ ligands. Employing a grand

canonical *ab initio* thermodynamic approach we investigate the relative stability of a multitude of configurations possibly realized at the NC-ligand interface. Our study highlights the importance of different structural details and their strong impact on the resulting composite's properties. We show that to obtain a detailed understanding of experimental data it is necessary to take into account complex interfacial structures beyond simplified NC-ligand model interfaces.

O 12.14 Mon 18:15 S051

A research concept for understanding morphology evolution and nanoscale atomic arrangement in multicomponent thin films — VIKTOR ELOFSSON¹, GEORGIOS ALMYRAS¹, BO LÜ¹, ROBERT BOYD², and ●KOSTAS SARAΚINOS¹ — ¹Nanoscale Engineering Division, Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden — ²Plasma and Coatings Physics Division, Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden

Synthesis of multicomponent thin films using vapor fluxes with a modulated deposition pattern is a potential route for accessing a wide gamut of atomic arrangements and morphologies for property tuning. In the current study, we present a research concept that allows for understanding the combined effect of flux modulation, kinetics and thermodynamics on the growth of multinary thin films. This concept entails the combined use of thin film synthesis by means of multiatomic vapor fluxes modulated with sub-monolayer resolution, deterministic growth simulations and nanoscale microstructure probes. Using this research concept we study structure formation within the archetype immiscible Ag-Cu binary system showing that atomic arrangement and morphology at different length scales is governed by diffusion of near-surface Ag atoms to encapsulate 3D Cu islands growing on 2D Ag layers. The knowledge generated and the methodology presented herein provides the scientific foundation for tailoring atomic arrangement and physical properties in a wide range of miscible and immiscible multinary systems.