ICII-2021 International Conference on Internal Interfaces

10 – 14 October 2021 Castle Rheinfels, Germany



Program and Abstracts





ICII-2021 International Conference on Internal Interfaces

10 – 14 October 2021 Castle Rheinfels, Germany

Interfaces between solids play a decisive role in modern materials sciences and their technological applications. ICII-2021 provides an expert forum for the discussion of recent progress as well as of experimental and theoretical challenges in fundamental research of solid/solid interfaces. Scientific topics include: interfaces of two-dimensional semiconductors, organic/inorganic interfaces, hybrid organic/layered materials interfaces, interfaces with carbon-based materials, ultrafast charge transfer processes at interfaces, properties of interface excitons, chemical reactivity and interphase formation, synthetic interface chemistry, electronic and structural characterization of solid/solid interfaces, interfaces, interfaces, interfaces, electron microscopy at internal interfaces, advances in theoretical methods for solid/solid interfaces, computational materials design.

Organizers: Prof. Dr. Michael Gottfried Prof. Dr. Kerstin Volz Prof. Dr. Ulrich Höfer Dr. Johanna Heine

Philipps-Universität Marburg D-35032 Marburg, Germany **Conference Secretary:**

Dr. Stefan Renato Kachel Sonderforschungsbereich 1083 Philipps-Universität Marburg Hans-Meerwein-Straße 6 35032 Marburg, Germany

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Conference Location:

Hotel Schloss Rheinfels, Schlossberg 47, 56329 St. Goar, Germany

N 50° 9' 15.088" (50.1541910929) E 7° 42' 18.346" (7.7050960064)

Financial Support:

Collaborative Research Center "Structure and Dynamics of Internal Interfaces", SFB 1083, funded by the Deutsche Forschungsgemeinschaft (DFG)

Scientific Program

<u>Sunday, 10.10.2021</u>

From 17:00	Registration	Castle Rheinfels
19:00	Get together, discussions and Poster Session I (on-site)	

Monday, 11.10.2021

From 8:30	Registration
Session I	(Chair: Michael Gottfried)
09:00-09:05	Welcome
09:05 - 9:50	Hui Zhao, University of Kansas Ultrafast charge transfer across interfaces of two-dimensional semiconductors
9:50 - 10:35	Ulrich Höfer, University of Marburg Ultrafast electron transfer processes at internal interfaces
	Networking and discussion (with coffee)
Session II	(Chair: Ulrich Höfer)
11:00 - 11:45	Martin Wolf, Fritz Haber Institute (online) <i>Recent Advances in Probing Excited States at Interfaces by Time-resolved</i> <i>ARPES</i>
11:45 - 12:30	Hrvoje Petek, University of Pittsburgh Light MATTERs!!!
12:30 - 13:30	Lunch Break
13:30 - 15:30	Discussion

Session III	(Chair: Hrvoje Petek)
15:30 - 16:00	Kunie Ishioka, National Institute for Materials Science, Japan (online) Coherent phonons at lattice matched GaP/Si(001) heterointerface
16:00 - 16:45	Uwe Bovensiepen, University of Duisburg Essen
	Microscopic dynamics of propagating and localized excitations across interfaces analyzed by femtosecond solid state spectroscopy
	Networking and discussion (with coffee)
Session IV	(Chair: Uwe Bovensiepen)
17:15 - 18:00	Petra Tegeder, University of Heidelberg
	Electronic Properties of Interfaces with N-Heteropolycyclic Molecules
18:00 - 18:30	Marcel Reutzel, University of Göttingen
	Quantifying ultrafast energy dissipation pathways in exfoliated and stacked van der Waals materials with energy-, momentum-, and time-resolution
19:00 - 20:30	Dinner
20:30 - 22:00	Poster Session II (on-site)

<u>Tuesday, 12.10.2021</u>

Session V	(Chair: Petra Tegeder)
09:00 - 09:45	Junfa Zhu, University of Science and Technology of China (online)
	Different reaction mechanisms of two biphenyl-based molecules on Ag(111) surface
09:45 – 10:30	Karl-Heinz Ernst, EMPA Dübendorf / University of Zurich
	Planarization of non-planar aromatic hydrocarbons: Dehydrogenation versus hydrogenation
	Networking and discussion (with coffee)
Session VI	(Chair: Karl-Heinz Ernst)
11:00 - 11:30	Qitang Fan, University of Marburg
	Carbon Nanostructures from On-Surface Synthesis
11:30 - 12:00	Ulrich Koert, University of Marburg
	Cyclooctynes on Si(001): A synthetic chemist's perspective
12:00 - 12:30	Gregor Witte, University of Marburg
	Engineering of Printable and Air-Stable Silver Electrodes with High Work Function using Contact Primer Layer: From Organometallic Interphases to Sharp Interfaces
12:30 - 13:30	Lunch Break
13:30 - 16:30	Excursion and discussions (walk to Maria Ruh)

Session VII (Chair: Gregor Witte)

- 16:30 17:15Joan Redwing, University of PennState (online)Step-directed alignment of epitaxial transition metal dichalcogenide
monolayers on sapphire
- 17:15 18:00Oliver L.A. Monti, University of ArizonaInterfacial Interactions at Hybrid Organic / Layered Materials Interfaces
- 18:00 18:45Willi Auwärter, Technical University of MunichBorophenes made easy: Distinct polymorphs and heterostructures
- 19:00 20:30 *Dinner*
- 20:30 22:00 *Discussions*

Wednesday, 13.10.2021

Session VIII	(Chair: Thomas Michely)
09:00 - 09:45	Sheng Meng, Chinese Academy of Sciences (online) Manipulating quantum states by photoexcitation in two-dimensional quantum materials
09:45 - 10:30	Xavier Marie, Institute of Applied Sciences of Toulouse <i>Excitons in atomically thin 2D semiconductors</i>
	Networking and discussion (with coffee)
Session IX	(Chair: Kerstin Volz)
11:00 – 11:45	Erdmann Spiecker, University of Erlangen-Nuremberg (online) <i>Revealing the structure and orientation of organic nanocrystallites in bulk</i> <i>heterojunction solar cells using 4D Scanning Confocal Electron Diffraction</i> <i>(4D-SCED)</i>
11:45 – 12:30	Thomas Michely, University of Cologne <i>Chemical reactivity and electronic correlations in 2D-materials tuned by</i> <i>internal interfaces</i>
12:30 - 13:30	Lunch break
13:30 - 17:00	Poster session III (on-line)
Session X	(Chair: Robert Wallauer)
17:00 - 17:45	Christian Jooß, University of Göttingen (online) <i>Tuning energy conversion by correlations at perovskite oxide interfaces</i>
17:45 – 18:30	Christoph Tegenkamp, University of Chemnitz Electron transport along chiral nanostructures
18:30 - 19:00	Hanna Bishara, Max Planck Institute for Iron Research, Düsseldorf The effect of grain boundary structure on electrical resistivity for a pure metal
19:00 - 22:00	Dinner and Discussion

<u>Thursday, 14.10.2021</u>

Session XI	(Chair: Xavier Marie)
09:00 - 09:45	Chung-Lian Lin, National Chiao Tung University (online)
	Temperature-Dependent Electronic Structures of TMD Weyl Semimetals
09:45 - 10:30	Christoph Koch, Humboldt-University Berlin (online)
	<i>Exploring static and dynamic charges at interfaces by advanced TEM methods</i>
10:30 - 11:00	Robert Wallauer, University of Marburg
	Charge transfer and exciton formation dynamics in TMDCs imaged by time- resolved momentum microscopy
	Networking and discussion (with coffee)
Session XII	(Chair: Willi Auwärter)
11:30 - 12:15	Silvana Botti, University of Jena (online)
	Computational materials design: from bulk systems to 2D materials and interfaces
12:15 - 13:00	Peter Liljeroth, Aalto University (online)
	Designer electronic states in van der Waals heterostructures
13:00 - 13:15	Closing remarks
13:15 - 14:15	Lunch
14:15	Departure

Poster Sessions

Sunday, 10.10.2021 & Monday, 11.10.2021 (on-site) and Wednesday, 13.10.2021 (online). The posters should be presented at on-site and online poster sessions, except for the posters marked *online only*, which are presented only during the online poster session on Wednesday.

1 Klaus Stallberg, University of Clausthal

Temperature effects on the formation and the relaxation dynamics of metal-organic interface states

2 Felix Otto, University of Jena (online only)

Restoring the molecular properties: K intercalation of the flexible DBP on Ag(111)

3 Maximilian Schaal, University of Jena (online only)

Decoupled or not decoupled? Investigation of charge transfer in organic/2D insulator/metal interfaces

4 Lukas Eschmann, University of Münster

Impact of electron phonon interaction on metal-organic interface states

5 Philipp Marauhn, University of Münster

Theory and computation of dielectric image effects in two-dimensional materials

6 Marie-Christin Heißenbüttel, University of Münster (online only)

Valley-dependent interlayer excitons in magnetic WSe₂/CrI₃

7 Mark Hutter, Research Center Jülich

On-Surface porphyrin transmetalation with Pb/Cu redox exchange

8 Miriam Raths, Research Center Jülich

Tracing orbital images on ultrafast time scales: The PTCDA/Cu(001)-2O-system

9 Robert Wallauer, University of Marburg

Tracing orbital images on ultrafast time scales: Time-resolved photoemission tomography experiments

10 Pierre-Martin Dombrowski, University of Marburg

Experimental Quantification of Interaction Energies in Organic Monolayers

11 Maximilian Dreher, University of Marburg

Van der Waals Bound Organic Semiconductor/2D-Material Hybrid Heterosystems: Intrinsic Epitaxial Alignment of Perfluoropentacene Films on Transition Metal Dichalcogenides

12 Yurii Radiev, University of Marburg Prepare with Care: a Universal Approach to Improving the Contact Resistance of Organic Field Effect Transistors

- **13 Priya Ravi, University of Marburg (online only)** Single-domain molecular layers on Ag (110)
- 14
 Jan Herritsch, University of Marburg

 Nickel Tetrapyrrole Complexes at Metal/Organic Interfaces
- **15 David Krug, University of Marburg** In-situ TEM Investigations of III/V Semiconductor Materials
- 16
 Andreas Beyer, University of Marburg

 Quantification of Nanometer-Scale Electric Fields at Internal Interfaces
- **17 Oliver Maßmeyer, University of Marburg** Structural characterization of III/V semiconductor interfaces using quantitative STEM methods
- **18 Thilo Hepp, University of Marburg** Interface-Dominated Heterostructures for Long-Wavelength Emission on GaAs Substrates
- **19 Robin Günkel, University of Marburg** *MOCVD growth studies of III-VI monolayers*
- **20** Hendrik Weiske, University of Leipzig Design of New Interfaces and Moving to New Substrates: Ring-Opening Reaction of Tetrahydrofuran on Ge(001)
- 21 Carolin Kalff and Dominik Scharf, University of Marburg Synthesis of Organic Building Blocks for Internal Interfaces
- 22 Josefine Neuhaus, University of Marburg Electron-Hole Plasma-Induced Dephasing in Transition Metal Dichalcogenides for ICII-2021
- 23 Marleen Axt, University of Marburg Ultrafast charge-transfer dynamics in twisted TMDC heterostructures

24 Alexa Adamkiewicz, University of Marburg

Tip-induced modification of semiconductor/organic interfaces

25 Tim Bergmeier, University of Marburg

Experimental setup for THz-ARPES and THz-HHG of electric currents at interfaces of topological insulators

26 Jonas Zimmermann, University of Marburg

Time-Resolved SHG Imaging Microscopy for Systematic Studies of Two-Dimensional Materials

27 Lasse Münster, University of Marburg

Momentum-resolved observation of ultrafast interlayer charge transfer between the topmost layers of MoS_2

28 Sarah Zajusch, University of Marburg

Dark exciton formation dynamics in WS₂

29 Nico Hofeditz, University of Marburg (online only)

Dynamics of charge transfer processes in strongly interacting organic donor/acceptor compounds

Oral Abstracts Monday

Ultrafast charge transfer across interfaces of twodimensional semiconductors

<u>Hui Zhao</u>

Department of Physics and Astronomy, The University of Kansas, Lawrence, KS, United States e-mail: huizhao@ku.edu

Since 2010, two-dimensional (2D) materials beyond graphene have drawn considerable attention as new forms of nanomaterials. One of the most intriguing aspects of 2D materials is that they provide a new route to fabricating multilayer heterostructures. Such multilayers are formed by combining several 2D materials with certain stacking orders *via* van der Waals interlayer interaction. Since lattice match is no longer a constraint, this new approach can produce a vast number of new materials for many applications, and can potentially transform material discovery.

One key issue for harnessing emergent electronic and optoelectronic properties of 2D heterostructures is the efficient and controllable charge transfer between different 2D layers. Since 2014, ultrafast and highly efficient transfer of electrons has been observed in several van der Waals heterostructures by time-resolved pump-probe measurements [1-4]. In such experiments, an ultrashort laser pulse is used to photo-excite one layer of a van der Waals heterostructure. Transfer of the excited electrons and holes to another layer is time resolved by measuring the transient absorption of a probe pulse that is tuned to the excitonic resonance of the destination layer.

In this talk, after a brief introduction on the principles of the experimental techniques, I will discuss some of the latest developments in this field. First, I will present experimental results that highlight the importance of the layer-coupled states on charge transfer. Second, I will discuss results of using an electric field generated by a pre-pulse to control interlayer charge transfer. Third, time-resolved studies on the tunneling of electrons through atomically-thin boron nitride barriers will be introduced. Finally, charge transfer in mixed-dimensional van der Waals heterostructures will be discussed. These experimental results could be used to develop advanced theoretical models to understand interlayer charge transfer in the van der Waals heterostructures.

- [1] X. Hong et al., Nat. Nanotechnol. 9, 682 (2014).
- [2] J. He et al., Nat. Commun. 5, 5622 (2014).
- [3] F. Ceballos et al., ACS Nano 8, 12717 (2014).
- [4] F. Ceballos et al., Nano Lett. 17, 1623 (2017).

Ultrafast electron transfer processes at internal interfaces

<u>Ulrich Höfer</u>

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Solid/solid interfaces play a crucial role in diverse fields of materials sciences. In this talk, I will describe how we access the ultrafast charge-carrier dynamics at such interfaces experimentally in the time domain. I will present results for a number of model systems where we obtained microscopic insights into electron transfer processes in a detail not envisioned a decade ago.

With time-resolved optical second-harmonic generation (SHG), we have been able demonstrate the presence of interface-specific electronic states at the buried interface of GaP/Si(001). Upon optical excitation, carriers are injected form the interface to the bulk material. The build-up of the resulting electric field can be followed as function of time.

Ordered organic layers grown on single crystal metal surfaces present well-defined models for contacts in organic semiconductor devices. For a number of such systems, time-resolved photoemission experiments revealed the presence of interfacial electronic states, located between the Fermi level of the metal and the molecular LUMO. Experiments at organic heterolayer systems clearly show that such interface states efficiently mediate the electron transfer at the contact. In the future, time-resolved photoemission orbital tomography, is expected to provide detailed information for the electron as well as the hole transfer between the different constituents of such organic heterolayers and allow us to time-resolve the formation of charge-transfer excitons.

Two-dimensional heterostructures of transition metal dichalcogenides (TMDC) have proven to be very well-defined and at the same time highly versatile model systems of van-der-Waals interfaces. Many material combinations feature a type-II band alignment which can separate photoexcited electrons and holes into different layers leading to the formation of so-called interlayer or interface excitons. The dynamics of this process shows a strong dependence on the stacking angle as revealed with time-resolved SHG imaging microscopy. Time-resolved photoemission momentum microscopy can record full 2D bandstructure movies of the electron scattering processes in these materials.

Recent Advances in Probing Excited States at Interfaces by Time-resolved ARPES

Martin Wolf

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Ultrafast photoexcitation at interfaces may lead to non-equilibrium phenomena like ultrafast phase transitions or interfacial charge and energy transfer coupled to nuclear motion. Such processes are characterized by pronounced changes of in the electronic structure and occupation of electronic states. Here I discuss recent advances to probe such transient changes by a table-top 500 kHz HHG based XUV laser source enabling excited state band mapping throughout the complete Brillouin zone by time-resolved photoemission spectroscopy (trARPES) employing a hemispherical analyzer and a momentum microscope in the same setup [1]. Such trARPES experiments provide detailed insights into the photo-induced phase transitions [2], the extend of the excitonic wave function in WSe₂ [3], and the ultrafast interlayer electron and energy transfer dynamics in a monolayer-WSe₂/graphene heterostructure (see figure below).



Acknowledgement: Collaboration with Shuo Dong, Samuel Beaulieu, Chris Niocholson, Tommaso Pincelli, Michele Puppin, Julian Maklar, Laurenz Rettig and Ralph Ernstorfer

- [1] M. Puppin et al., Rev. Sci. Instr. 90, 023104 & J. Makler et al., Rev. Sci. Instr. 91, 123112 (2020)
- [2] C.W. Nicholson et al., Science 362, 821 & Beaulieu et al., Science Advances 7, eabd9275 (2021)
- [3] S. Dong et al., Natural Science e10010 (2021)

Light MATTERs!!!

Hrvoje Petek,¹ Andi Li,¹ Zehua Wang,¹ Marcel Reutzel^{1,2}

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Light interacting with solid-state matter under perturbative conditions excites primarily electric dipole transitions between *k*-vector dependent eigenstates of the periodic lattice potentials. A time-periodic light potential, however, can modify the electronic band structure of a solid through nonperturbative interactions entangling the light-matter interaction, and opening a route to tailor material properties with light at will.

I will describe two examples: 1) It will happen at zero field strength when the complex dielectric response function Re[$\varepsilon(\omega)$]~0 and Im[$\varepsilon(\omega)$] is small. This happens for ionic solids above the longitudinal optical phonon frequency and for metals where the $-\varepsilon_{\infty}(\omega) \sim \varepsilon_{Drude}(\omega)$, or near the interband absorption threshold. This epsilon near-zero (ENZ) response coincides with the excitation of collective ion or electron responses, *i.e.*, in case of metals, the bulk plasmon excitation. I will describe the ENZ response of single crystalline, low-index surfaces of Ag, as measured by ultrafast multiphoton photoemission (mPP) spectroscopy. This bulk plasmonic response of Ag is fundamentally responsible for all plasmonic responses of silver, and yet the observed mPP spectra fundamentally contradict significant aspects that we expect from theory.

2) I will also report the high field response of Cu(111) surface where light is sufficiently strong to dress the electronic bands through Floquet engineering and Stark shift effects. The optical dressing opens the way to modify quasiparticles in solids at will, where, for example, electrons can be transformed into holes on subfemtosecond time scale. Our studies inform how light, electronic, and atomic degrees of freedom in solids can overcome their natural performance boundaries.

Strongly coupled interface phonons and interface electronic states at lattice-matched GaP/Si(001)

<u>Kunie Ishioka</u>¹, Gerson Mette², Steven Youngkin², Andreas Beyer², Christopher J. Stanton³, Wolfgang Stolz², Kerstin Volz², Ulrich Höfer²

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Interface of GaP and Si(001) can serve as a model semiconductor heterojunction because of the small lattice mismatch between the two semiconductors [1]. Transient reflectivity measurements with below-bandgap excitation of GaP with a near infrared pulse reveal a rich variety of ultrafast phononic and electronic responses that are characteristic to the heterointerface. The polarization-dependence of the LO phonon of the GaP layer shows a clear deviation from that of bulk GaP under the same excitation, which is indicative of a sudden creation of charge carriers due to the ultrafast injection from the Si substrate. In addition, the transient reflectivity of the heterointerface is also modulated by an oscillation at 2 THz, which is not seen for the bulk semiconductors. For the GaP nucleation layer grown at a relatively low temperature, the amplitude of this low-frequency mode (LFM) shows a distinct peak at 1.4 eV as the excitation photon energy is swept. This resonance behavior agrees well with that of the sub-picosecond electronic response in the same transient reflectivity signal and in our previous second harmonic generation study [2]. These results unambiguously demonstrate the resonant transition between the interface electronic states and the interface phonon mode that is strongly coupled to it.



Fig. 1 (a,b) Pump wavelength-dependence of the electronic response (a) and the interface phonon (b). (c) Schematic band diagram at the GaP/Si(001) interface.

- [1] A. Beyer and K. Volz, Adv. Mater. Interfaces 6, 1801951 (2019).
- [2] G. Mette, J. E. Zimmermann, A. Lerch, K. Brixius, J. Güdde, A. Beyer, M. Dürr, K. Volz, W. Stolz, and U. Höfer, Appl. Phys. Lett. 117, 081602 (2020).

Microscopic dynamics of propagating and localized excitations across interfaces analyzed by femtosecond solid state spectroscopy

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An excited electron propagates in condensed matter with its momentum k at an energy $E(\mathbf{k})$ and experiences elastic and inelastic scattering processes, which lead to electronic relaxation and energy transfer to microscopic excitations of the lattice and spin systems. Experiments employing femtosecond time-resolved photoelectron spectroscopy exploited so far very successfully the surface sensitivity of the method and probed such scattering processes locally at or near the surface in the time domain [1]. Here, we report on experimental results which analyze the non-local dynamics of excited electrons in two-photon photoemission (2PPE) and demonstrate sensitivity to buried media [2]. In these experiments one photon excites in Au/Fe/MgO(001) heterostructures electrons in Fe. Electron propagation through the layer stack to the Au surface is detected in 2PPE in back side pump - front side probe experiments in a time-of-flight like scheme. We observe pronounced differences between front and back side pumping of the heterostructure which are attributed to electron transport contributions through the layer stack. Furthermore, competition of e-e with e-ph scattering will be discussed in [Fe/MgO]_n heterostructures. Pump-probe experiments of element specific spectroscopy in combination with electron diffraction provide here unprecedented insights regarding the mechanism of energy transfer across interfaces and emphasize the importance of coupling hot electrons to non-thermalized interface phonons [3]. Extension of these experimental tools to address effects of strong electron correlation [4] and spindependent dynamics across interfaces [5] will be discussed.

This work was funded by the Deutsche Forschungsgemeinschaft through the Collaborative Research Center CRC 1242.

- U. Bovensiepen, H. Petek, M. Wolf, *Dynamics at Solid State Surface and Interfaces*, Vol. 1, Wiley-VCH, 2010.
- [2] Y. Beyazit J. Beckord, P. Zhou, J. Meyburg, F. Kühne, D. Diesing, M. Ligges, U. Bovensiepen, Phys. Rev. Lett. 125, 076803 (2020).
- [3] N. Rothenbach, M. E. Gruner, K. Ollefs, C. Schmitz-Antoniak, S. Salamon, P. Zhou, R. Li, M. Mo, S. Park, X. Shen, S. Weathersby, J. Yang, X. J. Wang, R. Pentcheva, H. Wende, U. Bovensiepen, K. Sokolowski-Tinten, A. Eschenlohr, Phys. Rev. B 100, 174301 (2019).
- [4] M. Ligges, I. Avigo, D. Golez, H. U. R. Strand, Y. Beyazit, K. Hanff, F. Diekmann, L. Stojchevska, M. Kalläne, K. Rossnagel, M. Eckstein, P. Werner, U. Bovensiepen, Phys. Rev. Lett. 120, 166401 (2018).
- [5] J. Chen, U. Bovensiepen, A. Eschenlohr, T. Müller, P. Elliott, E. K. U. Gross, J. K. Dewhurst, S. Sharma, Phys. Rev. Lett. 122, 067202 (2019).

Electronic Properties of Interfaces with N-Heteropolycyclic Molecules

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For improvement and optimization of the performance of organic molecule-based devices, such as photovoltaic cells and thin-film transistors comprehensive insight into the physical and chemical properties of the organic molecules at surfaces is necessary.

N-heteropolycyclic aromatic compounds are promising candidates for n-channel semiconductors. The introduction of nitrogen atoms into the π -backbone of the polycyclic aromatic hydrocarbons stabilizes the frontier orbitals and increases the electron affinity, while the size of the HOMO–LUMO (optical) gap is nearly unaffected. By using two-photon photoemission spectroscopy (2PPE) and high resolution electron energy loss spectroscopy (HREELS) we determined quantitatively transport, singlet and triplet states as well as electronic spectra of serval N-heteropolycyclic molecules adsorbed on Au(111) [1-5]. Using angle-resolved 2PPE we identified strongly dispersing occupied and unoccupied electronic states, which result from hybridization between localized molecular states and delocalized metal bands at the metal/organic interface [4, 5].

We acknowledge funding by the German Research Foundation through the SFB 1249 (N-Heteropolycycles as Functional Materials) and the Cluster of Excellence (3D Matter Made to Order).

- [1] M. Ajdari, T. Schmitt, M. Hoffmann, F. Maaß, H. Reiss, U. H. F. Bunz, A. Dreuw, P. Tegeder, J. Phys. Chem. C 124 (2020) 13196.
- [2] M. Ajdari, A. Stein, M. Hoffmann, M. Müller, U. H. F. Bunz, A. Dreuw, P. Tegeder, J. Phys. Chem. C 124 (2020) 7196.
- [3] M. Ajdari, F. Landwehr, M. Hoffmann, H. Hoffmann, U. H. F. Bunz, A. Dreuw, P. Tegeder, J. Phys. Chem. C 125 (2021) 6359.
- [4] A. Stein, D. Rolf, C. Lotze, B. Günther, L. H. Gade, K. J. Franke, P. Tegeder, J. Phys. Chem. Lett. 12 (2021) 947.
- [5] A. Stein, D. Rolf, C. Lotze, S. Feldmann, D. Gerbert, B. Günther, A. Jeindl, J.J. Cartus, O.T. Hofmann, L.H. Gade, K.J. Franke, P. Tegeder, J. Phys. Chem. C 125 (2021) 19969.

Quantifying ultrafast energy dissipation pathways in exfoliated and stacked van der Waals materials with energy-, momentum-, and time-resolution

<u>Marcel Reutzel</u>, Marius Keunecke, David Schmitt, Jan Philipp Bange, Wiebke Bennecke, Marco Merboldt, Marten Düvel, Daniel Steil, G. S. Matthijs Jansen, Sabine Steil, Stefan Mathias

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The atomic thickness and large chemical variety of two-dimensional van der Waals materials make them an exciting playground to investigate and control energy conversion processes on the atomic scale. The full potential of these materials can be exploited by stacking them into three-dimensional architectures: the (opto-)electronic material properties are then not only defined by the separate material sheets, but by the interlayer coupling and the respective Moiré potential, which can be manipulated by the relative momentum mismatch of the monolayer sheets. In order to explore the response of such material systems to an optical excitation, typically, time-resolved all-optical spectroscopies are employed. However, such experiments lack information on the momentum of the charge carriers involved, which is crucial for a detailed quantification of ultrafast energy dissipation pathways.

In this contribution, we will describe our efforts to quantify the ultrafast carrier dynamics in exfoliated and stacked van der Waals materials with complete energy-, momentum-, and time-resolution. First, we will introduce our new time-resolved photoemission experiment that combines a 1 MHz table-top extreme ultraviolet light source with a time-of-flight momentum microscope [1]. Second, we will describe the excited charge carrier dynamics of epitaxial graphene and in doing so pinpoint the contribution of distinct e-e and e-p scattering pathways to the overall dynamics [2]. Finally, we will discuss our efforts to probe exfoliated and stacked van der Waals materials in the time-resolved momentum microscopy experiment [Fig. 1].



Fig. 1.: Time-resolved momentum microscopy on exfoliated monolayer graphene. (a) Energy- and momentumresolved photoemission spectra are selectively collected from few μ m sized sample areas by placing an aperture into the image plane of the microscope. Either the energy filtered (b) real or (b) momentum space image is projected onto the detector.

- [1] Keunecke et al., Rev. Sci. Ins. 91, 063905 (2020).
- [2] Keunecke et al., arXiv:2012.01256 (2020).

Oral Abstracts Tuesday

Different reaction mechanisms of two biphenyl-based molecules on Ag(111) surface

Zhiwen Zeng, Lin Feng, Tao Wang, Junfa Zhu*

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On-surface synthesis (OSS) has shown its great potential in the fabrication low-dimensional covalent nanostructures with atomic precision in the last decade.¹ To obtain the high-quality covalent nanostructures, there is a need for a greater understanding of the underlying mechanisms of OSS. Here, we report an example that demonstrates the clear interdependence between surfacesupported reactions and molecular adsorption configurations. Two biphenyl-based molecules with two and four bromine substituents, i.e. 2,2'-dibromo-biphenyl (DBBP) and 2,2',6,6'-tetrabromo-1,1'-biphenyl (TBBP), show completely different reaction pathways on a Ag(111) surface, leading to the selective formation of dibenzo[e,l]pyrene and biphenylene dimer, respectively.² By combining low-temperature scanning tunneling microscopy, synchrotron radiation photoemission spectroscopy, and density functional theory calculations, we unravel the underlying reaction mechanism. After debromination, a bi-radical biphenyl can be stabilized by surface Ag adatoms, while a four-radical biphenyl undergoes spontaneous intramolecular annulation due to its extreme instability on Ag(111). Such different chemisorption-induced precursor states between DBBP and TBBP consequently lead to different reaction pathways after further annealing. The precise regioselective aryl-aryl coupling will reduce the flexibility of the DBBP which lead to the formation of planar dibenzo[e,l]pyrene (DB[e,l]P) via hierarchical intermolecular aryl-aryl coupling and cyclodehydrogenation. In contrast, the high selectivity toward a biphenylene dimer is attributed to the special adsorption configuration of TBBP on Ag(111).



Fig. 1 Reaction pathways of (a) DBBP and (b) TBBP on the Ag(111) surfaces, respectively.

- T. Wang, J.F.Zhu, Confined On-Surface Organic Synthesis: Strategies and Mechanisms. Surf. Sci. Rep. 74, 97 (2019).
- [2] L. Feng, *et al.*, On-Surface Synthesis of Planar Acenes via Regioselective Aryl-Aryl Coupling. Chem. Commun. 56, 4890 (2020).

Planarization of non-planar aromatic hydrocarbons: Dehydrogenation *versus* hydrogenation

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Besides their interest for potential organic electronic devices, modification of polycyclic aromatic hydrocarbons (PAH) on surfaces is believed to play a role in new organic electronic devices, light sensors or for electron-spin filters. We will present different aspects of modification of various single crystal metal surfaces in ultrahigh vacuum with PAHs, such as carbohelicenes and buckybowls.

The buckybowl pentaindenocorannulene adsorbs on a Cu(100) surface in two different modes, namely, bowl cavity up and bowl cavity down [1,2]. The latter dehydrogenates and delivers the hydrogen for hydrogenation of the cavity-up species. Cleavage of C-C bonds in two steps leads to a planar PAH with surface-quenched open shell character (Fig. 1, top). Cyclodehydrogenation of 2,2'-bispentahelicene, on the other hand, proceeds stereospecifically to coronocoronene, which is chiral due to surface confinement (Fig. 1, bottom) [3]. The role of steps, adatoms and vacancies in these processes will be discussed.



Fig. 1. Two examples in which planarization occurs by hydrogenation and C-C bond cleavage or by dehydrogenation and C-C bond coupling.

- [1] L. Li et al. ACS Nano 15, 3578 (2021).
- [2] Wäckerlin et al. ACS Nano 14, 16735 (2020).
- [3] B. Irziqat, A. Cebrat et al. Chemistry-Eur. J. doi.org/10.1002/chem.202102069

Carbon Nanostructures from On-Surface Synthesis

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In recent years, reactions at solid surfaces have been found extremely promising for the synthesis of planar carbon nanostructures, e.g., nanographenes, graphene nanoribbons, and nanoporous graphene [1]. The quest for planar carbon nanostructures with novel topologies persistently intrigues scientists because of their potentially remarkable properties. Here, by using custom designed organic precursors, we show the on-surface synthesis of carbon nanostructures with special topologies, including graphene nanorings, porous graphene nanoribbon, and nonbenzenoid graphene isomers (e.g., biphenylene sheet [2] in Fig. 1). Their electronic properties were studied with scanning tunneling spectroscopy and photoemission spectroscopy. The novel hierarchical on-surface reactions developed therein are expected to enrich the bottom-up toolbox for the synthesis of other theoretically proposed carbon nanostructures with exotic properties [3].



Fig. 1 Structural model of a new carbon allotrope: biphenylene sheet [2].

- [1] L. Talirz, P. Ruffieux, R. Fasel, Adv. Mater. 28, 6222-6231 (2016).
- [2] Q.T. Fan et al., *Science* **372**, 852-856 (2021).
- [3] S. Clair, D. G. de Oteyza, Chem. Rev. 119, 4717-4776 (2019).

Cyclooctynes on Si(001): A synthetic chemist's perspective

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The predictable synthesis of structurally defined interfaces is an important goal to regulate their physical, electronic, photophysical, and chemical properties. Here, progress towards the layer-by-layer synthesis of organic/semiconductor interfaces is reported. Functionalized cyclooctynes show a chemoselective reaction of the strained alkyne with the Si(001) surface. The achieved selectivity originates from a direct adsorption pathway of cyclooctyne as opposed to the majority of other organic functionalities. A layer-by layer synthesis can be achieved by combination of UHV-physics and solution chemistry.^[1] Alternatively, an UHV-only strategy is possible using 4+2 cycloadditions with inverse electron demand and strain-promoted azide/cyclooctyne 3+2 cycloadditions.^[2]



Fig. 1: UHV-only strategy using 4+2 cycloadditions with inverse electron demand and azide/cyclooctyne 3+2 cycloadditions.

[1] T. Glaser, J. Meinecke, C. Länger, J. Hepp, UK, M. Dürr, J. Phys Chem C 2021, 125, 4021

[2] T. Glaser, J. Meinecke, L. Freund, C. Länger, J. N. Luy, R. Tonner, UK, M. Dürr, Chem. Eur. J. 2021, 27, 8082.

Engineering of Printable and Air-Stable Silver Electrodes with High Work Function using Contact Primer Layer: From Organometallic Interphases to Sharp Interfaces

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Contact engineering is an important issue for organic electronics as it allows to reduce charge carrier injection barriers. While the use of molecular contact primer layers to control the energy level alignment is demonstrated in many concept studies mainly using (single crystalline) model substrates, the processability of electrodes, and their robustness (e.g., to air exposure) must also be considered in real devices. Although silver electrodes can be printed using silver ink, their low work function and sensitivity to oxidation severely limits their use for printable organic electronics. The present work demonstrates that contact primer monolayers of F4TCNQ and F6TCNNQ allow to meet these requirements and provide a reliable approach to engineer high work function silver electrodes, which is examined for Ag(111) as well as polycrystalline and silver ink substrates. Notably, upon multilayer growth of these organic acceptor films, a pronounced intercalation of silver into the molecular adlayer occurs at room temperature yielding an organometal interphase extending over the entire adlayer, which is stabilized by a charge transfer from the metal. It is shown that heating allows controlled desorption of this interphase leaving behind a well-defined monolayer that is further stabilized by an additional charge transfer into the acceptor molecules and causes a complete filling of the former LUMOs. Especially F6TCNNQ contact primer layers can also be prepared on oxidized silver electrodes and reliably yield work functions of 5.5–5.6 eV, which can even withstand air exposure. In addition, such contact primers show no interdiffusion into subsequently deposited layers of the prototypical p-type organic semiconductor pentacene, hence validating their use for organic electronic devices [1].



Fig. 1 Schematic summary of the structure and thermal stability of F₆TCNNQ films on silver electrodes.

[1] F. Widdascheck, D. Bischof, G. Witte. Adv. Funct. Mater. 10.1002/adfm.202106687 (2021).

Step-directed alignment of epitaxial transition metal dichalcogenide monolayers on sapphire

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Transition metal dichalcogenides (TMDs) form a compelling class of 2D materials with potential applications in optoelectronics, flexible electronics, chemical sensing and quantum technologies. At the monolayer limit, the semiconducting TMDs (*e.g.*, MX₂ where M = Mo/W and X = S/Se) exhibit direct band gaps within the visible range, large exciton binding energies and spin-valley polarization. The lack of out-of-plane bonding on the van der Waals surface of these materials enables heterostructure formation without the constraints of lattice matching.

Wafer-scale synthesis of semiconducting TMD monolayers is of significant interest for device applications. Promising results have been demonstrated for epitaxial films deposited by vapor phase techniques such as chemical vapor deposition (CVD) and metalorganic CVD (MOCVD). However, the three-fold symmetry of TMDs such as MoS₂ and WSe₂, typically results in two energetically equivalent domain alignments, often referred to as 0° and 60° domains, when grown on substrates such as c-plane sapphire and graphene. The oppositely oriented domains give rise to inversion domain boundaries upon coalescence which exhibit a metallic character.

In this study, we demonstrate the epitaxial growth of unidirectional TMD monolayers by MOCVD on 2" diameter c-plane sapphire substrates with a significantly reduced density of inversion domains [1]. Steps on the sapphire surface are shown to break the surface symmetry giving rise to a preferred domain orientation. The as-received sapphire substrates, which are miscut ~0.2° toward $<11\overline{2}0>$, consist of steps with sub-1 nm step height separated by 50-70 nm wide terraces. A threestep nucleation-ripening-lateral growth process, carried out at temperatures ranging from 850°C to 1000°C, was used to achieve epitaxial films of WSe₂ and WS₂ using W(CO)₆, H₂Se and H₂S as precursors in a H₂ carrier gas [2]. Nucleation was observed to occur at the step edge and the growing domains align epitaxially with the underlying (0001) sapphire lattice. As a result of the nucleation process, the domains grow with a zig-zag edge facing the top terrace edge which imparts a preferential direction to the domains. The percentage of domains with a preferred direction ranges from 75%-86% depending on MOCVD growth conditions. Continued lateral growth for times ranging from 10-30 minutes results in fully coalesced TMD monolayers that are epitaxially oriented on the sapphire, as assessed by in-plane x-ray diffraction, with a reduced density of inversion domain boundaries. The results demonstrate the important role of surface structure in nucleation and epitaxial growth of TMD monolayers.

[1] M. Chubarov et al., ACS Nano 15, 2532-2541 (2021).

[2] X. Zhang et al., Nano Lett. 18, 1049-1056 (2018).

Interfacial Interactions at Hybrid Organic / Layered Materials Interfaces

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Van der Waals layered materials offer an unprecedented sandbox for designing and probing quantum materials and strongly correlated materials. This is in large part due to their ease of fabrication and assembly into complex heterostructures with broadly tunable properties. Despite these unique advantages, the scope of functionalities and new physics of van der Waals layered materials has the potential to be enhanced even further if heterostructures beyond the layered materials are explored. Organic semiconductors are particularly advantageous in this context: They can be designed and synthesized essentially at will, and their internal interfaces reveal striking new properties that go beyond the organic materials on their own.

Here I will discuss two case studies where we investigate the new physics that arises at the interface of a layered materials and an organic semiconductor: I will show how the combination with carefully tailored organic semiconductors leads to the emergence of spin texture in a topological insulator [1], and how the combination of 2D materials and organic semiconductors creates hybrid excitons and strong Raman enhancement [2]. These two examples are showcases of the power of combining atomically hybrid heterostructures.

- [1] S. Jakobs *et al.*, Nano Lett. 15, 6022 (2015).
- [2] C. Muccianti et al., J. Phys. Chem. C 124, 18302 (2020)

Borophenes made easy: Distinct polymorphs and heterostructures

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Surface-supported two-dimensional (2D) materials keep attracting considerable interest. For example, borophene, a synthetic, boron-based 2D material, offers intriguing anisotropic electronic and mechanical properties [1,2]. Here, we present a versatile chemical vapor deposition (CVD) approach to grow atomically-thin 2D polymorphs of borophene by using diborane. This precursor originates from byproducts of commercial borazine, a popular material for growth of hexagonal boron nitride (h-BN). Specifically, borophene polymorphs with large single-crystalline domains are synthesized on Cu(111) and Ir(111) supports. Additionally, atomically-precise lateral interfaces or vertical van der Waals heterostructures combining borophene and h-BN can be achieved by sequentially dosing different precursors from the same supply (Fig. 1). Thereby, borophene is protected from immediate oxidation by a single h-BN overlayer. The borophene polymorphs and interfaces with h-BN are comprehensively characterized by low-temperature scanning tunneling microscopy and spectroscopy, x-ray photoelectron spectroscopy, and complementary density functional theory modeling. The ability to synthesize high-quality borophenes by a straightforward, scalable CVD approach opens up opportunities for the study of their fundamental properties and for device incorporation.



Fig. 1. Scheme (left panel) and atomically-resolved STM image (right panel) of a vertical heterostructure with h-BN covering borophene on Ir(111).

- [1] A.J. Mannix et al., Nat. Rev. Chem. 1, 1 (2017).
- [2] P. Ranjan et al., Adv. Mater. 32, 2000531 (2020).
Oral Abstracts Wednesday

Manipulating quantum states by photoexcitation in two dimensional

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Photoexcitation is a powerful means in distinguishing different interactions and manipulating the states of matter, especially in complex quantum systems. Here we demonstrate photoexcitation induced ultrafast dynamics in two-dimensional quantum materials using time-dependent density functional theory molecular dynamics. In particular, we discover a novel mechanism which involves self-amplified exciton-phonon dynamics for the formation of charge density wave (CDW), and we predict a new collective mode induced by photoexcitation which is significantly different from thermally-induced phonon mode. We will also discuss photoinduced electronic phases in other two-dimensional materials such as controlling the dynamics of Weyl quasiparticles in semimetal WTe₂ (Fig. 1). Our results provide insights from a new perspective on the coherent electron and lattice quantum dynamics in materials upon photoexcitation.



Figure 1. The dynamics of Weyl points distribution in response to different photoexcitation.

- M.X. Guan, E. Wang, P.W. You, J.T. Sun, S. Meng. Manipulating Weyl quasiparticles by orbital-selective photoexcitation in WTe₂. Nature Commun. 12, 1885 (2021).
- [2] H. Lakhotia, H.Y. Kim, M. Zhan, S.Q. Hu, S. Meng, E. Goulielmakis. Laser picoscopy of valence electrons in solids. Nature 583, 55 (2020).
- [3] C. Lian, S.J. Zhang, S.Q. Hu, M.X. Guan, S. Meng. Ultrafast charge ordering by self-amplied exciton-phonon dynamics in TiSe₂. Nature Commun. 11, 43 (2020).

Excitons in atomically thin 2D semiconductors

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In this talk I will first recall the general properties of 2D excitons in Transition Metal Dichalcogenides monolayers: giant binding energy, oscillator strength, exchange interactions, spin/valley...

Encapsulation of monolayers such as MoSe₂ in hexagonal boron nitride (hBN) yields narrow optical transitions approaching the homogeneous exciton linewidth [1,2]. We demonstrate that the exciton radiative rate in these van der Waals heterostructures can be tailored by a simple change of the hBN encapsulation layer thickness [3].

We also measured the exciton fine structure of MoS_2 and $MoSe_2$ monolayers encapsulated in boron nitride by magneto-photoluminescence spectroscopy in magnetic fields up to 30 T [4,5]. Finally I will present recent optical spectroscopy experiments on the control of interlayer excitons in MoS_2 bilayers [6,7]. We show that there is a correlation between the stacking order and the interlayer coupling of valence states in both as-grown MoS_2 homobilayer samples and in artificially stacked bilayers from monolayers. We also evidenced a giant Stark splitting of the interlayer excitons characterized by a large oscillator strength in bilayer MoS_2 .

[1] F. Cadiz et al, Phys. Rev. X 7, 021026 (2017)

- [2] G. Wang et al, Phys. Rev. Lett. **119**, 047401 (2017)
- [3] H. Fang *et al*, Phys. Rev. Lett **123**, 067401 (2019)
- [4] C. Robert et al, Phys. Rev. Lett . 126, 067403 (2021)
- [5] C. Robert et al, Nature Com. 11, 4037 (2020)
- [6] I. Paradisanos et al, Nature Com. 11, 2391 (2020)
- [7] N. Leisgang et al, Nature Nano. 15, 901 (2020)

Revealing the structure and orientation of organic nanocrystallites in bulk heterojunction solar cells using 4D Scanning Confocal Electron Diffraction (4D-SCED)

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The performance of bulk heterojunction (BHJ) organic solar cells is dictated by the nanomorphology and crystallinity of the organic blend, including size and orientation of (donor) nanocrystallites, donor-acceptor interfaces, and degree of percolation, which determine the efficiency of exciton dissociation and charge carrier transport. However, revealing the nanoscale structures at high spatial resolution using electron microscopy is challenged by radiation sensitivity of the organic materials. Nanobeam diffraction (NBD) imaging, also known as 4D-STEM, has recently emerged and demonstrated to map the orientation and study π -stacking structures in organic semiconductors molecular crystals, opening a new application field in beam sensitive soft materials [1]. In 4D-STEM, pixelated detectors are used to record the full 2D diffraction pattern at each probed sample position, allowing reciprocal space details of the scattered intensities to be analyzed afterwards. However, the NBD mode is intrinsically not optimized for dose efficiency as (i) a focused probe is interacting with a small sample region (high dose rate) and (ii) the far field diffraction disks are detected spreading over many pixels of the detector/camera, resulting in low signal to noise ratio (SNR). Moreover, for molecular crystals with relatively large unit cell parameters disk overlap severely limits the angular resolution of the technique.

Here, we propose a novel 4D-STEM modality based on a scanning confocal electron diffraction (SCED) setup, which combines high angular resolution with high contrast and low dose [2]. We use the 4D-SCED method to study the structure and orientation of molecular nano-crystallites in DRCN5T:PC71BM BHJ thin films. We show its high angular resolution for investigating the rich structural information of the molecular crystals, and demonstrate that this 4D-STEM modality is capable to improve dose efficiency by about one order of magnitude at identical dose budget compared to standard NBD setup. We furthermore show that 4D-SCED can even be used to monitor the growth and structural evolution of the nanocrystallites in situ during annealing at elevated temperatures.



Fig. 1 Visualization of the orientation of edge-on DRCN5T donor nano-crystallites (colored) and distribution of face-on grains (gray) from 4D-SCED. Scale bars: 500 nm (left), 2 mrad (right).

- [1] O. Panova et al., Nature Materials, 18, 860-865 (2019).
- [2] M. Wu et al., Microsc. Microanal., 27(S1), 194-197 (2021). doi:10.1017/S1431927621001306

Chemical reactivity and electronic correlations in 2D-materials tuned by internal interfaces

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Two dimensional materials are atomically thin and display a front- and a backside. Through interface interaction with a layer of atoms, another 2D layer, or a bulk substrate on its backside, the 2D layer electronic properties and its frontside interaction with the environment are largely changed.

Doping of graphene through intercalation layers on its backside changes the ionic binding of adsorbates to graphene, graphene's van der Waals interaction with organic molecules and even reaction pathways in organo-metallic synthesis on its frontside.

Doping graphene itself can also be used for non-invasive chemical gating of 2D layers placed on top. For MoS_2 grown on doped and un-doped graphene on Ir(111) we demonstrate shifts of the band structure by up to 1.1 eV, severe band gap renormalization, and an insulator-to-metal transition.

Thereby it is also possible to manipulate 1D internal interface states in MoS₂, e.g. the 1D electronic states in mirror twin boundaries. One fundamental consequence of the analysis of 1D band filling and bending is the confirmation of a long standing theoretical prediction for the quantized polarization charge on mirror twin boundaries.

Tuning energy conversion by correlations at perovskite oxide interfaces

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Transition metal perovskite oxides show very rich structure-property relations. Even small changes in chemical composition, strain or defect concentrations can have tremendous effects on the electronic structure and related materials properties. Particularly at interfaces, electro-chemical, mechanical and defect chemical equilibria are strongly coupled, giving rise to emerging, highly tunable interface properties. Detailed understanding of these properties requires advanced atomic scale experimental techniques such as *in situ* transmission electron microscopy, x-ray as well as ultrafast optical spectroscopy.

In my talk, I will present two examples of tuning energy conversion at manganite perovskite interfaces by correlations:

(i) Tuning highly dynamic states at the electrode-water interface during oxygen evolution via electronic overlap between metal 3d states and oxygen 2p states and the resulting impact on carrier localization. This has a strong impact on the activity and stability of the electrode interfaces under operando conditions.

(ii) Tuning charge and orbital order of polaronic charge carriers at interfaces between manganites and titanites in order to enable hot polaron photovoltaics. The ordering has a strong impact on the lifetime of excited charge carriers and thus photovoltaic energy conversion.

- S. Raabe, D. Mierwaldt, J. Ciston, M. Uijttewaal, H. Stein, J. Hoffmann, Y. Zhu, P. Blöchl, and Ch. Jooss, Adv. Funct. Mater. 22 (2012) 3378.
- [2] J. Scholz, M. Risch, K.A. Stoerzinger, G. Wartner, Y. Shao-Horn, C. Jooss, J. Phys. Chem. C 120 (2016) 27746.
- [3] M. Sotoudeh, S. Rajpurohit, P.E. Blöchl, D. Mierwaldt, J. Norpoth, V. Roddatis, S. Mildner, B. Ifland, C. Jooss, Phys. Rev. B 95 (2017) 235150
- [4] D. Raiser, S. Mildner, B. Ifland, M. Sotoudeh, P. Blöchl, S. Techert, C. Jooss, Adv. Energy Mater. (2017) 1602174, DOI: 10.1002/aenm.201602174
- [5] B. Kressdorf, T. Meyer, A. Belenchuk, O. Shapoval, M. ten Brink, S. Melles, U. Ross, J. Hoffmann, V. Moshnyaga, M. Seibt, P. Blöchl, Ch. Jooss, Phys. Rev. Appl. 14 (2020) 054006.
- [6] G. Lole, V. Roddatis, U. Ross, M. Risch, T. Meyer, L. Rump, J. Geppert, G. Wartner, P. Blöchl and Ch. Jooss, Communication Materials, 1 (2020) 68

Electron transport along chiral nanostructures

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The transmission properties of electrons through chiral systems attracts currently a lot of attention [1]. In DNA and polypeptides the so-called chiral induced spin selectivity (CISS) effect describes the built-up of an extraordinarily high spin-polarizations upon long-range electron transfer. Moreover, also in chiral carbon nanotubes strong spin-polarizations are reported. This is surprising since heavy-atoms are missing in these carbon-based compounds. It turns out, that also for weakly spin-orbit coupled systems the spin transmissions are strongly amplified by the helicity, giving rise to non-symmetric Green's functions [2].

Towards these intriguing effects, we studied the transport through various chiral nanostructures. By means of pre-structured SiC(0001) samples, epitaxial graphene nanoribbons (GNRs) of exceptionally high quality and well-defined edges were prepared by Si sublimation [3,4]. The symmetry of the ribbons can be tuned by the SiC substrate, allowing us to fabricate armchair, zigzag and chiral GNRs. In contrast to armchair GNRs, the hallmark for ribbons with zigzag and chiral edges is a probe-spacing and temperature independent conductance of e^2/h which strongly indicates fully spin-polarized ballistic transport. These robust signatures can be observed in a range of a few µm down to hundreds of nm at room temperature [5]. The spin-polarized and ballistic transport channel comes along with asymmetrically coupled edges. By means of nanoscale and spatially resolved transport experiments, the concomitant separation of bulk channels in 40nm wide ribbons was found and explained by tight-binding calculations [6]. In a further example, we performed first transport experiments through lysine-doped and cysteine-terminated single helical polyalanine molecules (PA). The conductance varied exponentially with the length of the molecules and depend not on temperature, thus electron tunneling is the dominating transport channel. The decay constant for the PA was found to be 0.35 1/Å, significantly smaller compared to saturated and π -conjugated molecules, underlining the high conductivity along the PA and reflecting a low tunneling barrier height. The conductance histograms of all PA molecules investigated revealed characteristic satellite peaks, which correlate to apparent molecule length in multiples of characteristic peptide sequences. We address this effect to a racheting of interdigitated molecules [7,8].

- [1] K. Banerjee-Ghosh et al., Science 360, 1331 (2018).
- [2] M. Zöllner et al., ChemRxiv, doi.org/10.26434/chemrxiv.8325248.v2
- [3] A. Zakharov et al., ACS Appl. Nano Mat., 2, 156 (2019).
- [4] J. Aprojanz et al., Nano Research (2019) https://doi.org/10.1007/s12274-019-2425-5
- [5] J. Baringhaus et al., Nature, 506, 349 (2014).
- [6] J. Aprojanz et al., Nature Communications, 9, 4426 (2018).
- [7] T.N.H. Nguyen et al., J. Phys. Chem. C 123, 612 (2019).
- [8] T.N.H. Nguyen et al., J. Phys. Chem. C (2020), 10.1021/acs.jpcc.0c00246

The effect of grain boundary structure on electrical resistivity for a pure metal

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Grain boundaries (GBs) are internal interfaces which significantly increase the electrical resistivity of metals and alloys due to electronic scattering. However, the relationship between the interface atomic structure and its electrical behaviour is not fully understood yet, hindering the development and the design of novel electronic materials with boosted performance, such as conductors, photovoltaics, and thermoelectrics. Here, we provide a systematic study to correlate directly-measured resistivity of well-defined tilt Cu GB sub-micrometre segments with their structural and thermodynamic characteristics, e.g. misorientation, inclination, normal planes, atomic structures (phases), curvature, and excess volume and free energy.

To this aim, Cu thin films were sputtered on c-sapphire substrates and annealed to obtain abnormal grain growth and a variety of [111] tilt GB types, namely $\Sigma 3$, $\Sigma 7$, $\Sigma 19b$, $\Sigma 21a$, $\Sigma 37c$, and low angle GBs. Then, bi-crystals were created by focused ion beam (FIB), isolating a single GB. Electron backscatter diffraction (EBSD) and high-resolution transmission electron microscopy (TEM) were exploited to unravel the GB characteristics and the atomic structures. Subsequently, electrical resistivity measurements are conducted with four scanning probes positioned by micromanipulators inside a Scanning Electron Microscope (SEM). We found that the resistivity values span over more than one order of magnitude, while reporting a clear correlation with the excess volume and free energies of the interfaces as found by molecular dynamics simulations (MD).

Our results indicate that resistivity is highly dependent on the Σ -type of the GB. However, it does not noticeably change for structural variations of GB plane, phase, misorientation deviation from ideal Σ -type and inclination within the same Σ -type. Nevertheless, GB curvature increases resistivity up to 80% due to high density of defects. Overall, our novel results contribute to a better understanding of the structure-resistivity relation in GBs.

Oral Abstracts Thursday

Temperature-Dependent Electronic Structures of TMD Weyl Semimetals

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Transition metal dichalcogenides (TMDs) are layered materials with chemical compositions described as MX₂. Here, M represents an element of transition metals such as Nb, Mo, and W, and X a chalcogen atom such as S, Se, and Te. Most TMDs are semiconducting with valley degrees of freedom to generate an application in information processing. On the other hand, MoTe₂ and WTe₂ are TMDs and have been proposed as candidates for Weyl semimetals [1, 2]. Both of them have gathered a great deal of attention because of the quasiparticles on their crystal surface behave as massless chiral fermions –Weyl fermions. One of the unique characteristics of Weyl semimetals is the emergence of a topologically protected surface state called Fermi arc, which can be observed by Angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM) based quasiparticles interference (QPI).

Recently temperature-dependent transport properties of both WTe₂ and MoTe₂ are reported [3, 4]. Therefore, it is urgent to reveal the temperature-dependent electronic structures of these TMD Weyl Semimetals. By using STM and STM-QPI, both structure and electronic structures of MoTe₂ and WTe₂ are clearly revealed. Surprisingly, huge variations are found in between the results measured at 5K and 77K. For WTe₂, slight shifts of both two Fermi arc surface states (SS1 and SS2) and Weyl points (WPs) are shown in Fig. 1. Much large variations are found in the results of MoTe₂. The current work provides valuable insights into the temperature-dependent properties of TMD semimetals.



Fig. 1 Band dispersion of WTe₂ observed by STM-QPI at 77K and 4K. Shifts of both two topological surface states (SS1 and SS2) and Weyl points (WPs) can be seen.

- [1] C. L. Lin et al., J. Phys.: Condens. Matter 32, 243001(2020).
- [2] C. L. Lin et al., ACS Nano 11, 11459 (2017).
- [3] L. R. Thoutam et al., Phys. Rev. Lett. 115, 046602 (2015).
- [4] Q. L. Pei et al., Phys. Rev. B 96, 075132 (2017).

Exploring static and dynamic charges at interfaces by advanced TEM methods

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Fast electrons in the transmission electron microscope are very sensitive to local electric fields and with that the presence of charges that are not screened in the plane normal to the electron beam within a distance of less than about 1Å. Also interface and surface plasmons, i.e. the dynamics of charges at interfaces and surfaces can be detected by inelastic scattering of electrons with these quasi-particles, especially if the electron beam is very monochromatic. Charges and electric fields at interfaces can be detected by classical inline electron holography / focal series reconstruction [1]. But the detection of surface plasmons and other surface or interface specific electronic states typically requires monochromation. The ability to detect both spectra and electron diffraction patterns with a fast direct electron detector allows every electron to be counted without any readout noise and with high efficiency, since comparatively few electrons are thrown away due to the use of apertures or lossy detection [2]. This further enhances the sensitivity of the experimental apparatus. As an alternative to focal series reconstruction 4D-STEM data sets may also be used to recover the local electrostatic potential and charge density with deep sub-Ångstrom spatial resolution [3] and may even account for multiple scattering within the material [4]. EELS data being highly quantitative after having removed relativistic contributions to the spectrum and recovering the local dielectric function [5] – may then be used to map the dynamics of charges at interfaces.

- K. Song, S. Ryu, H. Lee, T.R. Paudel, C.T. Koch, B. Park, J.K. Lee, S. Choi, Y. Kim, J.C. Kim, H.Y. Jeong, M.S. Rzchowski, E.Y. Tsymbal, C. Eom, and S.H. Oh, *Direct imaging of the electron liquid at oxide interfaces*, Nature Nanotechnology 13 (2018) 198–203
- [2] B. Plotkin-Swing, G.J. Corbin, S. De Carlo, N. Dellby, C. Hoermannb, M.V. Hoffmana, T.C. Lovejoya, C.E. Meyer, A. Mittelberger, R. Pantelic, L. Piazza, O.L. Krivanek, *Hybrid pixel direct detector for electron energy loss spectroscopy*, Ultramicroscopy 217 (2020) 113067
- [3] C.M. O'Leary, B. Haas, C.T. Koch, P.D. Nellist, L. Jones, *Increasing Spatial Fidelity and SNR of 4D-STEM using Multi-frame Data Fusion*, Microscopy and Microanalysis (2021) DOI:10.1017/S1431927621012587
- [4] M. Schloz, T.C. Pekin, Z. Chen, W. Van den Broek, D.A. Muller, and C.T. Koch, Overcoming information reduced data and experimentally uncertain parameters in ptychography with regularized optimization, Optics Express 28 (2020) 28306
- [5] A. Eljarrat, C. Koch, Design and application of a relativistic Kramers–Kronig analysis algorithm, Ultramicroscopy 206 (2019) 112825
- [6] We acknowledge funding by the following DFG grants: KO 2911/12-1, KO 2911/13-1, BR 5095/2-1, SFB 951, SFB 1404, INST 276/721-1 FUGB, and INST 276/829-1

Charge transfer and exciton formation dynamics in TMDCs imaged by time-resolved momentum microscopy

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Two-dimensional heterostructures of transition metal dichalcogenides (TMDC) represent very well-defined and at the same time highly versatile model systems of van-der-Waals interfaces. They provide a rich playground to study interfacial charge transfer since parameters like stacking angle or band alignment can be changed systematically. To gain a microscopic understanding of exciton and charge carrier dynamics we employ time-resolved two-photon photoemission, which provides momentum-, energy- and time-resolved access to excited states. It allows us to study charge transfer processes extensively, including optically dark channels, and on their intrinsic time scales.

In our experiment, we combine a tunable pump, high-harmonic probe laser source with a 3D momentum imaging technique to map the photoemitted electrons. The high temporal resolution of the setup allowed us to trace the early-stage exciton formation dynamics and identity the momentum location of electron transfer between two layers. We were able to show that the Σ -point is crucial to explain the fast interlayer exciton formation times usually observed in optical experiments. In addition, we have shown, how the temporal evolution of the coherent excitonic polarization influences the dark exciton formation by comparing our experimental results with a fully microscopic theory.



Fig. 1 Left: Scheme of a 2PPE measurement that images the charge transfer across two TMDC layers. After optical excitation at K in the bottom layer, electrons are scattered towards Σ and transferred to the topmost layer subsequently. The delayed XUV probe pulse emits the electrons from the topmost layer. Right: Sketch of the momentum microscope with occupied band structure of WS₂. Momentum slices at certain kinetic energies are recorded at different time of flights and stacked together to a 3D data set.

Computational materials design: from bulk systems to 2D materials and interfaces

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How can new functional materials be designed using supercomputers?

In this talk I will show that extensive first-principles calculations, combined with crystal structure prediction and machine learning, can efficiently speed up the discovery of new materials. As an example, I will focus on the search of materials for photovoltaics.

Characterizing the electronic properties of crystalline bulk materials can however be insufficient. Interfaces are in fact at the heart of electronic devices: transistors, light-emitting diodes and solar cells, all exploit quantum processes involving electrons in tailored multilayers. The ability to shape potential gradients at interfaces opens up the possibility to manipulate electrons and develop new functionalities. The design of interfaces, as well as the deep understanding and control of their properties, is still a challenge beyond the current state of the art. I will discuss some recent progresses in this direction. In particular, I will present two *ab initio* density functionals that we have developed for accurate calculations of band diagrams at interfaces and surfaces.

- [1] Direct insight into the structure-property relation of interfaces from constrained crystal structure prediction, L. Sun, M.A.L. Marques, S. Botti, Nature Communications 12, 1-10 (2021).
- [2] Exchange-correlation functionals for band gaps of solids: benchmark, reparametrization and machine learning,
 P. Borlido, J. Schmidt, A.W. Huran, F. Tran, M.A.L. Marques, S. Botti, npj Computational Materials 6, 96 (2020).
- [3] Local Modied Becke-Johnson Exchange-Correlation Potential for Interfaces, Surfaces, and Two-Dimensional Materials, T. Rauch, M.A.L. Marques and S. Botti, J. Chem. Theory Comput. 16, 2654-2660 (2020).
- [4] Recent advances and applications of machine learning in solid-state materials science, J. Schmidt, M.R.G. Marques, S. Botti, M.A.L. Marques, npj Computational Materials 5, 83 (2019).
- [5] Local hybrid density functional for interfaces, P. Borlido, M.A.L. Marques, and S. Botti, J. Chem. Theory Comput. 14, 939-947 (2018).

Designer electronic states in van der Waals heterostructures

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Van der Waals (vdW) heterostructures have emerged as a playground for realizing and engineering exotic quantum states not found in naturally occurring materials. In these designer heterostructures, the desired physics through the engineered interactions between the different components. The use of vdW heterostructures further facilitates using these effects in future device structures and potentially allow further control through e.g. electrostatic gating.

I will outline our recent results on realizing topological superconductivity [1,2] and artificial heavy fermion systems in vdW heterostructures [3]. We use molecular-beam epitaxy (MBE) in ultra-high vacuum for the sample growth and low-temperature scanning tunneling microscopy (STM) for their characterization. Topological superconductivity can be realized by combining ferromagnetic CrBr₃ on a superconducting NbSe₂ substrate [1,2]. This brings together out of plane ferromagnetism, Rashba-type spin-orbit interactions and s-wave superconductivity, which are the necessary ingredients for topological superconductivity. On the other hand, artificial heavy fermion systems can be realized by coupling localized magnetic moments with mobile conduction electrons. We achieve this experimentally by bringing together 1T-TaS₂, where a strong charge-density wave modulation results in a formation of localized electronic states, and normal metal layer 1H-TaS₂ [3]. These examples highlight the versatility of vdW heterostructures in realizing quantum states that are difficult to find and control in naturally occurring materials.

- [1] S. Kezilebieke et al., Nature 588, 424 (2020).
- [2] S. Kezilebieke et al., arXiv: 2011.09760.
- [3] V. Vaňo *et al*, arXiv:2103.11989.

Poster Abstracts

Temperature effects on the formation and the relaxation dynamics of metal-organic interface states

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The performance of organic (opto-)electronic devices is determined by the efficiency of organic/metal contacts. Charge transfer across these contacts depends on many factors such as the chemical bond of the molecules at the interface, the interfacial energetic structure, or the electron-phonon interaction. Using two-photon photoemission (2PPE), we investigate the ultrafast electron dynamics at the interfaces of perylene- and naphthalene-tetracarboxylic dianhydride (PTCDA and NTCDA) with single-crystalline metals as prototype organic/metal contacts. We demonstrate that the Shockley-derived electronic interface states (IS) of these systems facilitate electron transfer from the photoexcited LUMO to the metal electrode, which is further corroborated by recent results from photoemission tomography. Experiments at systematically varied sample temperatures reveal that the IS lifetime strongly increases with the temperature, which we relate with a phonon-driven molecular lifting off the metal surface. The extraordinary strength of the lifetime increase, however, cannot be explained with the lifting effect alone and indicates strong electron-phonon interaction.



Fig. 1 left: Interface-state mediated charge transfer at PTCDA/Ag(111). right: Influence of the sample temperature on the IS energy and lifetime

Restoring the molecular properties: K intercalation of the flexible DBP on Ag(111)

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The polycyclic aromatic hydrocarbon tetraphenyldibenzoperiflanthene (DBP) has advantageous properties for applications in the field of organic electronics. These are a consequence of its chemical structure consisting of an aromatic backbone with four phenyl rings nearly perpendicular to the molecular plane. We are interested in the effect of potassium intercalation on the structural, optical, and electronic properties of DBP adsorbed on Ag(111). Several structurally reordered stable bonding stages were obtained with K intercalation. LEED and STM measurements combined with differential reflectance spectroscopy (DRS) as well as XPS and UPS including photoelectron momentum maps (PMMs) were used to investigate the system and yield a variety of different information. These results can only be interpreted unambiguously with the help of DFT calculations. We find that the added K atoms adsorb below the molecule and thereby obstruct the bonding channels between DBP and Ag. These alterations of the rather complex host molecule - guest atom - substrate system lead to severe changes of the electronic structure. The strong metalorganic hybridization of DBP and K₂DBP yields PMMs which cannot be explained by assuming free molecules. In contrast, K₆DBP essentially behaves like an electronically decoupled monolayer of DBP dianions. [1]

[1] F. Otto, J. Phys. Chem. C 124, 4114-4127 (2020).

Decoupled or not decoupled? Investigation of charge transfer in organic/2D insulator/metal interfaces

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2D materials like hexagonal boron nitride (h-BN) are widely used as interlayer to decouple organic molecules from metallic surfaces [1]. Nevertheless, there are also indications for a significant hybridization which results in a perturbation of the intrinsic molecular properties [2]. This raises the question: what are the specific conditions under which an h-BN monolayer is sufficient to efficiently decouple organic molecules?

In this work we deal with this question by comparing the electronic and optical properties as well as the lateral structure of about one monolayer 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and tetraphenyldibenzoperiflanthene (DBP) on h-BN/Ni(111).

Therefore, we combined *in situ* differential reflectance spectroscopy, ultra violet photoelectron spectroscopy, low energy electron diffraction and low temperature scanning tunnelling spectroscopy. Our results reveal that an integer charge transfer happens for PTCDA on h-BN/Ni(111). In contrast, the DBP molecules on h-BN/Ni(111) are well decoupled from the metal substrate, and no charge transfer occurs. Furthermore, we will discuss the mechanism and possible origins of the charge transfer.



Fig. 1 Schematic sketch of the investigated organic/h-BN/Ni(111) interface. The Ni(111) surface as well as the boron and nitrogen atoms of the h-BN interlayer are illustrated as green, light red and blue balls.

^[1] W. Auwärter, Surf. Sci. Rep. 74, 1-95 (2019).

^[2] M. Wang et al., ACS Nano 8, 5478-5483 (2014).

Impact of electron phonon interaction on metal-organic interface states

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Electron phonon interaction (EPI) plays a crucial role in many topics in condensed matter physics. For instance, it constitutes the basic effect for superconductivity and contributes to a temperature dependent renormalization of the band gap in semiconductors. Despite that, it is only rarely discussed in the context of metal-organic adsorbate systems and the occurring nearly-free electron like interface states (IS) whose energy E is strongly coupled to the vertical binding distance d with a coupling strength of $\lambda \approx \Delta E/\Delta d$ that is in the order of -1 eV/Å for several adsorbate systems.

We present an EPI-model that is based on ab-initio data and uses the nearly-free electron like character of the IS to obtain an analytic expression for the temperature induced renormalization of the latter. We find that the energy shift is dominated by the coupling to the out-of-plane phonon modes that change the average binding distance and scales quadratically with the coupling strength, i.e. $\sim \lambda^2$.

Applied to the system of a NTCDA layer adsorbed on Ag(111), our model predicts a renormalization of the IS onset energy through quantum mechanical coupling with the adsorbate phonons by -10 meV per 100 K. With this, we are able to explain the discrepancy between a classical lifting-effect and the experiment, thus revealing the important impact of EPI on spectroscopic states at metal-organic internal interfaces.

Theory and computation of dielectric image effects in twodimensional materials

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We present an efficient approach to study the interplay between dielectric effects and interlayer hybridization in multilayer 2D materials. Our approach extends previous work on dielectric effects in nanostructures of conventional semiconductors [1,2]. We show that the variation of dielectric screening along the stacking direction of multilayer crystals can be described by an anisotropic image potential. Combining empirical tight-binding (TB) with a semiclassical treatment of the GW self-energy, we are able to calculate quasiparticle band structures for large multilayer stacks of 2D materials.

By applying our approach to multilayer MoS₂, we find that dielectric effects can result in an energetic decoupling of the surface layer. Facilitated by weak interlayer hybridization at the K-point, the surface layer forms its own direct band gap which is distinctly larger from that of the total system.

- [1] M. Lannoo, C. Delerue, and G. Allan, Phys. Rev. Lett. 74, 3415 (1995).
- [2] C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. Lett. 90, 076803 (2003).

Valley-dependent interlayer excitons in magnetic WSe₂/CrI₃

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Heterostructures of two-dimensional transition metal dichalcogenides and ferromagnetic substrates are important candidates for the development of viable new spin- or valleytronic devices. For the prototypical bilayer of WSe₂ on top of a ferromagnetic layer of CrI₃ we find substantially different coupling of both WSe₂ K-valleys to the sublayer. Besides an energetic splitting of a few meV, the corresponding excitons have significantly different interlayer character with charge transfer allowed at the K⁻ point but forbidden at K⁺. The different exciton wave functions result in a distinctly different response to magnetic fields with g-factors of about -4.4 and -4.0, respectively. By means of ab-initio GW/Bethe-Salpeter equation calculations these findings establish g-factors as tool to investigate the exciton character and shed light on the detailed quantum-mechanical interplay of magnetic and optical properties which are essential for a targeted development of optoelectronic devices.

On-Surface porphyrin transmetalation with Pb/Cu redox exchange

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Metal complexes at surfaces play a significant role in many areas of modern technology, e.g., for surface reactions or catalytic processes. An important aspect in this context is the possible surfaceinduced exchange of the metal center of a molecule, because this reaction can drastically influence the properties of the metal complex and the interface. Several reports have claimed a transmetalation taking place, but the hard proof using mass spectrometry was lacking [1,2]. Here, we demonstrate a metal exchange reaction, proceeding at moderate temperatures even in the absence of solvents. Specifically, we studied the redox transmetalation of a monolayer of lead(II)tetraphenylporphyrin (PbTPP) with copper from a Cu(111) surface under ultrahigh-vacuum (UHV) conditions using multiple surface-sensitive techniques. Temperature-dependent X-ray photoelectron spectroscopy (XPS) reveals that the Pb/Cu exchange starts already below 380 K and is complete at 600 K. The identity of the reaction product, CuTPP, is confirmed by mass spectrometric detection in a temperature-programmed reaction (TPR) experiment. Scanning tunneling microscopy (STM) sheds light on the adsorbate structure of PbTPP at 300 K and uncovers the structural changes accompanying the transmetalation and side-reactions of the phenyl substituents. Moreover, individual free Pb atoms are observed as a product of the metal exchange [3].



Fig. 1 (a) Transmetalation of a Pb(II) porphyrin by reaction with a Cu(111) surface. (b) Molecular structure of Pb(II) 5,10,15,20-tetraphenylporphyrin (PbTPP).

- [1] C. M. Doyle et al., Chem. Commun. 50, 3447-3449 (2014).
- [2] K. Shen et al., RSC Adv. 7, 13827-13835 (2017).
- [3] J. Herritsch et al., Nanoscale 13, 13241-13248 (2021).

Tracing orbital images on ultrafast time scales: The PTCDA/Cu(001)-2O-system

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We combined time-resolved photoemission (using high laser harmonics) and time-of-flight momentum microscopy to establish a femtosecond pump-probe photoemission tomography experiment of unoccupied molecular orbitals. The full momentum-space distribution of electrons, transiently excited into the lowest unoccupied molecular orbital (LUMO), was measured [1].

The selection of the sample system was crucial for this experiment: On the one hand, photoemission tomography requires a sufficiently corrugated substrate that promotes a small number of well-defined azimuthal orientations of the adsorbed molecules. On the other hand, the molecules must be electronically decoupled from the substrate since electrons excited into otherwise unoccupied states shall be (photo)emitted. The PTCDA/ Cu(001)-2O-system fulfills both conditions: The ultrathin oxide layer provides a $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -2O reconstructed surface imposing only two, clearly defined azimuthal orientations of PTCDA (see Fig. 1), and at the same time suppresses any static charge transfer between the molecules and the metal surface. On this poster, we discuss the structure and the preparation of the PTCDA/Cu(001)-2O-system in detail.



Fig. 1 PTCDA on Cu(001)- $(\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ -2O: (A,B) Adsorption geometry (top and side view) of one of the four equivalent domains. In (B) adsorption heights are given according to [2]. (C,D) Measured and simulated LEED patterns.

- [1] R. Wallauer et al., Science **371**, 1056 (2021)
- [2] X. Yang et al., Chem. Commun. 54, 9039 (2018).

Tracing orbital images on ultrafast time scales: Time-resolved photoemission tomography experiments

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Photoemission tomography is a powerful tool to image the electron distribution in molecular orbitals in momentum space. However, unoccupied molecular orbitals have not been accessible. In our experiment, we combine time-resolved photoemission using high laser harmonics and a momentum microscope to establish a tomographic, femtosecond pump-probe experiment of unoccupied molecular orbitals [1]. We measure the full momentum-space distribution of transiently excited electrons within a single molecular layer of PTCDA on an oxygen-passivated Cu(001) surface.

Beside the identification of the lowest unoccupied molecular orbital and the determination of its lifetime, we were able to link the excited state dynamics to real-space excitation pathways. By changing the polarization of the pump pulses we induced either electron transfer from the substrate to the molecule or intramolecular excitation. Each process led to a distinct signature in the time evolution of the respective momentum map that allowed a clear assignment. Our results proof the potential of this technique to identify electron excitation and transfer processes at molecular surfaces and interfaces.



Fig. 1 Left: Experimental momentum maps at three different pump-probe delays integrated over an energy region corresponding to the LUMO of PTCDA. Right: Calculated Kohn-Sham LUMO of gas-phase PTCDA with polarization factor. Projected light incidence is indicated by two colored arrows.

[4] R. Wallauer et al., Science 371, 1056 (2021).

Experimental Quantification of Interaction Energies in Organic Monolayers

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The formation of molecular nanostructures is determined by the interplay of intermolecular and molecule-substrate interactions. However, these interactions are experimentally hardly accessible. Temperature-programmed desorption (TPD) is a fairly well-established experimental technique capable of quantifying both types of interaction, but its quantitative analysis is by no means trivial. In the present study, we analyse the desorption kinetics of the two organic semiconductors pentacene (PEN) and perfluoropentacene (PFP) from Au(111) and MoS₂ surfaces to show the potential of TPD, but also highlight challenges for larger adsorbates. Combining TPD with scanning tunneling microscopy, work function measurements and theoretical modelling, we show that intermolecular interactions are dominated by the intramolecular charge distribution, resulting in net intermolecular repulsion in unitary and attractive interactions in mixed PEN:PFP monolayers. We determine the coverage-dependent prefactor of desorption with unprecedented precision and correlate its evolution with the activation of specific degrees of freedom of motion of adsorbed molecules. Lastly, we compare differences in molecule-substrate interactions on Au(111) and MoS₂, revealing that (sub-) monolayers on MoS₂ are stabilized only by entropy, adopting a 2D gas phase rather than an ordered, crystalline structure. Taking advantage of the intermolecular attraction in mixed PEN:PFP monolayers, we show that it is nonetheless possible to process crystalline organic monolayers on 2D materials such as MoS₂.



Fig. 1 Schematic summary of the desorption kinetics of different PEN thin films adsorbed on MoS₂.

- [1] S. R. Kachel, P.-M. Dombrowski, T. Breuer, J. M. Gottfried, G. Witte. Chem. Sci. 12, 2021, 2575-2585.
- [2] P.-M. Dombrowski, S. R. Kachel, L. Neuhaus, J. M. Gottfried, G. Witte. Nanoscale 13, 2021, 13816-13826.

Van der Waals Bound Organic Semiconductor/2D-Material Hybrid Heterosystems: Intrinsic Epitaxial Alignment of Perfluoropentacene Films on Transition Metal Dichalcogenides

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Hybrid systems consisting of transition metal dichalcogenides (TMDCs) and organic semiconductors (OSCs) are promising candidates for future optoelectronic device architectures, as they combine the outstanding charge transport properties of TMDCs with the high photoabsorption cross-section and the ability to tailor the energy levels of OSCs through synthetic means. Since crystalline organic layers have very anisotropic optical absorption and emission characteristics, their azimuthal alignment is an important parameter for the efficiency of the optical coupling in such hybrid systems. The lack of dangling bonds makes surfaces of 2D materials quite inert and smooth and therefore allows an unrestricted growth of organic adlayers without the requirement of relaxation or commensurability at the interface, which is an important prerequisite for van der Waals (vdW) epitaxy. Here, we have studied the formation and azimuthal alignment of crystalline adlayers of the OSC perfluoropentacene (PFP) on the basal plane of MoSe₂, WSe₂, MoS₂, and MoTe₂ single crystals representing the most ideal TMDC surfaces, which are further compared with corresponding films on graphene and hBN. Combining specular X-ray reflectivity with polarization resolved optical reflection measurements allowed the azimuthal alignment of crystalline PFP domains to be precisely analyzed, which revealed characteristic twist angles between adlayer and substrate lattices for the various 2D materials. This orientational order can be rationalized as an on-line coincidence and is well reproduced by model calculations that are based on the scheme of projection of real-space adlayer lattice points onto the substrate unit cell. The extreme sensitivity of the resulting rotational alignment of epitaxial adlayers on the smallest changes of the lattice parameters is demonstrated by distinctly different twist angles for PFP films that were grown at an elevated temperature and thus show a slight thermal expansion. The presently introduced and validated model to describe the epitaxial alignment in weakly bound crystalline adlayers can also be applied to other vdW bound heterosystems and can be useful to elucidate the peculiarities of vdW epitaxy. [1]



Fig. 1 Epitaxial alignment of crystalline PFP films on the basal plane of MoS₂ and WSe₂[1] M. Dreher, D. Günder, S. Zörb, G. Witte. Chem. Mater. 32, 20, 10.1021/acs.chemmater.0c03482 (2020).

Prepare with Care: a Universal Approach to Improving the Contact Resistance of Organic Field-Effect Transistors

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The interface between the organic semiconductor active layer and the source and drain electrodes is known to affect the device characteristics of organic field-effect transistors (OFETs) due to the formed charge carrier injection barrier. The resulting contact resistance reduces the device performance by causing idle power, limiting the maximum operational frequency of transistors and also leads to erroneous values of the extracted charge carrier mobility. In the race for recordbreaking device performances, a precise and well-defined structure of the interfaces is often lost and important effects, such as doping due to ambient exposure, are neglected. This renders establishing connection between the interface properties and the device characteristics close to impossible. To address this issue, we have established a full high vacuum OFET preparation and characterization process chain that allows us to rigorously exclude the effects of ambient exposure and ensure the quality and well-defined structure of the interfaces. This allows us to bridge the gap between the microscopic interfacial properties and the performance of real devices. We have shown that, by careful treatment of a commercially available OFET substrate, PEN-based devices with pure gold electrodes and exceptionally low contact resistances can be produced [1]. Furthermore, by electronically decoupling PEN from the gold electrodes and improving the energy level alignment at the interface, either using gold oxide or organic contact primer layers such as F₆TCNNQ and various metal phthalocyanines, we can even further reduce the contact resistance of the devices. Finally, we have shown that this approach also works for n-type semiconductors, such as novel PhC₂-BQQDI, rendering it a promising candidate for a universal method of contact resistance reduction in OFETs.



Fig. 1. From left to right: photograph of a device during the electrical characterization, schematic model of an OFET and electrical characteristics of a PEN OFET.

[1] Radiev, Y. et al., Org. Electron. 89, 106030 (2021).

Single-domain molecular layers on Ag (110)

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Single domain molecular layers have been explored on the non-hexagonal Ag (110) substrate. The absence of rotational domains for fcc (110) metal substrates allows to grow layers with uniform azimuthal orientation of deposited molecules [1]. Also, the increased metal-molecule interaction on Ag(110) vs. Ag(111) leads to an extra energy shift of the LUMO, thereby having a significant impact on interfacial dynamic charge transfer (IDCT) of vibrational modes [2]. In this work we have identified various molecules and configurations that can form such single domain molecular layers. Specifically, PTCDA, NTCDA, phthalocyanines (CuPc, TiOPc) and regio-selectively substituted pentacene species (pentacene, pentacene-quinone, pentacene-tetrone, quinacridone) have been deposited and examined in terms of their structure using SPA-LEED, and their vibrational signature using IRAS. PTCDA, NTCDA and pentacene have been found to form single domain structures. In general, the formation of long-range ordered phases depends on the coverage and annealing temperature, so that different configurations can be prepared by applying according processing schemes. In the case of PTCDA the two prominent phases, the brick-wall (BW) and the herringbone (HB) phases exist and they are readily distinguished not only by their LEED patterns but also from their vibrational signatures.



Fig. 1 SPA-LEED images and corresponding real space lattices of PTCDA/Ag(110): the single domain brickwall (top) as well as the herringbone (bottom) structures.

- S. Lukas, G. Witte, and Ch Wöll. Novel mechanism for molecular self-assembly on metal substrates: Unidirectional rows of pentacene on Cu (110) produced by a substrate-mediated repulsion, Phys. Rev. Lett. 88, 028301 (2001).
- [2] P. Jakob and S. Thussing, Vibrational Frequency used as Internal Clock Reference to access Molecule - Metal Charge - Transfer Times, Phys. Rev. Lett. 126, 116801 (2021).

Nickel Tetrapyrrole Complexes at Metal/Organic Interfaces

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Nickel tetrapyrrole complexes whose structure is related to biologically relevant molecules (e.g., F_{430} cofactor, tunichlorin, nibalamine) are promising precursors for novel functional surfaces and interfaces. Here, we report on the influence of the interaction at the metal/organic interface on the electronic structure of a nickel porphyrin (Ni(OEP), Fig. 1a) monolayer on coinage metal surfaces studied by XPS, UPS, STM, NEXAFS and LEED. On Ag(111), Ni(OEP) forms a mixed-valent adsorbate phase in which the Ni centers occur in two different oxidation states. The two separate peaks in the Ni 2p XP spectrum indicate that about 40% of the Ni centers are reduced. STM and LEED shows an incommensurate superstructure with an ordered arrangement of the metal centers in different oxidation states (Fig. 1b). Further insights into the valence electronic structure were obtained by UPS and NEXAFS. On the more reactive Cu(111) surface, Ni(OEP) forms a long-range ordered structure in which nickel centers are uniformly reduced; whereas on the most inert Au(111) surface, the oxidation state of the Ni centers remains unaffected by adsorbate interactions. By comparing Ni(OEP) on differently terminated single crystal surfaces (Ag(111), Ag(100), Ag(110)), the influence of the substrate lattice on the electronic state of the Ni centers is further investigated.

In a comparative study between Ni(OEP) and a nickel corrole complex (Ni(HEDMC), Fig. 1c) on Au(111), Ag(111) and Cu(111), we show how a small change in the ligand structure can be used to modify the interactions of the Ni center with the metal substrate. While the Ni center in Ni(OEP) is reduced depending on the substrate, the Ni(II) state is stabilized in case of Ni(HEDMC) even on the most reactive Cu(111) surface.



Fig. 1 (a) Molecular structure of Ni(OEP); (b) STM image of the mixed-valent Ni(OEP) monolayer on the Ag(111) surface; (c) molecular structure of Ni(HEDMC), which can be described as a ring-contracted porphyrin with one missing methine bridge and a direct pyrrole-pyrrole link (highlighted in blue).

In-situ TEM Investigations of III/V Semiconductor Materials

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In-situ (scanning) transmission electron microscopy ((S)TEM) allows to investigate dynamic processes, like the ones occurring during crystal growth, inside a TEM. To this end, a commercially available Protochips Inc. *in-situ* system has been modified to allow the usage of toxic and pyrophoric gases, so that the cell in the *in-situ* TEM holder acts as a metal organic vapor phase epitaxy (MOVPE) microreactor [1].

To investigate the comparability to MOVPE and the influence of the electron beam in TEM, a commercially residual gas analyzer has been added. With this the thermal decomposition of TBP (tertiarybutylphosphine) was investigated.

GaP VLS-nanowire growth has been realized to investigate the dynamics of crystal growth. Precursors used for growth were TBP and trimethylgallium (TMGa) at partial pressures between 10^{-1} and 10^{-2} hPa and a V/III ratio of around 10. Growth was performed at a temperature of 450 °C with N₂ as carrier gas at partial pressures of 400 hPa. Figure 1 a) shows the growth of such nanowires. The growth rates depend on the surface ratio of the catalyst droplet (gold) and the nanowire diameter (figure 1 b).

Furthermore, it was found that during growth the nanowires produce kinks after random distances. Statistics of these kinks show dominant kinking angles a 70.5°, 109.5° and 123.7°. The origin of these kinks was investigated by scanning precession electron diffraction (SPED) in post growth analysis. The results show that the predominant kinking angles result from microtwins of first $(70.5^{\circ} \& 109.5^{\circ})$ and second order (123.7°) .



Fig. 1: a) STEM images of two growing NWs. The deviating surface ratios lead to different growth rates. b) Growth rate measurements of 13 NWs in dependence of their surface ratio. Each color represents a single NW.

[1] R. Straubinger, et al., Microscopy and Microanalysis 23.4 (2017), pp. 751-757.

Quantification of Nanometer-Scale Electric Fields at Internal Interfaces

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Nanometer-scale built-in electric fields are the basis of many devices, like solar cells or batteries. Accordingly, measuring these fields directly would be very beneficial to optimize a device's performance. One prominent example is the field which forms at a p-n junction, i.e. the interface between two differently doped semiconductors. Scanning transmission electron microscopy (STEM) with its field-sensitive electron beam and sub-Å resolution is the right means for measuring these fields. The combination of STEM and fast pixelated detectors (4DSTEM) gives access to the center-of-mass shift of the diffraction pattern which is approximately proportional to a present electric field [1].

In an experimental study for the example system of a GaAs p-n junction it was shown that by using 4DSTEM it is possible to quantitatively determine the junction's built-in electric field, doping concentrations, polarity and the width of the depletion region [2]. In this study, typical conditions for high-resolution STEM were used, e.g. a rather high semi-convergence angle of 21 mrad.

In this contribution, we show STEM multislice simulation studies including beam deflection introduced by a p-n junction's built-in field. The simulations reveal that using smaller convergence angles may be beneficial for measuring long-range electric fields, due to an increased sensitivity.

Utilizing a NANOMEGAS precession electron diffraction (PED) system attached to a double aberration corrected JEOL JEM 2200FS, we realize 4DSTEM measurements with a nearly parallel beam with a convergence semi-angle of only 2 mrad. We will show that both illumination schemes are capable of measuring built-in electric fields. The advantages and disadvantages of both will be discussed in this contribution.

- [1] Müller, K., et al., Nature communicatons 5.1 (2014): 1-8.
- [2] Beyer, A., et al., Nano Letters 21(5) (2021): 2018–2025.
Structural characterization of III/V semiconductor interfaces using quantitative STEM methods

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A large variety of devices and technological applications like laser diodes, solar cells or high electron mobility transistors are based on III/V heterostructures. A thorough understanding of the formation of the interfaces involved would be beneficial to improve a device's performance or facilitate the realization of new semiconductor devices.

Due to its high spatial resolution, aberration-corrected scanning transmission electron microscopy (STEM) is an ideal method for the investigation of such internal interfaces. Accompanied by stateof-the art contrast simulations, it is possible to gain quantitative information on a sample's structure and composition, which was successfully demonstrated for ternary and even quaternary III/V semiconductors before [1,2]. However, due to their lack of scattering power, light substitutional elements, e.g. N, cannot be quantified accurately using the conventional methods. In this contribution, we will show our latest efforts to overcome these limitations.

To prove the feasibility of the quantification of light elements, we use the example of thin Ga(N,As) layers containing high amounts of N grown on GaAs (001) substrates. The epitaxial growth by metal organic vapor phase epitaxy (MOVPE) was conducted in an AIXTRON AIX 200 system. Different growth sequences were utilized to realize the most abrupt incorporation by ideally targeting for a monolayer of cubic GaN in the GaAs (001) matrix. Electron transparent focused ion beam (FIB) lamellae were prepared using a JEOL JB 4601 taking special care about minimizing amorphous layers during milling. Subsequently, STEM characterization is carried out in an aberration-corrected JEOL JEM 2200FS. We exploit the flexible detection schemes available using a fast pixelated pnCCD detector [3]. Moreover, we utilize the microscope's energy filter to select the elastic scattering signal only and avoid inelastic contributions, which would hinder a successful quantification. Complementary image simulation is carried out using the STEMsalabim code [4].

We will present the quantitative evaluation of nitrogen content and layer thicknesses of Ga(N,As) layers grown with different growth sequences. Our results are in good agreement with complementary high-resolution X-ray diffraction (HRXRD) measurements, which however, lack the high spatial resolution available in STEM.

- [1] L. Duschek et al., Ultramicroscopy. 200 (2019) 84–96.
- [2] P. Kükelhan et al., Ultramicroscopy. 206 (2019) 112814.
- [3] S. Firoozabadi et al., Ultramicroscopy. (2021) 113387.
- [4] J.O. Oelerich et al., Ultramicroscopy. 177 (2017) 91–96.

Interface-Dominated Heterostructures for Long-Wavelength Emission on GaAs Substrates

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This work will present the growth of Ga(N,As)/Ga(As,Bi)/Ga(N,As) W-type heterostructures (WQW) on GaAs (001). Due to the significant reduction of the band gap by incorporation of dilute amounts of nitrogen (N) and bismuth (Bi), respectively, it is possible to shift the emission wavelength of such structures into the mid-infrared region and beyond [1]. Since the electronegativities and covalent radii of Bi and N differ significantly from arsenic, such materials are considered as highly mismatched alloys (HMA).

Stacking both material systems on top of each other is a particular challenge during epitaxial growth using metalorganic vapor phase epitaxy since the material systems require considerably different growth conditions. While Ga(N,As) growth is conducted at 550 °C, Ga(As,Bi) growth requires growth temperatures around 400 °C. Moreover, the segregation of Bi is crucial to be considered during the growth of these interface-dominated heterostructures [2]. Therefore, the growth conditions at the interface require considerable adaptions by establishing growth interruptions.

The diffractogram exhibits clearly-resolved pendellösung fringes and an excellent fit to dynamical modeling suggests abrupt interfaces as shown in fig. 1 a). The inset shows the desired sample structure with applied growth interruptions.

The W-type structure's photoluminescence (PL) peak is red-shifted compared to the PL peak of test structures containing only the single quantum wells, respectively (compare fig. 1 b)). Hence, the origin of the PL peak at 1.1 eV is the spatially indirect type-II transition.



Fig. 1: a) Shows an HR-XRD diffractogram of a Ga(N,As)/Ga(As,Bi)/Ga(N,As) W-type structure. The inset sketches the sample structure. b) Shows the PL spectra of the W-type structure and the Ga(N,As) and Ga(As,Bi) test structures, respectively. The band structure is sketched in the inset.

[2] P. Ludewig et al., Semicond. Sci. Technol. 30, 094017 (2015)

^[1] C. A. Broderick et al., Sci. Rep. 7, 46371 (2017)

MOCVD growth studies of III-VI monolayers

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Two dimensional (2D) semiconductors have received great attention due to their extraordinary thickness dependent properties. One class of 2D semiconductors are the layered III-VI semiconductors such as GaS, GaSe and InSe which show a unique Mexican hat shape band structure. This band structure received high attention in the last years because it is expected to have properties such as unconventional superconductivity and ferromagnetism [1]. Further, 2D GaS and GaSe show a bandgap over 3 eV which makes them candidates for visible LEDs and also the composition tuning of multilayer GaSxSe1-x shows bandgaps between 2.0 and 2.5 eV [2]. Metal organic chemical vapor deposition (MOCVD) in general shows very high uniformity and reproducibility of growth on large areas making it suitable for large scale production. By investigating the growth of GaS on different amorphous and single crystalline substrates with metal organic precursors in a MOCVD system we are establishing the growth of 2D structures. The produced samples are characterized by means of atomic force microscopy (AFM), scanning electron microscopy (SEM), Raman spectroscopy and transmission electron microscopy (TEM).



Fig. 1 a) shows an AFM image of GaS monolayer plus 3D grain and b) shows the respective height profile of one monolayer. c) shows the Raman maspectrum of GaS of the same sample.

- [1] Hui Cai et al. Appl. Phys. Rev. 6, 041312 2019
- [2] Chan Su Jung et al. ACS Nano 2015, 9, 10, 9585–9593

Design of New Interfaces and Moving to New Substrates: Ring-Opening Reaction of Tetrahydrofuran on Ge(001)

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The investigation of interfaces between organic and inorganic materials has come a long way, especially for silicon, which was studied extensively. The step towards different substrates is coupled with major challenges in w.r.t the experimental setups. While silicon is heavily studied from a theoretical and experimental perspective, other semiconductor substrates have not been studied intensely. However, other substrates may exhibit different physical and chemical properties relevant for the design of optoelectronic devices. The first step within this project is to extend the previous work [1,2] in order to study the ring-opening reaction of tetrahydrofuran (THF) on the Ge(001) surface using density functional theory (DFT) applied within numerous methods such as Born-Oppenheimer molecular dynamics (BOMD), simulate STM-experiments using the Tersoff-Hamann approximation. Additionally, the focus is on the energy decomposition analysis for extended systems (pEDA) [3,4] of the ground- and transition states of the possible reactions.

Here, we will showcase the work on the THF-Ge(001) system in comparison to THF-Si(001) especially in terms of the pEDA and give an overview of the properties of the THF-Ge(001) system itself. Furthermore, an outlook on the design of new interfaces with cyclooctyne will be presented.





Fig. 1 Sampling of the O-atom in 10 randomized Fig. 2 pEDA of the datively bonded structure of BOMD-simulations of a molecular cannon with the time step in fs as color gradient.

THF on Ge(001).

- L. Pecher, S. Laref, M. Raupach, R. Tonner, Angew. Chem. Int. Ed. 56, 15150 (2017). [1]
- S. Park, K. Kim, Y.-S. Youn, ACS Omega 5, 22926–22930 (2020). [2]
- [3] M. Raupach, R. Tonner, J. Chem. Phys. 142, 194105 (2015).
- [4] L. Pecher, R. Tonner, WIREs Comput Mol Sci. 9, e1401 (2019).

Synthesis of Organic Building Blocks for Internal Interfaces

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As shown in the past, polycyclic aromatic and heteroaromatic molecules feature a distinct molecular dipole and show promising electronic properties in the solid state as well as in thin film and single crystal.^[1] Here we report on the synthesis of new partially fluorinated compounds, e.g. **1-3**, including the more stable and new core structure of DNTT's (dinaphthothienothiophene). Within the completion of this variety of compounds, the analytics regarding their molecular and optoelectronical properties are investigated.^[2,3]

Another goal is the synthesis of bridged annulenes like compounds **5-6** which can be used as precursors for interfacial synthesis of annulene-based chains, ribbons, and 2D+ carbon nanostructures.^[4,5] Introduction of substituents on the methylene-bridge as orthogonal linkers will allow STM manipulation.



Fig. 1 Structures of substituted pentacene, tetracene, DNTT and bridged annulenes.

- [1] J. Schwaben et al., Chem. Eur. J. 2015, 21, 13758-13771.
- [2] P. Hofman et al., Angew. Chem. Int. Ed. 2020, 59, 16501-16505.
- [3] M. Tripp, D. Bischof, M. Dreher, G. Witte, U. Koert, Eur. J. Org. Chem. 2021, 2021, 1295-1304.
- [4] E. Vogel, W. Klug, A. Breuer, Org. Syn. 1974, 54, 11-16.
- [5] E. Vogel, H. Königshofen, K. Müllen, J. F. M. Oth, Angew. Chem. 1974, 86, 229-231.

Electron-Hole Plasma-Induced Dephasing in Transition Metal Dichalcogenides for ICII-2021

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Excited carriers in a sample influence its electronic and optical properties in manifold ways, which is especially the case in ultrathin materials like monolayer transition metal dichalcogenides, where the Coulomb interactions and its modification due to the presence of additional carriers play a crucial role. Here, we focus on the influence of incoherent carrier populations on the dephasing and its manifestation in the excitonic absorption and the degenerate four-wave mixing spectra in an hBN encapsulated monolayer MoS₂. In particular, we analyze the dependence of the dephasing on the distribution of the carriers in different valleys of the bandstructure and for different carrier temperatures. We employ a microscopic approach combining density-functional theory calculations with advanced many-body techniques, namely the Dirac Bloch equations (DBE) that are based on the massive Dirac-Fermion model. We find that the influence of the excitation-induced dephasing depends only weakly on the exact shape of the carrier distribution for small densities, whereas details on the distribution become more important with increasing density.

Ultrafast charge-transfer dynamics in twisted TMDC heterostructures

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Two-dimensional heterostructures of transition metal dichalcogenides (TMDC) represent very well-defined and at the same time highly versatile model systems of van-der-Waals interfaces. Many material combinations feature a type-II band alignment, which can separate photoexcited electrons and holes into different layers through ultrafast charge transfer leading to the formation of so-called interlayer excitons. Since the coupling within these structures depends considerably on the layer stacking, a strong influence of the interlayer twist on the ultrafast charge-transfer, recombination and other properties of the interlayer excitons has been expected.

Here we present our investigation of ultrafast charge-transfer dynamics in twisted MoS_2/WSe_2 heterostructures by employing time- and polarization-resolved second-harmonic imaging microscopy. Stacking-dependent differences could be identified due to our excellent time resolution of ~ 10 fs, unattained in previous measurements. Electron transfer from WSe₂ to MoS_2 (Fig. 1) after resonant excitation (1.70 eV) was found to depend considerably on the twist angle. The transfer time is reduced from 85 fs down to 12 fs when going from a larger rotational mismatch (16°) towards 2H-stacking (52°). At higher excitation energy (1.85 eV), the corresponding decay dynamics show no significant dependence on the stacking angle indicating that radiative recombination of indirect Γ -K excitons becomes the dominant decay route for all samples.



Fig. 1 Schematic band alignment of MoS₂/WSe₂ and hexagonal Brillouin zones of the studied heterostructures showing the individual K-points and the hybridized Γ-point.

[1] J. E. Zimmermann et al., ACS Nano, DOI: 10.1021/acsnano.1c04549 (2021).

Tip-induced modification of semiconductor/organic interfaces

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Well-controlled interfaces between organic and semiconductor materials may open a wide range of possible applications. In particular, interfaces between organic molecules and silicon are of wide interest as they offer compatibility with conventional silicon technology and benefit from the broad variety of functionalities available in organic chemistry. In order to better understand and control the chemical interaction between the two classes of materials, the investigation of the adsorption process of organic molecules on silicon surfaces and possible means of manipulating the adsorbates can play a key role.

Here, we study the chemical modification of surface-adsorbed ether molecules and their reaction products on Si(001) by means of scanning tunneling microscopy (STM). At low surface temperature (T < 150 K), ether molecules such as diethyl ether (Et₂O) and tetrahydrofuran (THF) adsorb on Si(001) via a datively bound intermediate state. Thermal activation at T > 150 K induces C-O cleavage leading to covalently bound final states [1-3]. Whereas thermal activation leads to one single (in the case of THF) or two very similar final states (in the case of Et₂O), electronic excitation of the intermediate state was found to lead to a variety of additional, covalently bound final states [4,5]. Most interestingly, when we compare the final states of Et₂O and THF after electronic excitation, we find distinct differences between the two molecules, despite a similar excitation mechanism. We trace this back to the differences in the molecular structure of the two molecules: whereas the ring-like THF molecule forms one single entity in the final state on the surface, the linear Et₂O molecule leads to two covalently bound fragments in the final configuration. The latter allow for a better interaction between the molecules and reactive surface sites during the reaction.

In addition, we show that not only weakly bound intermediates can be manipulated on silicon by means of tip-induced electronic excitation but also covalently bound molecular adsorbates could be further reacted in this way. As an example, tip-induced β -hydrogen dissociation in an alkyl group bound on Si(001) was demonstrated [6]. Such processes may lead the way to more complex reaction schemes to be employed for the controlled modification of semiconductor/organic interfaces.

- [1] G. Mette et al., ChemPhysChem 15, 3725 (2014).
- [2] M. Reutzel *et al.*, J. Phys. Chem. C 119, 6018 (2015).
- [3] M. Reutzel et al., J. Phys. Chem. Lett. 6, 3971 (2015).
- [4] G. Mette et al., Angew. Chem. Int. Edit. 34, 3417 (2019).
- [5] A. Adamkiewicz et al., (in preparation).
- [6] A. Adamkiewicz et al., J. Phys.: Condens. Matter 33, 344004 (2021).

Experimental setup for THz-ARPES and THz-HHG of electric currents at interfaces of topological insulators

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Angle-resolved photoemission spectroscopy (ARPES) combined with terahertz (THz) excitation and subcycle temporal resolution opens up new opportunities to investigate the ultrafast dynamics of surface currents [1]. Recently, we succeeded in extending THz-ARPES to the frequency range of 25-40 THz and incoming electric field strengths of up to 10 MV/cm. Under these conditions, a large fraction of electrons in topological surface states (TSS) rapidly switch the direction of motion when their trajectories in momentum space come close the Dirac point. This gives rise to a novel type of THz high-harmonic generation [2].

In the framework of SFB 1083 we plan to extend this previous work on Dirac currents of topological insulators and embed the TSS under thin protecting layers for device applications. For those investigations, we will combine subcycle-resolution multi-THz ARPES with THz-HHG measurements.

Our setup consists of a high-repetition laser system (200 kHz, 40 W), which utilizes three OPAs to tune the wavelengths of pump and probe beams independent from each other. The THz-pulses are generated via difference frequency generation (DFG) from the Idler beams of two of the OPAs in a LiGaSe₂ crystal. Thus, the setup is capable of tuning the THz-frequency over a wide frequency range (12-42 THz) with high field strengths and a stable carrier envelope phase, which is characterized by electro-optic sampling (EOS). The HHG-experiments will be carried out under UHV condition in a small vacuum chamber, while the HHG spectra will be detected in reflection geometry by a high-sensitivity spectrometer in the visible range. For the subcycle ARPES experiments at high THz frequencies, the use of ultrashort UV-pulses (400 nm, <15 fs) for photoemission is necessary. This will be achieved by spectral broadening of the 20-fs, 800-nm pulses from the third, non-collinear OPA (NOPA) and subsequent frequency doubling with a thin BBO.

J. Reimann *et al.*, Nature, **562**, 396-400 (2021)
C. P. Schmid *et al.*, Nature, **593**, 385-390 (2021)

Time-Resolved SHG Imaging Microscopy for Systematic Studies of Two-Dimensional Materials

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Optical second-harmonic generation (SHG) imaging microscopy is a powerful tool for timeresolved investigations of charge-transfer processes between TMDC monolayers. By imaging the SHG signal via a camera lens on a CCD chip, we obtain a lateral resolution of 2 μ m without the need to comprise in terms of time resolution. By means of polarization dependent measurements, the crystalline orientation of monolayers as well as the stacking angles of heterostructures can then be evaluated for the whole field of view (Fig.1a). Moreover, by selecting the proper probe polarization, we can tune the sensitivity to individual layers of a heterostructure (Fig. 1b-d.). Images taken for different pump-probe delays allow to correlate observed transient changes of the second-harmonic response with the underlying structure. For a rotationally mismatched WSe₂/MoSe₂ heterostructure, we demonstrate a bi-directional ultrafast charge transfer between the layers with our setup [1]. Following the resonant excitation of one layer, we were able to identify a subsequent charge transfer into the other layer and vice versa. We found that the hole transfer from MoSe₂ into WSe₂ occurs with a time constant of 210 fs while the reversed direction shows a slower transfer time of 610 fs.



Fig. 1 a) False colour plot illustrating the crystal orientation of every flake within the field of view.b,c) Microscope image of a hBN capped heterostructure. d,e) Second-harmonic image of the same heterostructure measured for different probe polarizations [1].

[1] J. E. Zimmermann et al., Nanoscale Horizons, 5, 1603-1609 (2020).

Momentum-resolved observation of ultrafast interlayer charge transfer between the topmost layers of MoS₂

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Here, we report on the direct observation of electron transfer between the surface and the second layer of the prototypical transition-metal dichalcogenide $2H-MoS_2$ [1]. In our time-resolved two-photon photoemission experiment, we could disentangle the excitation and the transfer process. Thereby, we determined both, the momentum location and the duration of the electron transfer between the first two layers.

Our GW-based tight-binding calculations reveal that the band gap in the surface layer is considerably larger than in deeper layers and that the coupling between surface and deeper layers is strongly momentum-dependent throughout the Brillouin zone. At the conduction band minimum Σ , we find strong coupling, which explains the ultrafast interlayer charge transfer observed in our experiment at this location.



Fig. 1 Left: Experimental scheme. After optical excitation in the K-valley of the lower layer, electrons are scattered towards Σ and transferred to the topmost layer subsequently, where they are probed by a delayed XUV pulse. Right: Delayed rise of the signal at Σ for pump photon energies, which are below the first layer gap. The transfer time between layers is reflected in the time offset.

[1] R. Wallauer et al., Phys. Rev. B 125, 125417 (2020).

Dark exciton formation dynamics in WS₂

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The dynamics of momentum-dark exciton formation in transition metal dichalcogenides is difficult to measure experimentally, as many momentum-indirect exciton states are not accessible to optical interband spectroscopy. Here, we combine a tunable pump, high-harmonic probe laser source with a 3D momentum imaging technique to map photoemitted electrons from monolayer WS₂. This provides momentum-, energy- and time-resolved access to excited states on an ultrafast time scale. The high temporal resolution of the setup allows us to trace the early-stage exciton dynamics on its intrinsic time scale and observe the formation of a momentum-forbidden dark K Σ exciton a few tens of femtoseconds after optical excitation. By tuning the excitation energy, we manipulate the temporal evolution of the coherent excitonic polarization and observe its influence on the dark exciton formation. The experimental results are in excellent agreement with a fully microscopic theory, resolving the temporal and spectral dynamics of bright and dark excitons in WS₂ [1].



Fig. 1 Left: Experimental scheme. After optical excitation in the K-valley, momentum-dark excitons are forming at Σ and K' subsequently, which are probed by a delayed XUV pulse. Right: Momentum distribution of excited electrons 60 fs after optical excitation.

[1] R. Wallauer et al., Nano. Lett. 21, 5867 (2021).

Dynamics of charge transfer processes in strongly interacting organic donor/acceptor compounds

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Doping is a widely employed strategy to tailor the electronic properties of organic semiconductors. It is therefore of great interest to understand the kinetic processes that govern the efficiency of exciton transport or charge transfer processes in these systems. Here, we investigate the photoexcitation dynamics of blend systems comprised of the prototypical semiconductor tetracene, doped with different concentrations of the strong electron acceptor F4-TCNQ by means of time-resolved photoluminescence spectroscopy. Thin films of the blends comprise two phases: A relatively pure tetracene phase and a second phase where donor and acceptor molecules are intimately mixed. In the mixed phase, donor and acceptor molecules form charge transfer complexes with pronounced interaction in the ground state, which act as efficient quenching sites for excitons from the pure phases. As a consequence, the photoluminescence (PL) dynamics of the blends is faster with respect to neat Tc. Global and target analysis of the time and spectrally resolved low temperature PL reveals the underlying quenching dynamics and a highly dispersive transport, which is attributed to localization effects and energetic disorder in the tetracene domains.



Fig. 1 Left: Schematic representation of the three different species (F1, F2, F') generated by photoexcitation; Center: Energy scheme with possible energy transfer and loss processes; Right: PL data of a sample with a 1:1 mixing ratio.

- 1. Nico Hofeditz et al. J. Phys. Chem. C 125, 17194 (2021)
- 2. Christoph P. Theurer et al. J. Phys. Chem. C 125, 6313 (2021)

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