

Interfacing Machine Learning and Experimental Methods for Surface Structures

Abstract Book



Conference venue (HS P2)



IMPRESS	2018 S	chedule
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	Wednesday July 11	Thursday July 12	Friday July 13
9:00	Registration		
9:30	Hinderhofer	Fritz	Meyer
10:00	Panosetti	Frolov	Discussion
10:30	Forster-Tonigold	Karttunen	and
11:00	Coffee	Coffee	Coffee
	Jeindl	Pilz	Turner
	Todorović	Hartl	Hinuma
12:00			
12:30	Lunch	Lunch	
13:00	Lunch	Lunti	
13:30			
14:00	Discussion	Discussion	
14:30	Discussion	Discussion	
15:00	Coffee	Coffee	
15:30			
16:00	Zeppenfeld	Wegner	
16:30	Packwood	Rahman	
17:00	Resel	Fukushima	
17:30	Postor Sossion		
18:00	(catered)		
18:30	(catered)		
19:00			
19:30		Dinner (Open End)	
20:00			

Lunch: Complimentary lunch will take place at the "Rooftop" Mensa (Stremeyergasse 16, see map at the back). Please mention "IMPRESS" to the cashier.

<u>Dinner</u>: The conference dinner takes place on Thursday night at the hotel Weitzer, Grieskai 12-14. Directions will be provided on thursday after the talks.

Wifi: Eduroam works throughout the building. Alternatively, a WiFi token is available from the registration or the organizers.

FOLLOWING MOLECULAR THIN FILM STRUCTURE FORMATION IN REAL-TIME BY X-RAY SCATTERING

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Organic molecular semiconductor (OSC) thin films have attracted substantial research interest in recent years, in an effort to complement inorganic semiconductors, due to their attractive optical and structural properties (Fig. 1a-b).

We will present several state-of-the-art X-ray diffraction real-time studies on the growth and nucleation of molecular thin films [1-3]. We will demonstrate how X-ray diffraction can be applied to follow thickness dependent transitions between amorphous and crystalline states as well as between different polymorphs [2-3].

In addition, for more complex binary mixed films, which are widely used for electronic devices, we will show that the degree of mixing or phase separation can depend on the film thickness [1]. For example, the co-evaporation of C60 and Diindenoperylene results in a well-mixed film in the mono-layer regime. However, during further deposition the degree of phase separation is steadily increasing (Fig. 1c).

Finally, we will comment on the specific challenges of analyzing large low-symmetry unit cells and non-ideal samples (partial disorder and phase coexistence), and we will discuss the possibilities to apply advanced analysis methods on large sets of real-time data.



Figure 1: Sketches of Fullerene C60 (a) and Diindenoperylene (b). c) (Left) Contour plot of real-time GIXD data measured during growth of 1:1 mixed film. Contour lines indicate levels with equal intensity. GIXD data from the final thickness have been plotted at the bottom. The blue lines indicate the peak maxima. (Right) Schematic representation of the model proposed for the kinetically driven phase separation during the growth of a co-evaporated DIP and C60 thin film. The molecules phase-separate into domains of crystallites which grow laterally with increasing thickness of the film.

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[2] C. Lorch, R. Banerjee, C. Frank, J. Dieterle, A. Hinderhofer, A. Gerlach, and F. Schreiber, J. Phys. Chem. C, **119**, 819–825 (2015)

[3] V. Belova, B. Wagner, B. Reisz, C. Zeiser, G. Duva, J. Rozbořil, J. Novák, A. Gerlach, A. Hinderhofer, and F. Schreiber, J. Phys. Chem. C, 122, 8589–8601 (2018)

BETTER (RANDOM) WALKING THROUGH CHEMISTRY: HOW NOT TO GET LOST IN VAST CONFIGURATIONAL SPACES

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Ab initio structure prediction can systematically aid the computational discovery and rational design of new materials, as well as providing interpretative insights when atomistic details are difficult to resolve experimentally. However, global geometry optimization – the method of choice for finding chemically relevant (meta-)stable structures– is rarely applied to large-scale systems. The main challenge lies in the necessity of efficient ways to traverse configurational spaces in which the number of minima explodes with system size.

We adapt the basin hopping [1] global geometry optimization scheme to employ automatically-generated collective curvilinear coordinates. Due to the physical correspondence of these coordinates with vibrations, this enhances the generation of chemically meaningful trial structures for covalently bound systems. [2] In the application to hydrogenated Si clusters we concomitantly observe a significantly increased efficiency in identifying lowenergy structures and a reduction of unphysical geometries when compared to the same number of typical random Cartesian trial moves.

We further propose to combine this and the ab initio thermodynamics idea [3] in a grandcanonical global optimization framework, where the function to minimize is no longer the total energy, but rather the Gibbs free energy at several values of the chemical potential of the components, in order to target systems with unknown or variable stoichiometry, such as metal silicides synthesized directly at surfaces, or non-stoichiometric surface reconstructions.



Figure 1:

Following the fil rouge of the exploitation of chemically motivated trial moves, we further extend this to the study of organic molecules on surfaces [4] –by suitably imposing partial constraints– and to complex interfaces with variable or unknown stoichiometry –by applying strategies to alleviate the strain of newly generated structures upon grandcanonical particle insertion. A selection of prototypical results, with particular focus on hydrogenated silicon clusters and silicon surface reconstructions, will be presented to illustrate how all relevant portions of chemical space can be accessed with this approach, whereas "conventional" sampling often even struggles to produce sensible structures besides the starting geometry at all.

- [1] D. J. Wales, J. P. K. Doye, J. Phys. Chem. A 101, 12209–12011 (1997).
- [2] C. Panosetti, K. Krautgasser, D. Palagin, K. Reuter, R. J. Maurer, Nano Lett. 15 (12), 8044–8048 (2015).
- [3] J. Rogal, K. Reuter. Ab Initio Atomistic Thermodynamics for Surfaces: A Primer. In Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Supersonic Flights, pages 1–18 (2007).
- [4] K. Krautgasser, C. Panosetti, D. Palagin, K. Reuter, R. J. Maurer, J. Chem. Phys. 145 (8), 084117 (2016).

INTERACTIONS OF IONIC LIQUIDS AT (SEMI)METAL SURFACES

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Ionic liquids (ILs), i.e. salts composed of organic cations and mostly inorganic anions with melting points below 100°C, enjoy increasing popularity as solvents/electrolytes in Li ion batteries. Particularly interesting is the electrode/electrolyte interface, where during initial cycles of battery operation the electrolyte decomposes. This leads to the formation of the so-called solid/electrolyte interphase (SEI). The SEI plays a crucial role as it allows the transfer of Li ions, but it is electrolyte. In model studies we aim to get some insights into the initial stages of the formation of the SEI taking place already under open circuit voltage conditions by looking at the electrode/IL interface (see Figure 1). In close collaboration with experimentalists, who use scanning tunneling microscopy and photoelectron spectroscopy under ultrahigh vacuum conditions, we employed dispersion corrected density functional theory calculations to study the interactions and structure formation of an IL at graphite and metal surfaces [1-3]. We find a subtle interplay of dispersion interactions, electrostatic interactions and charge transfer both in between the adsorbates and between the adsorbate and the substrate. Finally, the interaction of the resulting IL adlayer with lithium is studied.



Figure 1: Modelling the electrode|*electrolyte interface in batteries*

[1] F. Buchner, K. Forster-Tonigold, B. Uhl, D. Alwast, N. Wagner, A. Groß, and R. J. Behm, ACS Nano 7, 7773-7784 (2013).

[2] F. Buchner, K. Forster-Tonigold, M. Bozorgchenani, A. Groß and R. J. Behm. J. Phys. Chem. Lett. 7, 226-233 (2016).

[3] F. Buchner, B. Uhl, K. Forster-Tonigold, J. Bansmann, A. Groß, and R. J. Behm, J. Chem. Phys. **148**, 193281 (2018).

UNDERSTANDING THE DRIVING FORCES OF SURFACE POLYMORPH FORMATION FOR ACENEQUINONES ON Ag(111)

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A variety of properties of metal-organic interfaces are determined by the polymorph the molecules assume on the (metal) surface. In order to engineer functional interfaces, it is therefore imperative to predict which polymorphs form for a given material combination and to understand the driving forces of their formation. Still, there are surprisingly few systematic studies that allow to infer reliable relationships between the molecular structure and the kinds of interface polymorphs that form. This is because experimentally, the vacuum deposition of molecules often leads to kinetically trapped phases which depend on the preparation conditions. Conversely, computational studies are hindered by the intractably vast number of possible polymorphs, also known as "configurational explosion".

In this contribution we overcome this configurational explosion utilizing the SAMPLE^[1] approach, which uses a combination of physically-motivated coarse graining of the configurational potential energy surface and machine learning in the form of Bayesian linear regression.

We apply the method to computationally investigate the influence of molecule size on the formation of surface polymorphs for acenequinones on Ag(111). Therefore we present the low energy polymorphs and surface patterns for monolayers of four different acenequinones, starting from the small benzoquinone over naphta- and anthraquinone to the larger pentacenequinone.

For a deeper understanding, we elucidate the driving forces of polymorph formation in two ways. First we investigate the molecule-substrate interaction by finding preferred adsorption sites for single molecules on the substrate. As a second step we illustrate the molecule-molecule interactions and therewith explain the energetic preferentiability of the low energy polymorphs found.

[1] Scherbela, Hörmann, Jeindl, Obersteiner and Hofmann, Physical Review Materials 2(4), 043803

BAYESIAN INFERENCE FOR ORGANIC/INORGANIC INTERFACES

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Quantum mechanical accuracy is required to simulate the structures and properties of molecules on surfaces. However, accurate calculations are costly and extensive sampling is prohibitive, so studies into molecular assembly and surface-supported processes like diffusion are guided by human intuition. To promote unbiased studies into molecular surface structures and phenomena, we have combined atomistic simulations with Bayesian optimisation - an artificial intelligence (AI) technique designed for complicated optimisation tasks [1]. We demonstrate how the AI was adapted to learn surface and property landscapes of molecules on surface with minimal computational sampling [2], delivering most stable surface structures with favorable designer properties. Energy landscapes can be further data-mined for low energy paths and associated trajectories to reveal the atomistic mechanisms behind key processes. We showcase the capability of AI to infer complex properties on several examples of atomic and molecular surface adsorbates.



Figure 1: AI applied to different organic/inorganic interface problems: a) complex oxide adsorption energy lanscape for coronene/Cu(110)-Oc(6x2); b) simultaneous inference of adsorption energy and charge transfer landscapes for benzene/Cu(100).

M. U. Gutmann, J. Corander, J. Mach. Learn. Res. 17, 1 (2016).
 M.Todorović, M. U. Gutmann, J. Corander and P. Rinke, *arXiv*:1708.09274 (2017).

ADSORPTION, CONDENSATION AND DESORPTION OF ATOMS AND MOLECULES ON SURFACES

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When atoms or molecules are deposited on surfaces, they can form different ordered or disordered phases depending on the delicate balance between (1) the interaction of the adsorbed particles with the substrate (V_{AS}) and (2) the lateral interaction between the adsorbed particles (V_{AA}). The effective lateral interactions between atoms or molecules on surfaces may be substantially weaker than in the corresponding 3D condensed phase and may even become repulsive. Overall attractive lateral interactions may result in a phase transition from an initial 2D lattice gas phase into a 2D condensed phase above a threshold coverage which depends on the substrate temperature. I will give an overview of the basic physical concepts governing the adsorption, condensation and desorption of atoms and molecules on surfaces and how these processes can be studied experimentally. In particular, I will illustrate how adsorption isotherms and temperature programmed desorption (TPD) can yield quantitative information on the adsorption enthalpy of atoms and molecules and provide access to the interaction parameters V_{AS} and V_{AA} [1,2].

While the case of atoms is rather straightforward, the many internal degrees of freedom of molecular adsorbates provide additional complexity but also novel physical phenomena, such as the possibility of an azimuthal reorientation of molecules during the 2D condensation [3,4]. I will stress the importance of transition states for the adsorption/desorption *kinetics* as well as the for the diffusion and nucleation of molecules on surfaces. The quantitative investigation of such transition states and their correct statistical treatment presents a major challenge in the field.

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- [2] B. Lehner, M. Hohage and P. Zeppenfeld, Chem. Phys. Lett. 336, 123 (2001);
 Chem. Phys. Lett. 369, 275 (2003); Chem. Phys. Lett. 379, 568 (2003).
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ORAL

INFORMATICS FOR SURFACE-ASSISTED MOLECULAR SELF-ASSEMBLY AND NANOSTRUCTURE PREDICTION

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Self-assembly of organic precursors on metal surfaces is widely used to create graphene nanoribbon and other exotic nanomaterials. In order to discover new nanomaterials by this approach, theoretical methods which can predict the outcome of the self-assembly process, as well as identify precursors which from target structures upon self-assembly, are desirable. In this presentation, we will introduce three informatics-based methods for studying on-surface molecular self-assembly processes. The first of these methods, which uses a combination of Monte Carlo sampling and supervised learning, can predict the shapes of self-assembled structures at thermodynamic equilibrium [1, 2]. The second of these methods uses an unsupervised learning strategy to explain how the chemical properties of the precursor molecules determine the shape of the self-assembled structure [3]. The third of these methods uses an optimization technique [4, 5] to predict a precursor molecule needed to form a desired self-assembled structure. We will introduce these methods in the context of graphene nanoribbon fabrication, and will also discuss our efforts to obtain experimental confirmation of our predictions.

- [1] D. M. Packwood, P. Han, and T. Hitosugi. Chemical and entropic control on the molecular self-assembly process. *Nat. Commun.* **8**, 2017, 14463
- [2] D. M. Packwood, P. Han, and T. Hitosugi. State-space reduction and equivalence class sampling for a molecular self-assembly model. *Roy. Soc. Open. Sci.* **3**, 2016, 150861
- [3] D. M. Packwood and T. Hitosugi. Materials informatics for self-assembly of functionalized organic precursors on metal surfaces. *In press* (2018)
- [4] D. M. Packwood and T. Hitosugi. Rapid prediction of molecule arrangements on metal surfaces *via* Bayesian optimization. *Appl. Phys. Express* **10**, 2017, 065502
- [5] D. M. Packwood. *Bayesian Optimization for Materials Science*. SpringerBriefs in the Mathematics of Materials 3, Springer, Tokyo (2017)

EPITAXIAL ORDER OF 3-DIMENSIONAL ORGANIC CRYSTALS: THE CASE OF ROD-LIKE CONJUGATED MOLECULES

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Rod like conjugated molecules like sexiphenyl, sexithiophene or pentacene are intensively studied in terms of their application in organic electronics like light emitting devices or thin film transistors. It turned out that the structural properties are one key to understand the performance of devices. This talk will present the epitaxial growth of sexiphenyl at different surfaces: muscovite(001), gold(111), KCl(100), rubbed polymer surfaces and isotropic silicon oxide [1,2]. The morphologies of the films are investigated by microscopic methods (AFM, TEM, SEM), the crystallographic properties are studied by diffraction methods (XRD related methods, TED) and the properties of the first monolayers at the substrate surface by surface science methods (LEED, TDS). Theoretical calculation based on energy minimization supplement the experimental results (see Figure 1) [3]. Based on different surfaces the different mechanisms for the formation of epitaxial thin films are discussed. The interaction of the molecules with the substrate surface is a key to understand the epitaxial thin film formation. While at systems with high molecule / substrate interactions (like a metal surface) the crystal growth follows rather the adsorption geometry of the first monolayers, while weak molecule / substrate interactions allow the formation of crystalline clusters directly at the substrate surfaces. Different mechanisms for the formation of epitaxial order of rod-like molecules is suggested which includes besides the molecule / substrate interaction also the corrugation of the substrate surface as well as the role of step edges. Additional the influence of polymorphism is discussed in terms on surface selected phases or surface induced crystal structures [4,5].



Figure 1: The epitaxial order of sexiphenyl on a muscovite (001) surface: alignment of a single molecule (left part) and of a crystalline cluster (right part) as obtained by energy calculations based on force field methods (middle part);

- [1] T. Haber, et al., J. Crys. Growth 284, 209 (2005).
- [2] T. Haber, et al., Phys. Rev. B, 74, 454191 (2006).
- [3] C. Simbrunner, et al., J. Am. Chem. Soc. 133, 3056 (2011).
- [4] T. Djuric, et al., PhysChemChemPhys 14, 262 (2012).
- [5] A.O.F. Jones, et al., Adv. Funct. Mater. 26, 2233 (2016).

ORAL

EPITAXY WITHOUT COINCIDENCES – THE STABILIZING ROLE OF STATIC DISTORTION WAVES

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Organic semiconductor materials are nowadays the basis for many types of devices such as light emitting diodes, solar cells, or field effect transistors. While applications typically feature polycrystalline layers, from the scientific point of view highly ordered molecular films are especially interesting as they allow for an undisturbed insight into the physical properties of molecular layers and interfaces.

The epitaxy of many organic films on inorganic substrates can be classified within the framework of rigid lattices. There, the total energy of a film of an organic material, growing under distinct orientations on top of a crystalline substrate, is minimized if both lattices share common sets of lattice lines. In reciprocal space this is tantamount to coincidences of recipro-cal adsorbate and substrate lattice points. Besides such different types of lattice epitaxy a highly reproducible growth mode with fixed lattice orientation but locally varying spacings has been discussed in literature for some decades. In my talk I will represent the first direct experimental observation of such 2-dimensional static distortion waves in a molecular film [1]. A model will be presented which allows not only to reproduce the observed molecular displacements in both size and direction, but which can be used to calculate the energy gain accompanying the local relaxations. Further, the epitaxial orientation angle of the film is accurately reproduced. The parameters for the model are obtained from DFT calculations.



Figure 1: Static distortion waves in one monolayer of the organic molecule HBC on graphite. Left: Experimentally determined average lattice (blue dots) and displacements (red; magnification factor 15). Right: Total adsorption energy per molecule of an HBC domain of approx. 10.000 molecules, initially separated by the experimental average incommensurate lattice constant of 13.95 Å, versus rotation angle θ . The lattice relaxation produces an energy gain of 85 meV/molecule. Inset: Chemical structure of HBC.

[1] M. Meissner, F. Sojka, L. Matthes, F. Bechstedt, X. Feng, K. Müllen, S.C.B. Mannsfeld, R. Forker, and T. Fritz: ACS Nano 10, 6474–6483 (2016).

MODELING TRANSITIONS AT GRAIN BOUNDARIES

T. Frolov, Q. Zhu, A. Oganov and R. E. Rudd

Recent years have seen a rapid growth of evidence suggesting that materials interfaces are capable of first-order structural transformations in which the interface properties undergo discontinuous changes. Experiments have linked these transitions to abnormal grain growth in ceramics, activated sintering and liquid metal embrittlement and raised a number of fundamental questions concerning the atomic structures and kinetic properties of these interface phases. This talk will review recent advances in modeling methodology that enable discovery of grain boundary phases. Applications of this methodology to several materials systems are discussed. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

EVOLUTIONARY STRUCTURE PREDICTION FOR MAGNETIC INORGANIC -ORGANIC COORDINATION POLYMERS

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A number of crystalline inorganic-organic coordination polymer (CP) thin films have been recently fabricated using Atomic/molecular layer deposition (ALD/MLD) [1], [2]. So far, mainly thin-films composed of alkali metals or earth-alkaline metals and organic building blocks have been structurally characterized. However, ALD/MLD process with terephthalic acid and a suitable iron precursor also results in a crystalline CP thin film (Fig. 1). We have used USPEX evolutionary crystal prediction approach together with DFT calculations to predict the atomic-level structure of the CP thin film [3]. We define the inorganic-organic coordination polymer as a pseudo-molecular structure with rigid building blocks to speed up the USPEX structure search. To properly describe the Fe-O bonding in the structure, we have used our recently developed USPEX/CRYSTAL interface to enable efficient hybrid-DFT calculations in combination with USPEX. Magnetism of the Fe(III) cations has also been taken into account. We will discuss the most stable structures predicted by our approach and compare them with the experimental GIXRD and FT-IR data.



Figure 1: Crystalline Fe-TP (terephthalate) coordination polymers have been prepared using ALD/MLD. One of the predicted structures is shown on the right (USPEX/DFT)

- [1] E. Ahvenniemi, M. Karppinen, Chem. Mater. 2016, 28, 6260.
- [2] M. Nisula, J. Linnera, A. J. Karttunen, M. Karppinen, Chem. Eur. J. 2017, 23, 2988.
- [3] A. R. Oganov, A. O. Lyakhov, M. Valle Acc. Chem. Res. 2011, 44, 227.

INFLUENCE OF SUBSTRATE TEMPERATURE ON STRUCTURAL, OPTICAL, AND ELECTRICAL PROPERTIES OF ZNO DEPOSITED BY PLASMA-ENHANCED ATOMIC LAYER DEPOSITION

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ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices (e.g., gas, bio, and UV sensors, piezoelectric nanogenerators and actuators). Being able to tailor these material properties to meet specific technological requirements is crucial for enhancing the device efficiency or sensitivity. In a previous study [1], the effect of plasma power on plasmaenhanced atomic layer deposited (PE-ALD) ZnO had been investigated at room temperature. By tuning the power, several material properties had been tailored (see Figure 1). However, the power had shown little influence on the texture of the crystalline films. In this study, we investigated the effect of substrate temperature in the range 25 $^{\circ}C$ – 250 $^{\circ}C$ on the ZnO properties. The films were grown by direct PE-ALD adapting diethylzinc and O₂-plasma as reactants. By adjusting the substrate temperature, it was possible to switch the texture of the films from (100) at room temperature to (002) above 150 °C. The growth per cycle (obtained by spectroscopic ellipsometry, SE) ranged from 1.6 to 4.0 Å/cycle, suggesting a temperature dependent growth behavior. Further SE analysis showed a range of refractive index (at 633 nm) from 1.87 to 1.94 and a bandgap range of 3.255 to 3.270 eV. X-ray photoelectron spectroscopy survey scans pointed out a non-detectable carbon while high-resolution scans of the O1s-peak showed a decrease in OH-content with increasing temperature. Further analysis will focus on resistivity (and its relation to OH-content), transparency, and piezoresponse.



Figure 1: (a) Growth per cycle, (b) refractive index, (c) extinction coefficient spectra, and (d) bandgap with respect to RF-power. Image reprinted from [1].

[1] Pilz et al., J. Vac. Sci. Technol. A 36.1 (2018): 01A109.

MOLECULAR SELF-ASSEMBLY AT SOLID LIQUID INTERFACES UNDER ELECTROCHEMICAL CONTROL

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In recent experiments [1] the spontaneous and reversible transition between two- and threedimensional self-assembly scenarios of a supramolecular system (PQPClO₄) at a solid–liquid interface under electrochemical conditions [Au (111) in 0.1 M HClO₄] has been demonstrated. By a simple variation of the interfacial potential, it was possible to selectively organize the target molecules (i) in an open porous pattern, (ii) to fill these pores to form an auto-hostguest structure or (iii) to stack the building blocks in a stratified bilayer.

In our complementary theoretical investigations effort is dedicated to rationalize these experimental observations. To this end the molecules are modeled as rigid entities composed of atomistic constituents. Based on ab initio calculations we take into account long-range electrostatic– and short-range Lennard Jones–potentials for intermolecular interactions, describe the solid–liquid interface in terms of a slab–geometry with a lower perfectly conducting soft wall and allow for an external electrostatic field.

The self-assembly scenarios of these molecular models at an interface is studied and identified via optimization tools that are based on evolutionary algorithms. The complexity of the problem forces us to use advanced techniques of these optimization tools, including a basin hopping memetic approach combining the heuristic nature of evolutionary strategies with deterministic local gradient descent algorithms. The gradient descent method – relying on LAMMPS potentials and gradients – deterministically evaluates every basin's local minimum with high accuracy while the evolutionary search gradually adapts its population to the energetically most favorable solution, exploring the search space for the global optimum.

Our theoretical results allow predicting, on the basis of the model above, the experimental conditions under which the various self-assembly scenarios can be observed. Moreover, our algorithm does not only apply to the PQPClO₄ system but we implemented a framework which can cope with arbitrary (rigid) molecules in any kind of periodic or non periodic system. We demonstrate that we are able to make reliable predictions for the ground state for a variety of combinations of cations (PQP⁺, PQPC₆⁺) and anions (ClO₄⁻, AQDSA²⁻, BS⁻) at a solid–liquid interface under electrochemical control [1, 2]. In addition, our findings indicate the location of the ClO₄⁻ anion relative to the cation, an information which is – due to the anion's high mobility – not, or only very limited [2], accessible experimentally.

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[2] K. Cui et al., Small 13, 1702379 (2017)

WHEN THERE IS MORE THAN MEETS THE EYE – STM/STS OBSERVATIONS OF SPATIAL AND ELECTRONIC STRUCTURES OF SELF-ASSEMBLED MOLECULAR STRUCTURES

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Scanning probe microscopy (both STM and AFM) is a very powerful tool to study the structural and electronic properties of surfaces with atomic-scale resolution, as evidenced by its more than 30 years and still ongoing triumphal procession through all fields of solid state research. However, in case of molecular adsorbates, the situation is often more complex than it appears at first glance. This has two reasons: firstly, STM "sees" only electronic local density of states and not atomic structure; secondly, STM only provides a "top view" of surfaces (LDOS), and additional atoms may be hidden underneath or between close-packed molecular self-assemblies. The latter is especially more likely to occur for non-innocent molecules exhibiting stronger interactions with the substrate. While the newly established combination of STM and AFM in a single measurement provides complimentary information [1], it cannot always help to discriminate different possible structural models. Even worse, for more sophisticated molecules the top-view projection of the LDOS in scanning tunneling spectroscopy (STS) can lead to misinterpretations when trying to assign spectral maps to molecular orbitals.

In my talk, I will give an overview of recent insights from adsorption of tetracyanoethylene (TCNE) onto various noble-metal surfaces, which features a surprisingly large variety of patterns [2-4]. I will show examples of complex self-assembly that can only be explained by adsorbate-induced strong relaxations and reconstructions of the substrate or by trapping of metal adatoms within the molecular layer [4,5]. In the last part of my talk, I will provide examples of submolecularly resolved spectroscopic mapping where orbitals seem to be located on parts of the molecular structure that cannot possibly be the origin [5,6]. I will discuss this in terms of tunneling combined with intramolecular transport, giving an outlook toward future requirements to correctly model scanning probe results.



Figure 1: STM images of TCNE adsorption on various noble-metal surfaces.

- [1] N. Hauptmann et al., Nano Lett. 17, 5660 (2017).
- [2] D. Wegner et al., Nano Lett. 8, 131 (2008).
- [3] S. Bedwani et al., Phys. Rev. Lett. 101, 216105 (2008).
- [4] D. Wegner et al., Nano Lett. 13, 2346 (2013).
- [5] V. Obersteiner et al., Nano Lett. 17, 4453 (2017).
- [5] P. Ewen et al., Phys. Rev. Lett. 111, 267401 (2013).
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INTERFACE MODULATED ACTIVE SITES ON AU NANOPARTICLES: IS IT REALLY ALL LOCAL?*

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In the three decades since Haruta's discovery of the unexpected reactivity of oxide-supported Au nanoparticles, we have come a long way in the application of nanoparticles as catalysts for a variety of reactions. Yet, the phenomenon is far from being fully understood as a number of factors control both active sites and product selectivity of these nanocatalysts: the size, the shape, the support, the coadsorbates are all important. In this talk, the local electronic structure and geometric environment for active sites on Au nanoparticles on three different supports, single-layer MoS_2 , single-layer *h*-BN and the $TiO_2(110)$ surface, will be compared. We will show that while the interface plays a major role in methanol decomposition [1] and CO

oxidation for Au nanoparticles supported on $TiO_2(110)$ and singlelayer *h*-BN, the same is not the case when the support is single-layer In fact, the Au/MoS_2 MoS₂. favors formation of composite methanol (and higher alcohols) from syn gas [2]. These differences may be traced to Au-support interaction, the ensuing charge transfer, the role of vacancies, and the extent to which the system frontier orbitals are shifted towards the Fermi level.



- [1] S. Hong and T. S. Rahman, JACS, **135**, 7629 (2013)
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ORAL

SOLID-SURFACE MODIFICATION WITH HIGHLY ORIENTED MOLECULAR FILMS WITH 2D STRUCTUTRAL ORDER

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The surface properties of solid substrates have a considerable impact on many physical, chemical, and electrochemical events occurring at a materials interface. Thus, the control of chemical and physical properties of solid surfaces, *e.g.*, surface morphology and energy, wettability, and adhesiveness, provides a key technology in many practical applications. As a useful approach for this purpose, the formation of self-assembled monolayers (SAMs) has widely been used, which relies on specific bonding between polar functional groups of organic molecules and outermost surface elements of inorganic substrates. However, this approach cannot be applied for the modification of polymer substrate surfaces, which are devoid of any effective binding site against polar functional groups. Recently, we reported new tripodal molecules that undergo controlled self-assembly not only on inorganic substrates but also on polymer substrates, resulting in a completely oriented molecular thin film like SAMs (Figure 1).^{1–3} The formation of this molecular film relies on a unique assembling property of the molecular building block capable of forming 2D (hexagonal triptycene array) + 1D (layer stacking) structure regardless of the types of substrates. In this presentation, the formation and applications of the molecular films will be described.



Figure 1: Highly ordered oriented organic thin films formed by the controlled assembly of tripodal molecules (tripodal triptycenes).

- [1] N. Seiki, Y. Shoji, T. Kajitani, F. Ishiwari, A. Kosaka, T. Hikima, M. Takata, T. Someya, T. Fukushima, *Science* **2015**, *348*, 1122–1126.
- [2] F. K.-C. Leung, F. Ishiwari, T. Kajitani, Y. Shoji, T. Hikima, M. Takata, A. Saeki, S. Seki, Y. M. A. Yamada, T. Fukushima, *J. Am. Chem. Soc.* **2016**, *138*, 11727–11733.
- [3] T. Yokota, T. Kajitani, R. Shidachi, T. Tokuhara, M. Kaltenbrunner, Y. Shoji, F. Ishiwari, T. Sekitani, T. Fukushima, T. Someya, *Nature Nanotech.* **2018**, *13*, 139–144.
- [4] F. Ishiwari, Y. Shoji, T. Fukushima, Chem. Sci. 2018, 9, 2028–2041.

STRUCTURE PREDICTION FOR SELF-ASSEMBLED MONOLAYERS AT THE SOLID/LIQUID INTERFACE

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Functionalization of oxide surfaces, i.e. the controlled attachment of functional organic molecules, for example in dye-sensitized solar cells, molecular electronics or nanoparticle synthesis, is usually done by wet-chemical processes. Linker units such as phosphonic acids or silanol groups are used, which facilitate binding of the organic molecules to the oxide surfaces via single or multiple condensation reactions, i.e. by elimination of water molecules. However, the preferred binding mode and the packing density (surface coverage) of the molecules and how both can be tuned by a specific choice of solvent and experimental processing conditions are basically unknown.

In the first part of my talk I will show how first insights can be obtained by the thermodynamic surface phase diagram technique. The advantage of this approach is that the solvent molecules are not explicitly included in the calculations but are represented by appropriate chemical potentials. Furthermore, it allows to assess the thermodynamic stability of the self-assembled organic layers. In the second part I will discuss an example of how accelerated molecular dynamics techniques such as metadynamics can be used for exploring adsorbate structures and reaction mechanisms. Here we frequently observe processes that cannot be simulated using implicit solvent models but require an explicit treatment of the solvent molecules.



Figure 1: Example of a free energy landscape for the reaction of a methylsilanetriol molecule with an alumina surface.

ORAL

KINETIC MONTE CARLO SIMULATION OF THE SOLUTION-PHASE GROWTH OF GOLD NANOPARTICLES

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The catalytic, electronic, and optical properties of metal nanoparticles strongly depend on their three-dimensional atomic structure. In this work, we have developed a kinetic Monte Carlo (KMC) simulation approach for modeling the atomistic growth behavior of Au nanoparticles, in order to provide a direct link to the experimentally-observed growth behavior. Such a model can provide information about the impact of individual system events on the final atomic-scale structural features of the Au nanoparticles. In contrast to traditional molecular dynamics simulations, we can track the atomistic nanoparticle structural evolution on time scales that approach the actual experiments. This allows us to perform direct comparisons against experimental benchmarks, and thus, transition our KMC simulations from a hypothetical toy model into an experimentally-relevant tool. Here, we report the effects of synthesis temperature and initial precursor concentration on the Au nanoparticle growth behavior, and we find that our model can be trained (via automated feedback) to adequately reproduce the experimental growth curves at the same conditions. The fitting procedure results in reasonable parameter values, including activation energy barriers that are consistent with related experimental measurements. In addition, since our KMC simulations preserve the atomistic details of our growing Au nanoparticle, this allows for detailed structural analyses. Also, our surface texture analysis highlights the changes in the surface structure as a function of time. While the nanoparticles show similar surface structures throughout the growth process, there can be some significant differences during the initial growth at different synthesis conditions.



Figure 1: Illustration of the local coordination analysis of the Au nanoparticles. (solid lines) fitted parameters (dashed lines) perturbed parameters for sensitivity analysis.

[1] C. H. Turner, Y. Lei, and Y. Bao, Nanoscale 8, 9354-9365 (2016).

HIGH-THROUGHPUT GENERATION OF NONPOLAR STOICHIOMETRIC SLAB-AND-VACUUM MODELS

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High-throughput first principles investigation of surface properties is impossible without high-throughput generation of atomistic slab-and-vacuum models. Making a nonpolar slab is very important when calculating surface energies because the two surfaces must be identical. Moreover, the electrostatic potential at the

two sides of the slab must be the same when comparing energy levels including the ionization potential, work function, and electron affinity, otherwise the vacuum level becomes ill-defined. Obtaining a nonpolar and stoichiometric slab can be obvious in some cases and could be prepared by hand, such as the rocksalt (100) surface, but is not trivial in many crystals, especially with complicated structures.

Core techniques that are critical to pursue this field of research will be outlined in the presentation, such as (1) robust and rigid definition of a nonpolar slab based on crystallography [1], (2) quick identification of whether an orientation is always polar or not based on the space group [2], (3) finding where to cleave bulk to automatically generate a nonpolar and stoichiometric slab by simple cleaving, if possible [1], and (4) how to automatically reconstruct the topmost and bottommost layers of a nonpolar slab that can be made stoichiometric by removing half of the atoms at both sides of the slab. In particular, technique (4) allows automatic generation of nonpolar slabs of some important crystal structures, most notably perovskite and spinel, that always require reconstruction to obtain a nonpolar and stoichiometric slab...



Figure 1: Making a nonpolar stoichiomentric perovskite (001) slab--and-vacuum model.

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- [2] Y. Hinuma et al., in preparation.

SURFACE INDUCED THIN FILM PHASES A BENZOTHIENO-BENZTIOPHENE DERIVATIVE

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A main advantage of organic semiconductors compared to inorganics is their processability in solution under ambient conditions. With them low-cost production of flexible and large-area electronics are expected. Therefore, organic molecules with suitable solubility, thermal stability and semiconducting properties have to be found and their crystallization behavior studied. So far benzothieno[3,2-b][1]benzothiophene (BTBT) derivatives are very promising candidates. Out of them 2-decyl-7-phenyl-[1] benzothieno[3,2-b][1] benzothiophene (Ph-BTBT-10) drew attention after uniform and molecularly flat polycrystalline thin films of its SmE liquid crystalline phase were successfully produced that exhibited high thermal durability and mobility.¹ Recently it was shown that the family of BTBT-molecules show polymorphic phases so called substrate-induced phases. They exhibit significantly different structure to that found in single crystals.² In this work these surface induced thin film phases are investigated for Ph-BTBT-10. Thin films starting from the monolayer regime up to thick films are prepared by spin coating. The films are investigated in terms of crystalline properties and thin film morphology by X-ray diffraction, X-ray reflectivity and grazing incidence X-ray diffraction, optical microscopy and atomic force microscopy. Additionally, the annealing behavior was studied trough in-situ diffraction measurements. It is shown that at low concentrations a uncompleted mono layer of standing molecules is obtained while at higher concentrations strong island growth is observed. At higher concentrations a new polymorph of the molecular Ph-BTBT-10 is found which differ in the molecular packing from the known bulk structure of the molecule.



Figure 1: The process of surface induced crystallization for the molecule 2-decyl-7phenyl-[1] benzothieno[3,2-b][1] benzothiophene

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C. Ruzie, O. Werzer, M. Sferrazza, ACS Appl. Mater. Interf. 7, 1868 (2015).

TOWARDS COMPUTATIONAL STRUCTURE PREDICTION OF ORGANIC THIN FILMS: TCNE ON Cu(111)

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Organic thin films often crystallize in unique, surface-induced phases, which exhibit physical properties that are superior to the bulk structures. However, resolving the surface-induced thin film phases remains a huge challenge, in particular for first-principle calculations. While efficient structure determination strategies exist for the adsorption of isolated molecules and to a limited extend also for molecular monolayers, none of these are efficiently applicable to organic thin films.

In this contribution, we demonstrate a strategy to bridge this gap with the SAMPLE^[1] approach: By combining single molecule adsortion geometries we first create an exhaustive set of monolayer structures. We then choose a small subset of these structures using experimental design (D-optimality criterion) and calculate their adsortion energies using dispersioncorrected density functional theory (DFT). Based on these adsorption energies we apply Bayesian linear regression to find an energetically optimized first adsorbate layer as well as the phase diagram for this layer. In order to predict multilayer structures we then consider this first layer as new surface on which a second layer adsorbes.

Here, we demonstrate the applicability of this approach on TCNE (tetracyanoethene) on Cu(111). For this system, we found that structures consisting of face-on geometries are energetically favourable at low coverage. We then investigate whether at increasing coverage a phase transition to densely packed, upright standing molecules occurs, or whether - and in which structure - a TCNE bilayer forms.

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CRYSTAL STRUCTURE SOLUTION FROM THIN FILMS

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A change in the structural order of organic molecular crystals is observed often for films, that are thin enough to interact strongly with the substrate, they are grown upon [1]. New polymorphic phases can be accessed this way, known as substrate-induced phases (SIPs), the most prominent example being pentacene [2]. The structure solution of such phases is challenging, as there are no well-established methods like when dealing with crystalline powders or large single crystals. A combined approach of using grazing incidence x-ray diffraction (GIXD) to measure and index the Bragg peaks as well as computational refinement with methods like molecular dynamics (MD) simulations, to determine the exact packing, is a promising methodology [3]. One set of samples are molecular crystals of 2-decyl-7-phenyl-[1]benzothieno[3,2-b][1]benzothiophene (Ph-BTBT-10). Thin films are prepared by physical vapour deposition and by spin-coating from toluene solutions on silicon oxide surfaces. Additionally, a mixed crystal film from p-sexiphenyl (6P) and α -sexithiophene (6T) deposited onto silicon as well as highly oriented pyrolytic graphite (HOPG) is studied.



Figure 1: a) Methodology to solve a crystal structure from a thin film. b) Structure of Ph-BTBT-10. c) Packing of 6P (top) and 6T (bottom) mixed crystals on HOPG.

- [1] A. O. F Jones, et al, Adv. Funct. Mater. 26, 2233 (2016)
- [2] D. Nabok, et al., Phys. Rev. B 76, 235322 (2007)
- [3] A. O. F. Jones, et al., CrystEngComm 19, 1902 (2017)

SAMPLE SURFACE STRUCTURE PREDICTION FROM FIRST PRINCIPLES

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Monolayers of organic molecules on inorganic substrates often show rich polymorphism with diverse structures in differently shaped unit cells. Determining the different commensurate structures from first principles is far from trivial due to the large number of possible polymorphs. Using the example of naphthalene on Cu(111), we introduce the SAMPLE approach^{[1][2]}, which employs coarse-grained modeling in combination with Bayesian linear regression to efficiently map the entire the potential energy surface and ab initio thermodynamics to generate phase diagrams. For naphthalene on Cu(111) we predict the adsorption energies for a large number of structures and determine the phase diagram.

Therefore, we first determine adsorption geometries, which isolated molecules adopt on the substrate. Secondly, we generate all possible unique substrate super cells, whose area lies within predefined boundaries. Thirdly, we combine the local adsorption geometries with each super cell to generate possible structures. For a subset of these structures, we determine the adsorption energies using dispersion-corrected density functional theory (DFT). This subset serves as training data for a Bayesian linear regression algorithm, which allows to predict the adsorption energies of all possible polymorphs. Finally, we employ ab initio thermodynamics by assuming that the adsorbed layer is in thermodynamic equilibrium with an ideal molecule gas. Evaluating the Gibbs free energy of adsorption of all polymorphs then allows to generate a phase diagram and identify stable polymorphs at different temperatures and pressures.

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Strategy to modelling the growth process of Co-Salen structures using multi scale methods, from Density Functional Theory to Empirical Force Fields.

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The self-assembly of metal-organic molecules Co-Salen ((Co(C16H14N2O2)) on the bulk NaCl(100) surface, has been measured using non-contact atomic force microscopy. These room temperature measurements, observe two different morphologies, a metastable nanowire and a stable nanocrystallite, both believed to consist of Co-Salen dimers [1]. To model this bimodal growth process, several levels of computational theory is needed. Density Functional Theory (DFT), is used to study single molecule adsorption on flat surfaces and step edges, which allow us to understand the interaction regimens involved in the system. However, DFT is unable to scale beyond a few molecules adsorbed on a surface. Therefore, a more approximate method is required. To reach the desired larger model sizes, empirical force fields is required. However, no parametrisation of a force field exists in the literature that is able to describe the three crucial interaction regimes required; Intermolecular, intramolecular and molecule-surface interactions. The force field parameters will be optimised using DFT reference data. Due to the large number of parameters required, a direct approach is unsuitable, and an approach using a genetic algorithm (GA) has been used [2]. In this work, the GA generated force field for the intramolecular and molecule-surface interactions is presented.



Figure 1: Proposed growth mechanism of Co-Salen structures observed on NaCl(100) [1]

- [1] S. Fremy, et al "Nanotechnology, vol. 20, no. 40, p. 405608, 2009.
- [2] D. Gao, et al, J. Comput. Chem., vol. 36, no. 16, pp. 1187-1195, 2015

EVALUATION OF A NOVEL SCHIFF BASE POLYPYRROLE ACTUATOR - A DFT AND FTIR STUDY

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To improve the electrical conductivity, elctropolymerized polyphenazine-2,3-diimino(pyrrole-2-yl) (PDPP) was doped with the sodium salt of polyvinyl sulphonic acid (PVSA) as a surfactant.[1,2] This study presents a combined electrochemical and theoretical investigation through CV and FTIR techniques of the PDPP polymers supported with theoretical DFT calculations on oligomer models of DPP. The role of the imino-pyrrole moiety was investigated by detection of their band frequencies (Figure 1), and it was confirmed that the orientation of PDPP at the electrode connects through the pyrrole linkage with adsorption of PVSA taking place within the pores in the polymer microstructure.



Figure 1: The DPP electropolymerization and its radical cation trimer structure (left) and the FTIR of the doped PDDP actuator (right)

F.J. Iftikhar, P.G.L Baker, A.M. Baleg, P.M. Ndangili, S.N. Mailu, E.I.Iwuoha, Electrochim. Acta 56, 5214 (2011).
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MODELING METAL/SELF-ASSEMBLED MONOLAYER INTERFACES USING DENSITY FUNCTIONAL THEORY

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Self-assembled monolayers (SAMs) of organic molecules covalently bonded to surfaces are widely used for numerous technological applications in many research areas, in view of their ability to modify surface and interfacial properties. In the increasingly growing field of organic electronics, SAMs are mostly employed to tune carrier injection/extraction barriers from the metal electrode to the (organic) semiconductor layer, being therefore particularly useful for devices such as organic thin film transistors (OTFTs).

The inclusion of SAMs in real devices, however, requires deep understanding and detailed characterization of the metal/SAM interface. In this regard, quantum mechanical simulations are an extremely powerful tool that allows investigating the systems of interest up to the atomistic level.

In this contribution I give some examples of how density functional theory (DFT) calculations, applied together with periodic boundary conditions and the repeated slab approach, can be used to characterize such interfaces. The electronic and structural properties of the systems are investigated, in order to precisely correlate the specific molecular building blocks to the induced surface modifications. The comparison of calculated and experimental results is discussed as well, emphasizing the importance of combining calculations and experiments for an exhaustive understanding of material properties.

In particular, originally designed dithiocarbamate (DTC) and triptycene based SAMs bonded to coinage metal substrates are considered, which have the peculiarity of adsorbing on the surfaces in a bidentate and tridentate fashion, respectively. Such unconventional docking groups represent new promising platforms for surface modifications.

BOTTOM-UP SYNTHESIS OF HIGH THERMOELECTRIC POWER IN B₃N₃-DOPED GRAPHENE: A FIRST-PRINCIPLES DESIGN ^A

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Based on the density functional theory simulations, we design a novel B_3N_3 -doped graphene sheet based on the bottom-up synthesis approach through the polymerization of BN-phenanthryne molecules [1,2,3], as shown in Figure 1. The B_3N_3 -doped graphene sheef is a semiconductor with a direct band-gap of 0.64 eV. On the other hand, we also find that the B_3N_3 -doped graphene exhibits large thermopower factor of 5.8 (mW/mK²) at room temperature, comparable to that of commercial Bi_2Te_3 (4 mW/mK²). This large thermopower could be ascribed to the large density of states near the valence and conduction band edges of B_3N_3 -doped graphene [4]. These findings demonstrate that B_3N_3 -doped graphene is a promising atomic-layer material for thermoelectric devices.



Figure 1: The schematic synthesis and energy band structure of B_3N_3 -doped graphene by covalent assembling of BN-Phenanthryene molecules

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INITIAL ZNO CRYSTALLITE FORMATION BY PLASMA ENHANCED ATOMIC LAYER DEPOSITION

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ZnO is a wide direct bandgap semiconductor, extensively studied as thin film because of its unique opto-electrical properties. Its crystalline structure has a crucial impact on the material characteristics and its applicability in opto-electronic devices. Therefore, control over the preferred crystallographic orientation in ZnO thin films has been often investigated.

Atomic layer deposition (ALD) is a self-limiting deposition method, mainly adopted for the delivery of (ultra-)thin films. Due to its layer-by-layer nature, details on the nucleation and growth of materials can be investigated. Next to ALD, plasma enhanced ALD (PE-ALD) is an alternative method which employs reactive plasma as co-reactant. Thin films deposited with PE-ALD show several differences when compared to ALD, such as different textures and lower defect formation. Therefore, for ZnO thin films the growth mechanism and initial crystallite formation may be greatly influenced by the use of plasma when compared to classical ALD.

In this contribution, the initial growth of direct PE-ALD ZnO grown on Si (100) is investigated. DEZ and pure oxygen plasma are adopted during the process. The first stages of growth are analysed using synchrotron light grazing incidence X-ray diffraction (GIXD), X-ray reflectivity (XRR), and spectroscopic ellipsometry (SE). The influence of substrate temperature (25 °C to 250 °C) on the crystal growth and orientation are studied. A closed layer was obtained within 7 cycles for all the temperature explored, suggesting island growth of the ZnO. However, GIXD showed no crystalline texture at this stage. An amorphous intermixed interface between the native SiO₂ and the growing layer was found, with a density in between pure SiO₂ and ZnO. Irrespective of the deposition temperature, the first crystal structure was measured at around 3 nm, with a preferential out-of-plane orientation transiting from (100) to (002).



Figure 1: Schematics of the PE-ALD reactor and GIXD map showing the (100) preferential orientation obtained for PE-ALD ZnO layers deposited at 25 °C.

A MOMENTUM-RESOLVED VIEW ON ULTRAFAST EXCITON DYNAMICS: FROM SEMICONDUCTORS TO MOLECULAR CRYSTALS

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The interaction of electrons and holes, as well as the formation of localized bound states, govern the optical properties of semiconductors and molecular crystals. While excitons have been typically investigated experimentally with optical spectroscopic techniques, studies providing momentum resolution are rare. In our group, we use time- and angle-resolved photoemission spectroscopy (trARPES) to study ultrafast exciton dynamics, resolved both in energy and momentum. In this pump-probe approach, an optical femtosecond laser pulse creates an excitonic excitation, while a time-delayed femtosecond extreme ultraviolet (XUV) pulse probes the system undergoing dynamics via trARPES [1-3], revealing the distribution and the evolution of the excited states within the Brillouin zone, as well as their potential spin- and pseudospin-polarization [1]. As recently shown theoretically [4], many-body states exhibit characteristic features in trARPES spectra. We applied this approach to the layered semiconductor (e.g. semiconducting transition metal dichalcogenide WSe₂) and discuss spectroscopic observable in the context of exciton binding energy and size as well as exciton-phonon coupling. We additionally discuss the application of this technique to the investigation of excited states in molecular systems.



Figure 1: Schematic of the experimental trARPES approach.

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EXPERIMENTAL AND DFT CALCULATION OF INTERFACE FOR MG₂SI AND AL MATRIX AFTER T6 HEAT TREATMENT

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Aluminium is the third most abundant element in the Earth's crust, after oxygen and silicon. Before the start of the last century, aluminium started to come into wide use as a structural material. Since then, it has reached the position of being the second most used metal in the world, with only steel beating it to the throne. One important structural limitation of aluminium is their fatigue strength. Precipitation hardening is utilized to strengthen a wide variety of alloy systems especially for Aluminum Alloys. An example is the class of commercially important Al–Mg–Si based alloys which are strengthened by a number of metastable precipitate phases, where the needle-shaped β ''-Mg5Si6 precipitates are often the main contributor to hardening. Beginning with the supersaturated solid solution (SSS), the generic precipitation sequence in Al–Mg–Si alloys is generally believed to be :

SSS -> Mg/Si clusters -> Guinier-Preston zones -> β '' -> β ' -> β

In practice, the sequence can be even more complex and a number of other metastable phases, depending on alloy composition and the heat treatment time and temperature. In this research, interface energy was calculated by Quantum Espresso with super cells designed on VESTA as shwon on Fig. 1. For comparison, in this research, experimental was also carried out to determine effects of strengthening precipitates on mechanical properties. T6 heat treatment was done starting from solid solution treatment, quenching and finished my artificial aging. Hardness was done to determine mechanical properties and SEM-EDS and XRD were done to characterize the materials.



Fig. 1 Supercell of Mg₂Si and Al

STRAIN EFFECTS IN DEFECTED MONOLAYER TRICHALCOGENIDES

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Recent experimental realizations of a few layer CrSiTe₃ and CrGeTe₃ have sparked a lot of interests in this class of layered materials. CrSiTe₃ is a Vander-waal stacked 2D-layered ferromagnet. Long range magnetic ordering is suppressed by thermal fluctuations in 2D materials (Mermin-Wagner theorem). The magnetic ordering in this class of 2D materials is protected by their high magnetic anisotropies. In this work, monolayers of CrSiTe₃ have been studied by introducing point defects in the Cr-sites. 2% compressive biaxial strain can drive the pristine monolayer from ferromagnetic ground state to antiferromagnetic ground state. The overall changes in electronic structure and magnetic ground state due to the combined effect of point defects and biaxial strain will be presented. Such a layered material can have potential applications in spintronics and flexible optoelectronic devices.



Figure 1: Defected monolayer CrSiTe₃

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[2] S. Chabungbam, P. Sen Phys. Rev. B 96, 045404 (2017)

EPITAXIAL FILM GROWTH OF PENTACENEQUINONE ON GRAPHENE AND Au(111)

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The formation of epitaxial order is studied for pentacenequinone (P2O) thin films with a nominal thickness of approximately 3.5 nm. Films were prepared by physical vapor deposition under ultra-high vacuum conditions on a Au(111) surface and on top of a graphene monolayer prepared at a silicon carbide substrate. The deposition process was monitored using differential reflectance spectroscopy starting from the bare substrate up to approximately 10 monolayers of coverage. Indexation of the low energy electron diffraction (LEED) measurements successively allowed the determination of the crystallographic unit cell of the adsorbate layer and its epitaxial relationships to the substrate. In a subsequent step the epitaxial order of P2O crystallites is investigated by grazing incidence X-ray diffraction (GIXD). The threedimensional crystal structure can be determined from these measurements by presenting reciprocal space maps and pole figures. Results obtained for P2O on Au(111) and graphene (see Figure 1) show two different surface unit cells as obtained from LEED images. GIXD measurements confirm the appearance of two different crystal structures (cf. Figure 1). One is the known bulk phase [1], the other one the recently reported surface-induced phase of P2O on graphite [2]. This work shows the combination of different experimental approaches to study epitaxy in films ranging from the monolayer regime up to thick films.



Figure 1: Low energy electron diffraction pattern (a), reciprocal space map (b) and pole figure of the 001 diffraction peak (c) of a pentacenequinone film with a nominal thickness of 3.5 nm.

[1] A. V. Dzyabchenko, V. E. Zavodnik, V. K. Bel'skii, Acta Crystallographica B, **35**, 2250 (1979).

[2] J. Simbrunner, C. Simbrunner, B. Schrode, C. Röthel, I. Salzmann, R. Resel, Acta Crystallographica A, accepted.

CRYSTAL STRUCTURE SOLUTION FROM THIN FILMS: INDEXATION OF GRAZING INCIDENCE X-RAY DIFFRACTION PATTERNS

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Crystal structure solution from thin films requires indexation of the diffraction pattern which means the assignment of Laue indices to the observed Bragg peaks. The focus of interest are molecular crystals at surfaces where usually low symmetry structures - either triclinic or monoclinic unit cells - are observed. The diffraction experiments for thin films are performed under grazing incidence condition of the primary x-ray beam which yield the reciprocal lattice vectors of the Bragg peaks splitted in two components: an in-plane part q_{xy} and an out-of-plane part q_z. Therefore, for this specific case two components of the reciprocal lattice vectors are available for the indexation process.¹ This is considerably different for the indexation procedure of single crystal diffraction pattern where all three components of the reciprocal lattice vectors are measured and powder diffraction on polycrystalline materials where only the lengths of the scattering vectors are detected. In a first step of our work analytical expressions were derived to calculate the lattice constants for a triclinic unit cell with the *ab*-plane parallel to the substrate surface.² But in the general case the rotation matrix must be included which introduces additional unknown parameters.³ We use a mathematical formalism by including the specular diffraction peak so that the system of unknown parameters can be reduced from the 3- to the 2dimensional space. Thus in the first part of the indexation routine the lattice parameters a, b, γ and the Laue indices h and k are determined followed by the second part calculating the residual parameters c, α , β and the Laue indices 1.



Figure 1: Grazing incidence diffraction pattern of pentacenequinone crystals on a graphite (0001) surface without indexation (left) and with indexation (right).

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EVALUATING DIFFERENT MODELS FOR THE ANALYSIS OF TUNNELING CURRENT-VOLTAGE CURVES IN METAL-MOLECULE-METAL MOLECU-LAR JUNCTIONS

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When characterizing molecular and monolayer junctions one of the key-parameters used is the so-called transition voltage. Unfortunately, its relation to the intrinsic electronic properties of the junction is still poorly understood, although Baldea, Frisbie and coworkers have recently obtained an excellent correlation between the energetic positions of the electronic transport channels extracted from a simple one-state model and the positions of the peaks in the density of states obtained via photoelectron spectroscopy measurements.

This raises the question, to what extent a model building on a single, discrete energy level can be sufficient to represent the complex electronic structure of the junction. We investigated the applicability of the aforementioned model especially in view of the vastly different coupling strength between substrates and molecules upon changing the docking chemistry.

For this, we simulated the electronic structure of a wide range of molecular junctions using density functional theory based methods and calculated the current-voltage characteristics by employing the Landauer-Büttiger formalism. Finally, from these characteristics we fitted the energetic position of the above-mentioned discrete "transport" level. Its properties are then compared to the actual electronic structure of the junction.