ICII-2016

International Conference on Internal Interfaces

31 May – 3 June 2016
Philipps-Universität Marburg, Germany

Program and Abstracts

Philipps Universität Marburg

SFB 1083
Structure and Dynamics of Internal Interfaces

ICII-2016
International Conference on Internal Interfaces

31 May – 3 June 2016
Philipps-Universität Marburg, Germany

Interfaces between solids play a decisive role in modern materials sciences and their technological applications. ICII-2016 provides an expert forum for the discussion of recent progress as well as of experimental and theoretical challenges in basic research of solid/solid interfaces. Scientific topics include: organic/inorganic interfaces, organic donor/acceptor interfaces, type-II semiconductor interfaces, interfaces of two-dimensional semiconductors, interfaces of topological materials, charge transfer processes at interfaces, properties of interface excitons, chemical reactivity and interphase formation, electronic and structural characterization of solid/solid interfaces, interface-specific optical spectroscopies, advances in theoretical methods for solid/solid interfaces.

Organizers:

Prof. Dr. Ulrich Höfer,
Dr. Gerson Mette,
Prof. Dr. Michael Gottfried,

Philipps-Universität Marburg
D-32032 Marburg, Germany

Conference Secretary:

Dr. Helen Pfuhl
Sonderforschungsbereich 1083
Renthof 5, Room 01006

E-Mail: sfb@internal-interfaces.de
Phone: +49 6421 28 24223

Conference Location:

Philipps-Universität Marburg

Alte Aula	Alte Universität, Reitgasse 2 (50°48'28.897"N, 8°46'16.215"E)
Renthof	Grosser Hörsaal, Fachbereich Physik, Renthof 5 (50°48'41.785"N, 8°46'9.299"E)
Fürstensaal	Landgrafenschloss (50°48'36.432"N, 8°46'02.193"E)

Financial Support:

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

Corporate Sponsors:

Coherent (Deutschland) GmbH, Dieselstrasse 5b, D-64807 Dieburg
SPECS Surface Nano Analysis GmbH, Voltastrasse 5, D-13355 Berlin
Scienta Omicron GmbH, Limburger Strasse 75, D-65232 Taunusstein

Scientific Program

Tuesday, 31.05.2016

09:00 – 09:30	Registration	**Alte Aula**
Session I	**(Chair: Ulrich Höfer)**	
09:30 – 09:40	*Welcome*	
09:40 – 10:20	**Torsten Fritz, Jena** *Epitaxy without coincidences – the stabilizing role of static distortion waves*	
10:20 – 11:00	**Kerstin Volz, Marburg** *Unravelling the structure of buried semiconductor interfaces and its correlation to opto-electronic properties*	
	Coffee break	
11:30 – 12:10	**Martin Aeschlimann, Kaiserslautern** *Controlling the spin texture of topological insulators with organic molecules*	
12:10 – 12:50	**Michael Rohlfing, Münster** *Electronic spectra of layered materials and monolayer adsorbates*	
	Break	

Tuesday, 31.05.2016

Poster Session I **Fürstensaal**

13:10 – 15:40 Lunch & Poster Session

Session II **(Chair: Michael Gottfried)** **Renthof**

16:00 – 16:40 **Yoshiyasu Matsumoto, Kyoto**
Structures of water at interfaces of ice crystal films grown on metals

16:40 – 17:00 **Martin Schmid, Marburg**
Hard X-ray photoelectron spectroscopy: a tool for chemical depth-profiling across buried interfaces

17:00 – 17:20 **Ulrich Koert, Marburg**
Functionalized cycloocytnes: potential building blocks for layer-by-layer synthesis at Si(001)

17:20 – 18:00 **Stefan Tautz, Jülich**
The backside of graphene

Wednesday, 01.06.2016

Session III **(Chair: Friedhelm Bechstedt)** **Renthof**

09:00 – 09:40 **Silvana Botti, Jena**
Materials design at interfaces for photovoltaics

09:40 – 10:00 **Daniel Niesner, Erlangen**
Electronic structure at interfaces and surfaces of organic-inorganic perovskites

10:00 – 10:40 **James Hone, Columbia University, New York**
2D materials in the ultraclean limit: basic science and applications

Coffee break

11:10 – 11:50 **Henning Riechert, Paul-Drude-Institut, Berlin**
Growth of two-dimensionally bonded materials – fiction, facts and surprises

11:50 – 12:30 **Steven Louie, UC Berkeley**
Interaction and correlation effects at ultimately thin interfaces: atomically thin quasi-2D crystals

Break

Wednesday, 01.06.2016

Session IV **(Chair: Gerson Mette)** **Renthof**

16:00 – 16:40 **Ursula Wurstbauer, TU München**
Light matter interaction, exciton-phonon coupling and optoelectronic properties in TMDCs

16:40 – 17:00 **Harald Jeschke, Frankfurt**
Effects of oxygen defects or pressure on the electronic states of $SrTiO_3$ at surfaces and interfaces

17:00 – 17:40 **Hrvoje Petek, University of Pittsburgh**
Plasmonically enhanced multiphoton photoemission at metal nanoparticle decorated surfaces

Poster Session II **Fürstensaal**

18:00 – 20:30 Poster Session & Snacks

Thursday, 02.06.2016

Session V	**(Chair: Gregor Witte)**	**Renthof**
09:00 – 09:40	**Norbert Koch, HU Berlin** *Energy level tuning at inorganic/organic semiconductor heterojunctions*	
09:40 – 10:00	**Derck Schlettwein, Gießen** *Light-induced charge transfer from dyes adsorbed to ZnO*	
10:00 – 10:20	**Andreas Opitz, HU Berlin** *Structural and electronic properties of planar organic heterojunction interfaces and their impact on diode characteristics*	
10:20 – 10:40	**Tobias Breuer, Marburg** *Effects of molecular orientation in acceptor-donor interfaces between pentacene and C_{60} and Diels-Alder adduct formation at the molecular interface*	
	Coffee break	
Session VI	**(Chair: Yoshiyasu Matsumoto)**	**Renthof**
11:10 – 11:50	**Julia Stähler, Fritz-Haber-Institut, Berlin** *Charge carrier and exciton dynamics at hybrid inorganic/organic interfaces*	
11:50 – 12:10	**Olga Turkina, HU Berlin** *Electronic and optical excitations at the pyridine@ZnO hybrid interface*	
12:10 – 12:30	**Sangam Chatterjee, Marburg** *Charge transfer excitations at the pentacene/C_{60} interface*	
	Break	

Thursday, 02.06.2016

Session VII	**(Chair: Torsten Fritz)**	**Renthof**
14:00 – 14:40	**Toshiaki Munakata, Osaka** *Unoccupied electronic structures of rubrene: from evaporated films to single crystals*	
14:40 – 15:00	**Cornelius Gahl, FU Berlin** *Electron and exciton dynamics in sexithiophene on Au(111)*	
	Coffee break	
Session VIII	**(Chair: Martin Aeschlimann)**	**Renthof**
15:20 – 15:40	**Alexander Lerch, Marburg** *Influence of the interface state on charge transfer processes at well-defined metal/organic interfaces*	
15:40 – 16:00	**Juliana Maria Morbec, Duisburg-Essen** *First-principles study of anthracene and pentacene adsorbed on coinage metal surfaces: the effects of the van der Waals interactions*	
16:00 – 16:20	**Stefan Mathias, Göttingen** *Spin filtering at a Bi superstructure on Au(111) interface*	
	Break	
19:00 – 22:00	**Conference dinner**	**Fürstensaal**

Friday, 03.06.2016

Session IX	**(Chair: Martin Koch)**	**Renthof**
09:00 – 09:40	**Mackillo Kira, Marburg** *Dynamic transport of quantum clusters*	
09:40 – 10:00	**Thomas Hannappel, Ilmenau** *GaP-on-Si(100) heterointerfaces studied in situ*	
10:00 – 10:20	**Kunie Ishioka, NIMS, Tsukuba** *Ultrashort acoustic pulses generated at buried GaP/Si interfaces*	
10:20 – 10:40	**Christopher Stanton, University of Florida, Gainesville** *Ultrafast coherent optical phonon probing of electronic properties of surfaces and interfaces*	
	Coffee break	
Session X	**(Chair: Stephan W. Koch)**	**Renthof**
11:10 – 11:30	**Wolfgang Stolz, Marburg** *Realization of interface-dominated type-II-(GaIn)As/Ga(AsSb)/(GaIn)As "W"-quantum well lasers in the near infrared emission wavelength range*	
11:30 – 11:50	**Anna Persson, Lund** *Electron diffusion in Ni studied with time-resolved X-ray diffraction*	
11:50 – 12:30	**Friedhelm Bechstedt, Jena** *Topological states at semiconductor interfaces: a view from first principles*	
12:30 – 12:40	*Closing remarks*	

Timetable

	Tuesday, 31.05.2016	Wednesday, 01.06.2016	Thursday, 02.06.2016	Friday, 03.06.2016	
09.00 - 09.20	Registration	Botti	Koch	Kira	09.00 - 09.20
09.20 - 09.40	Welcome				09.20 - 09.40
09.40 - 10.00	Fritz	Niesner	Schlettwein	Hannappel	09.40 - 10.00
10.00 - 10.20		Hone	Opitz	Ishioka	10.00 - 10.20
10.20 - 10.40	Volz		Breuer	Stanton	10.20 - 10.40
10.40 - 11.00		Coffeebreak	Coffeebreak	Coffeebreak	10.40 - 11.10
11.00 - 11.30	Coffeebreak	Riechert	Stähler	Stolz	11.10 - 11.30
11.30 - 11.50	Aeschlimann			Persson	11.30 - 11.50
11.50 - 12.10		Louie	Turkina	Bechstedt	11.50 - 12.10
12.10 - 12.30	Rohlfing		Chatterjee		12.10 - 12.30
12.30 - 12.50		Break	Break	Closing Remarks	12.30 - 12.40
12.50 - 13.20	Lunch & Poster Session I				12.40 - 13.00
13.20 - 13.40					13.00 - 13.20
13.40 - 14.00					13.20 - 13.40
14.00 - 14.20			Munakata		13.40 - 14.00
14.20 - 14.40					14.00 - 14.20
14.40 - 15.00			Gahl		14.20 - 14.40
15.00 - 15.20			Coffeebreak		14.40 - 15.00
15.20 - 15.40			Lerch		15.00 - 15.20
15.40 - 16.00			Morbec		15.20 - 15.40
16.00 - 16.20	Matsumoto	Wurstbauer	Mathias		15.40 - 16.00
16.20 - 16.40			Break		16.00 - 16.20
16.40 - 17.00	Schmid	Jeschke			16.20 - 16.40
17.00 - 17.20	Koert	Petek			16.40 - 17.00
17.20 - 17.40	Tautz				17.00 - 17.20
17.40 - 18.00		Poster Session II & Snacks			17.20 - 17.40
18.00 - 18.30					17.40 - 18.00
18.30 - 19.00					18.00 - 18.30
19.00 - 19.30					18.30 - 19.00
19.30 - 20.00			Conference Dinner		19.00 - 19.30
20.00 - 20.30					19.30 - 20.00
20.30 - 21.00					20.00 - 20.30
					20.30 - 21.00

Opening Session - Alte Aula, Old University

Talks - Renthof 5, main lecture-hall

Posters & Dinner - Castle

Poster Session I, Tuesday, 31.05.2016 **Fürstensaal**

1 **Marc Landmann, Paderborn**
Band offsets in cubic GaN/$Al_xGa_{1-x}N$ heterostructure

2 **Katharina Gries, Marburg**
3D investigation of InGaN nanodisks in GaN nanowires

3 **Han Han, Marburg**
Correlation of interface morphology and composition in GaInP/GaAs with growth conditions

4 **Henning Döscher, Marburg**
GaP-interlayer formation on epitaxial GaAs(100) surfaces in MOVPE ambient

5 **Anja Dobrich, Ilmenau**
Interface analysis on MOVPE grown InP-GaInAs-InP double heterostructures for application in infrared solar cells

6 **Christian Fuchs, Marburg**
Growth and characterization of (GaIn)As/Ga(AsSb)/(GaIn)As "W"-quantum well heterostructures for laser applications

7 **Christian Berger, Marburg**
Type-II quantum well structures for interface-dominated lasers

8 **Sebastian Gies, Marburg**
Charge transfer luminescence in (GaIn)As/Ga(AsSb) and (GaIn)As/Ga(NAs) quantum wells

9 **Julian Veletas, Marburg**
Excitonic transitions in type-II heterostructures

10 **Christian Lammers, Marburg**
Time-resolved gain spectroscopy on type-I and type-II VECSEL chips

11 **Christoph Möller, Marburg**
1.2 µm emitting VECSEL based on type-II aligned QWs

12 **Osmo Vänskä, Marburg**
Coherent control of correlation transport through interface between semiconductor quantum wells

13 **Osmo Vänskä, Marburg**
Hybrid cluster-expansion and density‑functional‑theory scheme and its application for optical absorption in TiO_2

14 **Abdul Samad Syed, Duisburg-Essen**
Polarization-dependent two-photon photoemission of unoccupied electronic states in Pb/Si(557)

15 **Lars Winterfeld, Ilmenau**
Two-dimensional metallic Na layers in Si stacking faults

16 **Ulrich Huttner, Marburg**
Strong terahertz excitations in semiconductors

17 **Markus Stein, Marburg**
Exciton mass anisotropy revealed by THz spectroscopy

18 **Jinghao Chen, Duisburg-Essen**
Ultrafast magnetization dynamics at the Co/Cu(001) interface investigated with time-resolved magnetization-induced second harmonic generation

19 **Jens Güdde, Marburg**
Spectroscopy and dynamics of a two-dimensional electron gas on top of ultrathin helium films on Cu(111)

20 **Rebecca Pöschel, Erlangen**
Unoccupied band structure of MgO/Ag(100)

21 **Johannes Reimann, Marburg**
Ultrafast dynamics of photocurrents in the Dirac cone surface state of a topological insulator

22 **Johannes Martin, Marburg**
Charge transport at an internal interface – turning the interface into an interphase

23 **Lorenz Maximilian Schneider, Marburg**
Gate voltage dependency of Förster resonance energy transfer in graphene - quantum dot photo-detection

24 **Eugenie Geringer, Marburg**
Functional binary and ternary organotin sulfide clusters

25 **Niklas Rinn, Marburg**
Chemistry of organofunctionalized Sn/Se clusters

26 **Johanna Heine, Marburg**
Organic–inorganic hybrid materials based on porphyrin dicacids and halogenidobismuthates

27 **Jonas Zimmermann, Marburg**
Time-resolved SHG-microscopy of 2D monolayer structures

28 **Robert Wallauer, Marburg**
Time- and angle-resolved photoemission from MoS_2

29 **Jan Kuhnert, Marburg**
Photoluminescence measurements of MoS_2 and WS_2 monolayers in magnetic fields up to 7 Tesla

30 **Oliver Supplie, Ilmenau**
A combined in situ RAS, in vacuo XPS and ab initio DFT study of the GaP/Si(100) heterointerface

31 **Ulrich Höfer, Marburg**
Time-resolved nonlinear spectroscopy at the buried GaP/Si interface

32 **Jan Oliver Oelerich, Marburg**
Computer simulation of anti phase domain formation at the GaP/Si interface

33 **Agnieszka Paszuk, Ilmenau**
Control over the GaP sublattice orientation on Si(111) and Si(100) by As-modifications of the heterointerface

34 **Christian Koppka, Ilmenau**
Suppressing rotational defects in GaP/Si(111) heterosubstrates for improved III-V nanowire growth

35 **Marcel Reutzel, Marburg**
Diethyl ether on Si(001) – an experimental study on adsorption configurations and energy barriers

36 **Tamam Bohamud, Marburg**
STM tip-induced manipulation of diethyl ether and tetrahydrofuran on Si(001)

37 **Franziska Maercks, Aachen**
Effects of surface modification with self-assembled monolayers on perylene thin film growth

38 **Josua Pecher, Marburg**
Computational study on the suitability of a bifunctional cyclooctyne molecule as a building block for growing interfaces on Si(001)

39 **Paul Nikodemiak, Marburg**
Functionalized cyclooctynes: potential building blocks for layer-by-layer synthesis in solution

40 **Michael Meyer, SPECS Surface Nano Analysis GmbH**
Spin-resolved time-of-flight momentum microscopy

Poster Session II, Wednesday, 01.06.2016 **Fürstensaal**

1 **Paul Beyer, HU Berlin**
Characterization of charge transfer in weakly interacting organic-organic heterostructures

2 **Qiankun Wang, HU Berlin**
Electronic properties of optically switchable photochromic diarylethene molecules at interface with organic semiconductors

3 **Marina Gerhard, Marburg**
Efficient dissociation of excitons at donor/acceptor interfaces in organic solar cells

4 **Sara Jäckle, Helmholtz-Zentrum für Materialien und Energie, Berlin**
Investigation of the PEDOT:PSS/silicon interface for hybrid heterojunction solar cells

5 **Ingo Meyenburg, Marburg**
Optical spectroscopy on organic-inorganic hybrids – charge transfer in type-II level systems

6 **Moritz Eyer, HU Berlin**
Hybrid charge transfer excitons and interface energetics at ZnMgO/P3HT heterojunctions

7 **Thorsten Schultz, HU Berlin**
Tuning the work function of GaN and the influence of surface states

8 **Reza Kakavandi, Tübingen**
Interfaces and surfaces in organic radical thin films: electronic structure and paramagnetic character

9 **David Nobis, Erlangen**
Electronic states of thin films of 1,3-diphenylisobenzofuran

10 **Nico Armbrust, Marburg**
Model potential for description of metal/organic interface states

11 **Felix Otto, Jena**
Investigation of the potassium doping of DBP on Ag(111) by photoelectron spectroscopy

12 **Malte Zugermeier, Marburg**
Metalation reactions of corroles at metal-organic interfaces

13 **Hazem Aldahhak, Paderborn**
Free-base 5,10,15-tris(pentafluorophenyl)corrole adsorption on Ag(111)

14 **Hazem Aldahhak, Paderborn**
PTCDA molecules on terraces and at steps sites of the KCl(100) and NaCl surfaces

15 **Eduard Baal, Marburg**
Probing PET with fluorescence switch off-on perylene diimides

16 **Andreas Namgalies, Marburg**
Energy transfer in thin layers of PTCDA on Ag(111) and Au(111) – a combined 2PPE and streak camera experiment

17 **Nikolay Zaitsev, Marburg**
Structure and vibrational properties of the PTCDA/Ag(111) interface: bilayer vs. monolayer

18 **Sebastian Thussing, Marburg**
Structure and thermal stability of molecular heterolayer structures on Ag(111)

19 **Alexander Mänz, Marburg**
Copper-phthalocyanine layer as contact primer for organic semiconductor films grown on coinage metals

20 **Laura Fernández, Marburg**
Growth and vibrational properties of ultra-thin TiOPc films on Ag(111)

21 **Stephan Jauernik, Kiel**
A combined 2PPE and LEED study of tin-phthalocyanine on Ag(111)

22 **Frederik Schiller, Marburg and CFM-CSIC, San Sebastián**
The electronic structure at the TiOPc/Ag(111) interface

23 **Martin Liebold, Marburg**
Experimental and computational study of soluble azaphthalocyanines and azasubphthalocyanines of varying number of aza units

24 **Jing Guo, Chemnitz**
Charge transfer channels between metal phthaloycanines and ferromagnetic substrates

25 **Michael Kothe, Marburg**
Low temperature deposition of oriented zinc phthalocyanine thin films and their optical characterization

26 **Gianluca Di Filippo, Erlangen**
Two-photon photoemission from tetraphenylporphyrins on Ag(100)

27 **Benedikt Klein, Marburg**
Analysis of buried metal-semiconductor interfaces with hard X-ray photoelectron spectroscopy (HAXPES)

28 **Gerson Mette, Marburg**
The metal-organic pyrphyrin/Au(111) interface

29 **Christian Udhardt, Jena**
Investigation of coronene thin-films on Ag(111) using photoelectron spectroscopy

30 **David Gerbert, Heidelberg**
Band formation at the F_4TCNQ/Au(111) interface

31 **Julia Rittich, Aachen**
Indium-tin-oxide (ITO) surface functionalization with organic self-assembled-monolayers

32 **Sebastian Jung, Aachen**
Optimization of charge carrier transfer in organic thin film transistors

33 **Anna-Katharina Hansmann, Marburg**
Theoretical description of electronic and vibronic properties at interfaces between pentacene derivatives

34 **Frederic Wagner, Marburg**
Pentacenes and azapentacenes as building blocks for internal interfaces: syntheses, molecular and solid-state properties

35 **Michael Klues, Marburg**
Electronic structure of fluorinated aromatic molecules

36 **Andre Rinn, Marburg**
Correlation of carrier dynamics and molecular packing in pentacene-perfluropentacene hybrids

37 **Rocío Félix, Marburg**
TEM analysis of codeposited pentacene:perfluoropentacene grown on SiO_2 substrate

38 **Robin Döring, Marburg**
Charge carrier dynamics at the pentacene - C_{60} interface

39 **Andrea Karthäuser, Marburg**
Controlling C_{60} layer morphology and crystallinity in organic heterostructures: influence of pentacene bottom layers

40 **Nicolas Bock, Marburg**
Electrospray ion-beam deposition (ESI-IBD) of organic molecules as an alternative to vapor deposition

Oral Abstracts Tuesday

Epitaxy without coincidences – the stabilizing role of static distortion waves

Torsten Fritz
Friedrich-Schiller-Universität Jena, Institute for Solid State Physics,
Helmholtzweg 5, 07743 Jena, Germany
e-mail: torsten.fritz@uni-jena.de

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

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

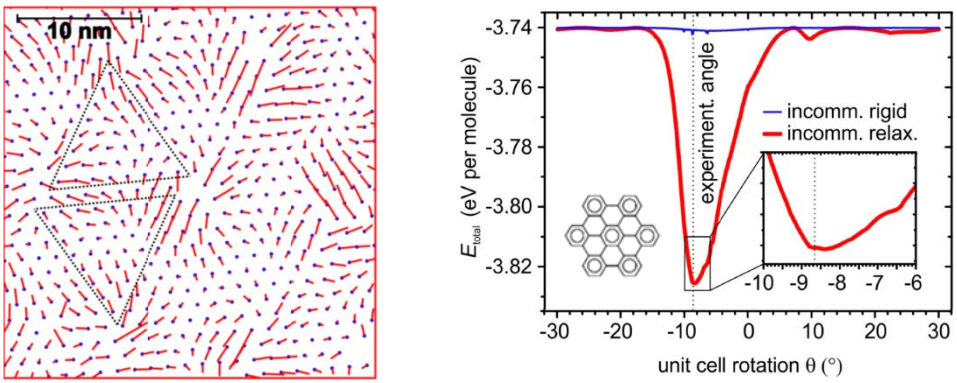


Fig. 1. Static distortion waves in one monolayer of the organic molecule HBC on graphite. *Left:* Experimentally determined average lattice (blue dots) and displacements (red; magnification factor 15). *Right:* Total adsorption energy per molecule of an HBC domain of approx. 10.000 molecules, initially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

Unravelling the structure of buried semiconductor interfaces and its correlation to opto-electronic properties

Kerstin Volz
Faculty of Physics and Materials Science Center, Philipps-Universität Marburg, Germany
e-mail: kerstin.volz@physik.uni-marburg.de

Modern semiconductor heterostructures are composed of several different materials grown on top of each other. The internal interfaces arising between these materials can have significant influence on device performance. Hence, it is important to first of all establish a knowledge on the composition and morphology of these interfaces and to correlate different structures to the optoelectronic properties of the heterostructure. Secondly, it is also fundamentally interesting to determine kinetic and thermodynamic driving forces leading to different interface morphologies depending on the properties of the two semiconductors forming the interface, like heteroepitaxial strain or charge.

Material systems have been chosen for this study, which can be used to examine the influence of different properties of the materials on the internal interface formation. (GaIn)As/GaAs is an example for a strained interface, where no charge is involved. (GaIn)P/GaAs is lattice matched with also no charge involved. In contrast, the GaP/Si interface could be charged due to the different polarity of the two semiconductors forming this interface. Nevertheless, GaP/Si is lattice matched so that strain effects on interface formation can be excluded.

All samples used for this study have been grown by metal organic vapour phase epitaxy.

Aberration-corrected scanning transmission electron microscopy in combination with “frozen phonon” contrast simulation for the different materials is applied to quantify the morphology and composition of the different internal interfaces at an atomic scale. Moreover, kinetic-Monte-Carlo and Density-Functional-Theory simulations have been conducted for certain examples to understand the kinetic and thermodynamic driving forces leading to intrinsic interface morphologies.

We find that (GaIn)P/GaAs is the sole interface under investigation that can be deposited atomically abrupt. (GaIn)As/GaAs shows an In-segregation profile due to strain and GaP/Si exhibits a triangular interface morphology. The latter one can be explained by kinetic aspects leading to intermixing and thermodynamic driving forces resulting in an interface structure that minimizes the charge present at the interface.

Controlling the Spin Texture of Topological Insulators with Organic Molecules

Martin Aeschlimann
Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Germany
e-mail: ma@physik.uni-kl.de

A rational design approach to customize the spin texture of surface states of a topological insulator will be presented. This approach relies on the extreme multifunctionality of organic molecules that are used to functionalize the surface of the prototypical topological insulator (TI) Bi_2Se_3. For the rational design we use theoretical calculations to guide the choice and chemical synthesis of appropriate molecules that customize the spin texture of Bi_2Se_3. The theoretical predictions are then verified in angular-resolved photoemission experiments. We show that, by tuning the strength of molecule–TI interaction, the surface of the TI can be passivated, the Dirac point can energetically be shifted at will, and Rashba-split quantum-well interface states can be created. These tailored interface properties (passivation, spin-texture tuning, and creation of hybrid interface states) lay a solid foundation for interface-assisted molecular spintronics in spin-textured materials.

S. Jakobs et al, Nano Lett. 15 (9), 6022 (2015)

Electronic spectra of layered materials and monolayer adsorbates

Michael Rohlfing
Inst. f. Festkörpertheorie, Westfälische Wilhelms-Universität Münster, Germany
e-mail: michael.rohlfing@uni-muenster.de

Many-body perturbation theory (MBPT) has emerged as a powerful tool for addressing electronic and optical spectra in low-dimensional systems.

Some recent examples:

(i) Topological insulators like Bi_2Se_3 exhibit metallic surface states (Dirac cone); in thin films these states hybridize and split [1];
(ii) Exciton states in monolayers of transition-metal dichalcogenides are considered important for future optoelectronics; these states are significantly affected by geometrical deformation, doping, and substrate polarizability [2];
(iii) Organic adsorbates on metal surfaces show characteristic molecular states which can even lead to Kondo resonances [3,4].

These system classes may appear quite diverse, but they share many common features and mechanisms that will be discussed in this talk, like e.g. the role of spatial extent and overlap of quantum-mechanical states, image-potential effects due to environment polarizability, etc., asking for a parameter-free ab-initio framework as provided by MBPT.

[1] T. Förster, P. Krüger, and M. Rohlfing: Phys. Rev. B 92, 201404(R) (2015)
[2] R. Schmidt, I. Niehues, R. Schneider, M. Drüppel, T. Deilmann, M. Rohlfing, S. Michaelis de Vasconcellos, A. Castellanos-Gomez, and R. Bratschitsch: submitted to 2D Materials.
[3] T. Esat, T. Deilmann, B. Lechtenberg, C. Wagner, P. Krüger, R. Temirov, F.B. Anders, M. Rohlfing, and F.S. Tautz: Phys. Rev. B 91, 144415 (2015).
[4] T. Esat, B. Lechtenberg, T. Deilmann, C. Wagner, P. Krüger, R. Temirov, M. Rohlfing, F.B. Anders, and F.S. Tautz: Nature Physics (2016), in print.

Structures of water at interfaces of ice crystal films grown on metals

T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe, and Y. Matsumoto
Department of Chemistry, Graduate School of Science, Kyoto University, Japan
e-mail: matsumoto@kuchem.kyoto-u.ac.jp

The structure of water crystalline ice is strictly restricted by ice rules: two hydrogen atoms must be positioned closer to each oxygen atom while two others further away from it. When crystalline ice is grown on solid surfaces, the structure of ice is influenced by water-surface interactions. Although the structure of crystalline ice films and the specific interactions at the interface have been extensively studied [1], the precise ice structure at interface including the orientation of molecules has not been thoroughly understood. In this talk, we focus upon the orientation of water molecules at ice/metal interfaces and how the orientation of water, i.e., proton ordering, propagates into the bulk ice films.

Because the ice/metal interfaces are buried interfaces, the vibrational structure and the orientation of molecules at the interfaces are difficult to probe with traditional vibrational spectroscopy such as infrared spectroscopy, high resolution electron energy loss spectroscopy, and inelastic He scattering. In this work, water molecules at an ice/Pt(111) interface has been probed with infrared-visible sum frequency generation spectroscopy (SFG) with heterodyne detection. In contrast to conventional homodyne detection probing $|\chi^{(2)}|^2$, where $\chi^{(2)}$ is the second-order nonlinear optical susceptibility, heterodyne-detected SFG allows us to determine $\chi^{(2)}$, whose imaginary part provides local configurations of water. Heterodyne signals were detected through the SFG intensity from the sample surface interfering with one from a local oscillator. To make an OH stretching band structure of water simpler, we have mainly targeted HDO ice films.

The $\mathrm{Im}\{\chi^{(2)}\}$ spectra show a single negative peak at around 3370 cm^{-1} in submonolayer coverages. As the coverage increases to form multilayer, a new negative peak at around 3275 cm^{-1} continues to grow. The negative sign of $\mathrm{Im}\{\chi^{(2)}\}$ of the first-layer water clearly indicates that the water molecules directly interacting with Pt(111) have a net orientation with one of their protons pointing toward the substrate; this agrees with the theoretical prediction [2]. Interestingly, the preference is kept in the multilayers. Namely, the specific orientation of first-layer molecules propagates into bulk, forming ferroelectric crystalline ice films.

[1] A. Hodgson and S. Haq, *Surf. Sci. Rep.*, **2009**, 64, 381-451.
[2] S. Nie, P. J. Feibelman, N. C. Bartelt, and K. Thümer, *Phys. Rev. Lett.*, **2010**, 105, 026102.

Hard X-ray photoelectron spectroscopy: a tool for chemical depth-profiling across buried interfaces

Martin Schmid
Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: schmidm5@staff.uni-marburg.de

Hard X-ray Photoelectron Spectroscopy (HAXPES) uses high-energy photons with energies of up to 10 keV to probe electronic states much deeper inside the bulk material compared to conventional X-ray Photoelectron Spectroscopy (XPS). In general, Photoelectron Spectroscopy (PES) is based on the photoelectric effect, i.e., the removal of electrons from discrete core states of atoms. This method is routinely used to obtain qualitative and quantitative chemical information about a given sample, since the kinetic energy of the photoelectrons carries information about the chemical nature of the source atom and its chemical state.

If applied to solid samples, only photoelectrons which were created close to the solid-vacuum interface have a chance of crossing this interface without being subject to inelastic scattering events en-route (and, as a consequence, the loss of 'chemical' information). Therefore, Photoelectron Spectroscopy is an inherently surface-sensitive method where the effective depth resolution is determined by the *escape depth* of the photoelectrons from the sample (λ); as a rule of thumb, 95% of all electrons in a given photoelectron peak emerge from a layer of the thickness of 3 λ. The escape depth, or more precisely *inelastic mean free path*, is a function of the electrons kinetic energy: On a logarithmic scale, λ follows approximately a U-shaped curve with the minimum at 50-100 eV kinetic energy. For smaller or larger energies, λ increases strongly. Accordingly, irradiating the sample at issue with photons of higher energy allows to probe and analyze chemical states of atoms deeper within the bulk, as the kinetic energy (and consequently λ) of the created photoelectrons will increase with the photon energy due to energy conservation.

Based on its ability to monitor the chemical states relatively deep within the sample material, HAXPES is ideally suited for destruction-free chemical depth profiling - in particular across buried solid-solid interfaces within a sample. For illustration, HAXPES analyses of buried Ca/α-sexithiophene and metal/2H-porphyrin, performed at the HIKE endstation at the BESSY II synchrotron facility, will be discussed in detail.

Functionalized cyclooctynes: potential building blocks for layer-by-layer synthesis at Si(001)

M. Reutzel[1], M. A. Lipponer[1], C. Länger[3], N. Münster[2], P. Nikodemiak[2], U. Höfer[1], U. Koert[2], M. Dürr[3]
[1] *Department of Physics, Philipps-Universität Marburg, Germany*
[2] *Department of Chemistry, Philipps-Universität Marburg, Germany*
[3] *Institute of Applied Physics, Justus-Liebig-Universität Gießen, Germany*
e-mail: koert@chemie.uni-marburg.de

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. Cyclooctynes of type **1** react with the Si(001) surface to form cycloadducts of type **2**.[1] Functionalized cyclooctynes **3** and **4** 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 model system for the layer-by-layer synthesis at surfaces via sequential chemoselective alkyne/azide cycloadditions is presented for solution chemistry using bisalkynes **5**, **6** and the bisazide **7**.

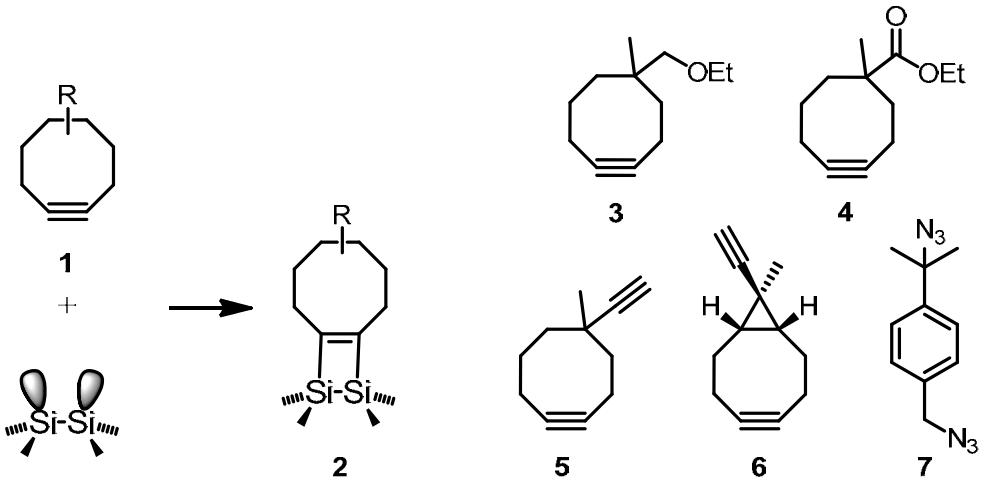


Fig. 1 Structures of substituted pentacenes and azapentacenes.

[1] G. Mette, M. Dürr, R. Bartholomäus, U. Koert, U. Höfer, *Chem. Phys. Lett*. **2013**, *556*, 70.

The Backside of Graphene

J. Sforzini[1], F.C. Bocquet[1], and F.S. Tautz[1,2]
[1] *Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany*
[2] *Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany*
e-mail: s.tautz@fz-juelich.de

Graphene, a strictly two-dimensional material, is considered to be a promising material for nanoelectronic applications. In practical devices, the graphene layer has to be supported by a substrate. By necessity, this creates an internal interface between the backside of graphene and the substrate. Because graphene is only one atomic layer thick, this interface will almost certainly influence the properties of the material and any active device made thereof.

In the present contribution we study the influence of the interface between graphene and 6H-SiC(0001), with particular attention to the structure (adsorption height, buckling, bonding, location of p and n-dopants) and electronic properties (band structure, charge carrier densities).

[1] Sforzini, J.; Nemec, L.; Denig, T.; Stadtmüller, B.; Lee, T.-L.; Kumpf, C.; Soubatch, S.; Starke, U.; Rinke, P.; Blum, V.; Bocquet, F. C.; Tautz, F. S., Approaching Truly Freestanding Graphene: The Structure of Hydrogen-Intercalated Graphene on 6H-SiC(0001). *Physical Review Letters* **2015,** *114*, 106804.
[2] Sforzini, J.; Telchyko, M.; Krejci, O.; Vondracek, M.; Svec, M.; Bocquet, F. C.; Tautz, F. S., Transformation of metallic boron into substitutional dopants in graphene on 6H-SiC(0001). *Physical Review B* **2016,** *93*, 041302(R).
[3] Sforzini, J.; Hapala, P.; Franke, M.; van Straaten, G.; Stöhr, A.; Link, S.; Soubatch, S.; Jelinek, P.; Lee, T.-L.; Starke, U.; Svec, M.; Bocquet, F. C.; Tautz, F. S., Structural and Electronic Properties of Nitrogen-Doped Graphene. *Physical Review Letters* **2016,** *116*, 126805.

Oral Abstracts Wednesday

Materials design at interfaces for photovoltaics

Silvana Botti
Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Germany
e-mail: silvana.botti@uni-jena.de

In the domain of photovoltaics it is by now clear that the optimization of existing technologies and the development of new ones passes through a better control of the physics of interfaces. *Ab initio* approaches for electronic excitations based and going beyond density functional theory ally accuracy and efficiency, and are therefore suitable for understanding the physics not only of simple bulk crystals, but also of interfaces and nanostructured systems. By combining high-throughput calculations, structural prediction and an accurate characterization of electronic properties we aim at designing improved interfaces for solar cells. I will present an overview of our most recent theoretical and computational developments, together with some examples of their application to the search of new materials.

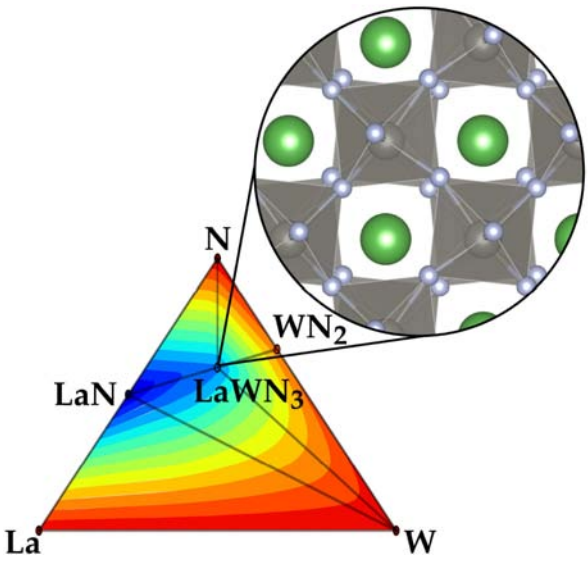


Fig. 1 Ternary phase diagram of a nitride perovskite from Chem. Mater. 27, 5957 (2015).

Electronic structure at interfaces and surfaces of organic-inorganic perovskites

D. Niesner[1,2], M. Wilhelm[1], T. Fauster[1], X. Wu[2], M. T. Trinh[2], H. Zhu[2], O. Yaffe[2], B. J. Kudisch[2], X.-Y. Zhu[2], I. Levchuk[3], and C. J. Brabec[3]

[1] Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany

[2] Department of Chemistry, Columbia University, New York, NY, USA

[3] Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany

e-mail: daniel.niesner@fau.de

Organic-inorganic perovskite compounds (OIPCs) have opened a new field in optoelectronics. Lifetimes and diffusion lengths of optically excited carriers in OIPCs are orders of magnitude longer than in purely inorganic semiconductors, making them excellent candidates for low-threshold nanolasers [1] and high-efficiency thin film solar cells [2]. The origin of these exceptional photophysical properties, however, remains a matter of discussion. Several mechanisms were proposed by theory, including electron-hole separation at microscopic ferroelectric domains [3], large polaron formation [4], suppression of electron-phonon scattering [5], and lifetime enhancement due to the spin structure of electronic states [6].

In experiments on commonly used OIPCs thin films, defects at surfaces and interfaces may detrimentally affect carrier lifetimes and diffusion lengths. Using transient absorption and fluorescence spectroscopy in combination with photoemission experiments, we compare the density of mid-gap states in $(CH_3NH_3)PbI_3$ thin films grown from PbI_2 and $PbCl_2$ [7]. While the former exhibit a significantly higher density of mid-gap states in bulk-sensitive optical spectroscopy, differences are less pronounced in surface sensitive photoelectron spectroscopy. Since thin films grown by the two techniques on the one hand exhibit very similar composition, but on the other differ in film morphology, we assign the observed traps predominantly to defects at internal and exposed surfaces.

As compared to thin films, the density of internal surfaces and surface defects is significantly reduced at surfaces of single crystals cleaved in ultrahigh vacuum. After cleaving, single crystal $(CH_3NH_3)PbBr_3$, which we use as a model system, exposes bulk-terminated surfaces. In photoemission experiments, no in-gap states are detectable. Angle-resolved experiments determining the dispersion of the highest-energy valence band become possible. We discuss the electronic structure of the system in its different structural phases and comment on effects of spin-orbit coupling.

[1] H. Zhu et al., Nature Mater. **14**, 636 (2015)
[2] W. S. Yang et al., Science **348**, 1234 (2015)
[3] J. M. Frost et al., Nano Lett. **14**, 2584 (2014)
[4] J. Ma et al., Nano Lett. **15**, 248 (2015)
[5] H. Kawai et al., Nano Lett. **15**, 3103 (2015)
[6] F. Zheng et al., Nano Lett. **15**, 7794 (2015)
[7] X. Wu et al., J. Am. Chem. Soc. **137**, 2089 (2015)

2D materials in the ultraclean limit: basic science and applications

James Hone
Department of Mechanical Engineering and Materials Research Science and Engineering Center, Columbia University, New York USA
e-mail: jh2228@columbia.edu

Two-dimensional materials offer a wide range of outstanding properties but are highly sensitive to disorder from the environment. We have developed techniques to stack 2D materials on top of each other to create 'van der Waals Heterostructures' with nearly perfect interfaces, and to achieve high-quality contacts to the one-dimensional edge of buried layers. These techniques provide an ideal platform to study and utilize 2D materials in the ultraclean limit.

Recent results in this area will be discussed, including: 1. Near-ideal performance in graphene monolayers and bilayers; 2. Novel physics in graphene / BN structures including Hofstader Butterfly physics, magnetic focusing, and Coulomb Drag; 3. Applications of graphene in high-performance optoelectronics and plasmonics; 4. Low-T magnetotransport in semiconducting MoS_2; 5. Studies of 2D metals and superconductors.

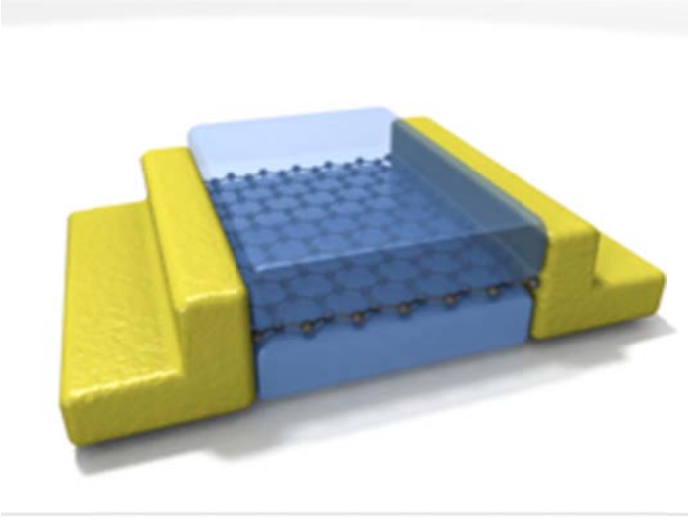


Fig. 1 Schematic representation of BN-encapsulated graphene with metal edge contacts

Growth of two-dimensionally bonded materials – fiction, facts and surprises

H. Riechert[1], J.E. Boschker[1], V. Bragaglia[1], R.N. Wang[1], K. Perumal[1], A. Giussani[1], L.A. Galves[1], T. Flissikowski[1], J.M.J. Lopes[1], R. Calarco[1], J. Momand[2], B.J. Kooi[2], M.A. Verheijen[3]

[1] Paul-Drude-Institut für Festkörperelektronik, Berlin
[2] University of Groningen, The Netherlands
[3] Eindhoven University of Technology, The Netherlands
e-mail: riechert@pdi-berlin.de

In this talk we report on the MBE growth of several combinations of two-dimensionally (van der Waals-) bonded materials. For tuning into the subject, we refer to early work which demonstrates some of the promises of van der Waals-epitaxy, above all the ease of combining materials with different lattice constants. The basis of our work at PDI are graphene and Sb_2Te_3. We grow the latter on graphene and on surfaces of Si(111) which are prepared in situ to obtain different amounts of surface bonds. Most surprisingly, the resulting surface reconstruction may influence the in-plane orientation in this process of heteroepitaxy. Moreover, we show that lattice matching remains an important issue in the epitaxy of van der Waals-bonded heterostructures.

Interaction and correlation effects at ultimately thin interfaces: atomically thin quasi-2D crystals

Steven G. Louie
Physics Department, University of California at Berkeley, and
Lawrence Berkeley National Lab, Berkeley, California 94720 U.S.A
e-mail: sglouie@berkeley.edu

Experimental and theoretical studies of atomically thin quasi two-dimensional (2D) materials and their nanostructures have revealed that these systems can exhibit highly unusual behaviors. Owing to their reduced dimensionality, quasi-2D materials present opportunities for manifestation of concepts/phenomena that may not be so prominent or have not been seen in bulk materials. Symmetry, many-body interaction, and substrate screening effects often play a critical role in shaping qualitatively and quantitatively their electronic and optical properties, and thus their potential for applications. In this talk, we present theoretical studies on quasi-2D systems such as monolayer and few-layer transition metal dichalcogenides and metal monochalcogenides, as well as other 2D crystals. Several phenomena are discussed including: novel exciton behaviors; tunable transport, optical, magnetic and plasmonic properties; and the central importance of substrate screening. We investigate their physical origins and compare theoretical predictions with experimental data.

This work was supported in part by the National Science Foundation and the U.S. Department of Energy.

Light matter interaction, exciton-phonon coupling and optoelectronic properties in TMDCs

Eric Parzinger[1,2], Bastian Miller[1,2], Alexander Holleitner[1,2], and Ursula Wurstbauer[1,2]
[1] *Walter Schottky Institute and Physics-Department, TU Munich, Garching, Germany*
[2] *Nanosystems Initiative Munich (NIM), München, Germany*
e-mail: wurstbauer@wsi.tum.de

Transition metal dichalcogenides such as MoS_2 are of current interest for optoelectronic, sensing and energy harvesting application, but also for studying fundamental aspects of light-matter interaction in strictly two-dimensional semiconductors. We access the complex dielectric function of MoS_2 flakes with a high lateral resolution by spectroscopic imaging ellipsometry [1]. The significant excitonic transitions close to the band gap as well as at high energies are only well observed in the in-plane component of the dielectric tensor and display a fascinating fine-structure. The importance of excitonic effects emerge also in resonant Raman spectroscopy, where unexpected polarization dependence point towards strong exciton-phonon coupling in MoS_2.

We further utilize non-resonant Raman spectroscopy on MoS_2 to study the effect of physisorbed environmental molecules [2] and to investigate the photo-stability in water [3]. The observed photo-catalytic stability highlights the potential of MoS_2 monolayers as high efficient photo-catalyst for solar driven water-splitting applications. In the scope of photo-catalysis and in general for optoelectronic application, the dissociation dynamics of photo-excited e-h pairs is of great relevance. Therefore, the dynamic of photo-excited charge carriers on a picosecond time scale is monitored by photocurrent measurements utilizing a recently developed pump-probe spectroscopy technique based on coplanar striplines [4-6]. These investigations provide access to the mechanisms for photocurrent generation, charge dissociation and the related charge transport dynamics.

We acknowledge support by BaCaTeC and DFG via cluster of excellence “Nanosystems Initiative Munich (NIM)”, “TUM IGSSE” and project “WU 637/4-1”.

[1] S. Funke et al., arXiv:1603.06644 (2016).
[2] B. Miller, et al., Appl. Phys. Lett. 106, 122103 (2015).
[3] E. Parzinger et al., ACS Nano, 9(11), 11302 - 11309 (2015).
[4] L. Prechtel, et al. Nature Communications 3, 646 (2012).
[5] A. Brenneis et al. Nature Nanotechnology 10, 135 (2015).
[6] C. Kastl et al. Nature Communications 6, 6617 (2015).

Effects of oxygen defects or pressure on the electronic states of $SrTiO_3$ at surfaces and interfaces

Harald O. Jeschke, Michaela Altmeyer, Vladislav Borisov, Roser Valentí
Institut für Theoretische Physik, Goethe-Universität Frankfurt, Germany
e-mail: jeschke@itp.uni-frankfurt.de

We investigate the electronic structure and spin texture at the (001) surface of $SrTiO_3$ in the presence of oxygen vacancies by means of *ab initio* density functional theory (DFT) calculations [1]. Relativistic non-magnetic DFT calculations exhibit Rashba-like spin winding with a characteristic energy scale ~10 meV. However, when surface magnetism on the Ti ions is included, bands become spin-split with an energy difference ~100 meV at the Γ point. This energy scale is comparable to the observations in SARPES experiments performed on the two-dimensional electronic states confined near the (001) surface of $SrTiO_3$. We find the spin polarized state to be the ground state of the system, and while magnetism tends to suppress the effects of the relativistic Rashba interaction, signatures of it are still clearly visible in terms of complex spin textures.

We also present *ab initio* pressure simulations of the 2D electron system (2DES) formed at the $LaAlO_3/SrTiO_3$ interface. Our results are strongly supported by recent experimental findings where substantial pressure effects have been observed. We clarify the mechanism of pressure-induced changes in the electronic system and analyze the role of the dielectric properties of both materials. We can explain both an increase of carrier density and a decrease of carrier mobility under pressure. Another important issue is whether the 2D electron system is truly two-dimensional. In the literature, there is no unified answer to this question, because of different experimental setups and theoretical models. We demonstrate that in the limit of thick STO films, the 2DES indeed approaches a well-defined two-dimensional behavior.

[1] M. Altmeyer, H. O. Jeschke, O. Hijano-Cubelos, C. Martins, F. Lechermann, K. Koepernik, A. Santander-Syro, M. J. Rozenberg, R. Valentí, M. Gabay, *Magnetism, spin texture and in-gap states: Atomic specialization at the surface of oxygen-deficient $SrTiO_3$*, Phys. Rev. Lett. **116**, 157203 (2016).

Plasmonically enhanced multiphoton photoemission at metal nanoparticle decorated surfaces

Shijing Tan, Adam Argondizzo, Hrvoje Petek
Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260 USA
e-mail: petek@pitt.edu

Excitation of plasmon resonances in metallic nanoparticles can enhance a variety of electromagnetic phenomena ranging from surface enhanced Raman scattering to photocatalysis. The topic of plasmonically enhanced photocatalysis is very popular, yet the mechanisms for the observed effects are difficult to establish because they involve complex chemical, electromagnetic, and electronic interactions between disparate materials. We employ multiphoton photoemission spectroscopy (mPP) with broadly tunable femtosecond excitation to investigate the photoemission mechanisms for the clean and metal nanoparticle (Ag and Au) decorated TiO_2 and graphite surfaces. On reduced TiO_2 surfaces, 2PP proceeds from t_{2g} symmetry Ti-3d defect states via a resonance with unoccupied e_g states [1]. In the case of graphite, mPP is predominantly of thermionic nature due to ineffectively screened Coulomb interactions, which are responsible for extremely efficient electron-electron scattering. In the presence of metal nanoparticles, the mPP processes are significantly enhanced, and provide clues to plasmon-substrate coupling that could be responsible for photocatalysis.

[1] Argondizzo, A., Cui, X., Wang, C., Sun, H., Shang, H., Zhao, J., & Petek, H. Ultrafast multiphoton pump-probe photoemission excitation pathways in rutile TiO_2. *Phys. Rev. B* **91**, 155429 (2015).

Oral Abstracts Thursday

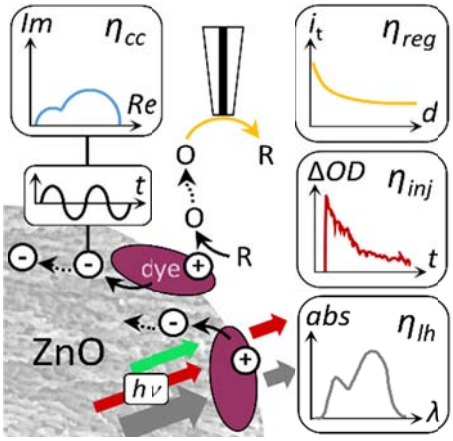
Energy level tuning at inorganic/organic semiconductor heterojunctions

Norbert Koch[1,2]
[1] *Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, Germany*
[2] *Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Germany*
e-mail: norbert.koch@physik.hu-berlin.de

The combination of inorganic and organic semiconductors provides for the potential to realizing high performance light emission or photovoltaic devices. While inorganic semiconductors feature high charge carrier mobility and support high excitation densities, organic semiconductors exhibit strong light-matter coupling and their energy spectrum can be tuned easily by molecular design. One of the key challenges to optimize inorganic/organic heterojunctions is controlling the interface electronic structure, which governs its functionality. To tune the "intrinsic" energy level alignment at the interface of a given material pair, e.g., to optimize energy transfer versus charge transfer, the work function of the inorganic semiconductor surface can be modified with appropriate monolayers of molecular donors or acceptors, so that the organic semiconductor levels are re-aligned accordingly. One mechanism that limits the range of level tuning is Fermi-level pinning at the frontier levels of the organic semiconductor. On the inorganic side, the energy and density of surface states turns out to play a crucial role for level tuning. Prototypical heterojunctions, comprising ZnO and GaN as inorganic component and intrinsic versus p-doped organic semiconductors, are discussed.

Light-induced charge transfer from dyes adsorbed to ZnO

Melanie Rudolph, Christoph Richter, Derck Schlettwein
Institute of Applied Physics, Justus- Liebig- University Giessen, Germany
e-mail: schlettwein@uni-giessen.de



The contact of dye molecules with oxide semiconductors and, in particular, charge transfer following illumination of the dye preferably to the semiconductor represent key steps of dye-sensitized solar cells (DSSCs). ZnO can serve as an alternative to the well-established TiO_2 and provides a number of advantages regarding the preparation of thin films of strongly varying morphology, typically at low temperatures. While these aspects can serve as advantages of ZnO over TiO_2, its most severe disadvantage consists in a generally lower efficiency of cells. While the injection into ZnO occurs on a sub-ps timescale, a detailed analysis revealed the presence of different injection channels, including also trap states at the surface of ZnO [1]. Such surface traps as well as aggregate formation of dyes can lead to significantly decreased injection and increased recombination rates [2] unless fast regeneration [5] can be achieved. The proper preparation of blocking, but still porous ZnO [3,4] as well as a proper choice of dyes and their environment on the ZnO surface [2], therefore, play a key role to tune the interplay of injection and regeneration versus parasitic recombination reactions in a way that favorable cell properties are achieved. In this contribution, recent results of spectroscopic as well as photoelectrochemical investigations will be discussed and an outlook provided to appropriate optimization strategies.

[1] I. Minda, E. Ahmed, V. Sleziona, C. Richter, M. Beu, J. Falgenhauer, H. Miura, D. Schlettwein, H. Schwoerer: Identification of different pathways of electron injection in dye-sensitised solar cells of electrodeposited ZnO using an indoline sensitiser, *Phys.Chem.Chem.Phys.* **2016**, 10.1039/C5CP07841E.

[2] M. Rudolph, T. Yoshida, H. Miura, D. Schlettwein: Improvement of Light Harvesting by Addition of a Long-Wavelength Absorber in Dye-sensitized Solar Cells Based on ZnO and Indoline Dyes, *J.Phys.Chem.C*, **2015**, 119, 1298–1311.

[3] C. Richter, M. Beu, D. Schlettwein: Influence of counter-anions during electrochemical deposition of ZnO on the charge transport dynamics in dye-sensitized solar cells, *Phys.Chem.Chem.Phys.*, **2015**, 17, 1883 - 1890.

[4] C. Lupo, M. Stumpp, D. Schlettwein: Diffusion-Controlled Electrochemical Growth of Porous Zinc Oxide on Microstructured Electrode Band Arrays, *J.Appl.Electrochem.*, **2015**, 45, pp. 105-113.

[5] U. M. Tefashe, M. Rudolph, H. Miura, D. Schlettwein, G. Wittstock: Photovoltaic Characteristics and Dye Regeneration Kinetics in D149-Sensitized ZnO with Varied Dye Loading and Film Thickness, *Phys.Chem.Chem.Phys.*, **2012**, 14, pp. 7533-7542.

Structural and electronic properties of planar organic heterojunction interfaces and their impact on diode characteristics

Andreas Opitz[1], Norbert Koch[1,2], Wolfgang Brütting[3], Ellen Moons[4]
[1] *Department of Physics, Humboldt-Universität zu Berlin, Berlin, Germany*
[2] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany*
[3] *Institute of Physics, University of Augsburg, Augsburg, Germany*
[4] *Department of Engineering and Physics, Karlstad University, Karlstad, Sweden*
e-mail: Andreas.Opitz@hu-berlin.de

The interface of organic heterojunctions plays a crucial role for charge separation in photovoltaic cells or for the charge carrier density in bilayer field-effect transistors. Foremost, the structural and electronic properties are of paramount importance. Here two prototypical interfaces for planar organic heterojunctions are discussed: the combination of diindenoperylene (DIP) with fullerene (C60) and the combination of copper-phthalocyanine (H16CuPc) with its perfluorinated analog (F16CuPc). Ultraviolet photoelectron spectroscopy (UPS) was performed to determine the energy level alignment together with angle resolved near edge X-ray absorption fine structure (NEXFAS) measurements to determine the molecular orientation at the interface.

The highest occupied molecular orbital (HOMO) energy levels do not shift upon deposition of the spherical C60 on top, and the orientation of the rod-like DIP is unaffected. In contrast, co-facial "lying" interface layers with π-orbital stacking of the two phthalocyanines were observed by UPS and NEXAFS. Here energy level pinning for both materials is found. These results can be related to the device performance of these two material combinations. Whereas DIP/C60 solar cells have an open circuit voltage of up to 0.9 V [1], the energy level pinning in planar structures of H16CuPc/F16CuPc leads to a charge generation layer [2,3]. The absence of a photovoltaic effect at the planar heterojunction of the phthalocyanines is thus explained by these findings.

The combined experimental approach results in a comprehensive model for the electronic and morphological characteristics of the interface between the two investigated organic semiconductors. The presence of a π-orbital stacking between different molecules at a heterojunction is also of interest for photovoltaic active interfaces or for ground-state charge-transfer. In all cases, the performance of the interface strongly depends on the relative orientation of the π-orbitals of the involved materials.

[1] J. Wagner et al., *Adv. Funct. Mater.* **20** (2010) 4295.
[2] A. Opitz et al., *Org. Electron.* **10** (2009) 1259.
[3] A. Opitz et al., *Sci. Rep.* **6** (2016) 21291.

Effects of molecular orientation in acceptor-donor interfaces between pentacene and C_{60} and Diels-Alder adduct formation at the molecular interface

Tobias Breuer, Andrea Karthäuser, Gregor Witte
Faculty of Physics, Philipps-Universität Marburg, Germany
E-mail: tobias.breuer@physik.uni-marburg.de

Interfaces between pentacene and Buckminster-Fullerene (C_{60}) have attracted interest due to their application as oligomeric model system for organic solar cells. As the actual device characteristics in such implementations are crucially controlled by the interface structure, detailed investigations of this interface on a molecular level are mandatory. Therefore, we have analyzed the influence of the orientation of the pentacene molecules in highly-ordered crystalline bottom layers on the characteristics of such interfaces. We show that the interface structure is driven by temperature-controlled diffusion of C_{60} molecules to the pentacene step-edges in the case of uprightly-oriented pentacene. For lying pentacene in the bottom layer, no step-edge decoration is observed and the wetting of the pentacene layer is enhanced. Furthermore, the stability of the interface against intercalation and re-orientation has been analyzed by means of NEXAFS spectroscopy, showing that the orientation of the pentacene molecules at the interface remains unchanged. Instead, we observe strong indication for a chemical modification of the molecular entities by the formation of Diels-Alder adducts between C_{60} and pentacene, which challenges the interpretation of this model system as chemically inert.

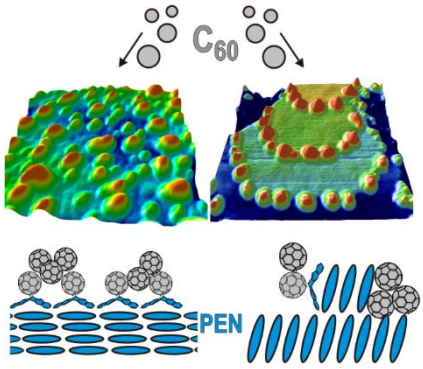


Fig. 1 Morphologies as determined by atomic force microscopy together with schematics of structural arrangements of pentacene / C_{60} interfaces in different molecular orientations.

Charge carrier and exciton dynamics at hybrid inorganic/organic interfaces

Laura Foglia, Jan-Christoph Deinert, Clemens Richter, Lea Bogner, Michael Meyer, Martin Wolf, Julia Stähler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin
e-mail: staehler@fhi-berlin.mpg.de

The functionality of hybrid inorganic/organic systems (HIOS) is governed by (i) the static interfacial electronic properties and, consequently, the energy level alignment, and (ii) the resulting charge and energy transfer rates (CT/ET). Both are investigated by a combination of complementary fs time-resolved techniques: two-photon photoelectron spectroscopy (tr-2PPE), transient excited state transmission (tr-EST) and time-resolved electronic sum frequency generation (tr-eSFG).

ZnO is an ideal candidate for a cheap, abundant and optically transparent inorganic semiconductor for HIOS. We show that hydrogen renders both mixed- and oxygen-terminated surfaces metallic by inducing strong downward surface band bending and, as a consequence, a charge accumulation layer at the surface. This is accompanied by a reduction of the work function by up to 1.6 eV. Our 2PPE measurements are supported by DFT calculations, which demonstrate that the associated changes to the electrostatic potential remain localized almost exclusively at the adsorption site for low hydrogen coverages [1]. Above band gap excitation is followed by hot electron relaxation to the Fermi level and the formation of a surface exciton (SX) within 200 fs, which exhibits a remarkable stability and lifetime up to nanoseconds [2]. tr-eSFG spectra of the non-centrosymmetric bulk of ZnO reveal that the non-equilibrium dynamics in the bulk are dominated by defect-induced states in the band gap. [3]

With regard to HIOS, we present first tr-2PPE results on the formation of a CT exciton at the ZnO interface with 5-phenyl-pyridine. The interfacial electronic structure is modified by adsorption [4] of the pyridine end group, elucidating the CT excitation mechanism. It decays through decay to the ZnO conduction band within 90 fs, indicating strong electronic coupling. Furthermore, we investigate the interface of ZnO with the organic dye 2,7-bis(biphenyl-4-yl)-2',7'-ditertbutyl-9.9'-spirobifluorene (SP6) by tr-EST and tr-2PPE. We observe two excited states populated for hundreds of ps, of which, remarkably, only one is depleted by charge transfer to the ZnO, showing that only one excited state diffuses to the interface. The charge separation competes with intersystem crossing to the SP6 triplet state and luminescence [5]. Moreover, we detect unexpected electron emission due to triplet-triplet annihilation of triplet states on microsecond timescales.

[1] J.-C. Deinert et al., *Phys. Rev. B* **91**, 2353131 (2015).
[2] J.-C. Deinert et al., *Phys. Rev. Lett.* **113**, 057602 (2014).
[3] L. Foglia et al., *in preparation* (2016)
[4] O.T. Hofmann et al., *J. Chem. Phys.* **139**, 174701 (2013).
[5] L. Foglia et al. *Chem. Phys. Lett.* **646**, 25 (2016)

Electronic and optical excitations at the pyridine@ZnO hybrid interface

Olga Turkina, Dmitrii Nabok, Caterina Cocchi, and Claudia Draxl
Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany
e-mail: turkina@physik.hu-berlin.de

Insight from *ab initio* theory is essential in order to gain an understanding of opto-electronic properties of hybrid materials, such as the correct level alignment and the creation of hybrid excitons. We investigate a prototypical hybrid inorganic/organic system composed of a pyridine molecule, chemisorbed on a non-polar ZnO(10-10) surface, using the interface geometry as optimized by Hofmann *et al.* [1] as a starting point for our calculations. We employ all-electron density-functional theory in combination with many-body perturbation theory (G_0W_0/BSE). The G_0W_0 approximation describing one-particle excitations is used to determine the electronic structure, while the Bethe-Salpeter equation describing two-particle excitations is solved to obtain the absorption spectrum. We focus on the nature of optical excitations at the interface, discussing the formation of hybrid electron-hole pairs.

[1] O. T. Hofmann, J.-C. Deinert, Y. Xu, P. Rinke, J. Stähler, M. Wolf, and M. Scheffler, J. Chem. Phys. **139**, 174701 (2013).

Towards disentangling charge-transfer excitations at the pentacene/C_{60} interface

Robin C. Döring[1], Andrea Karthäuser[1], Tobias Breuer[1], Gregor Witte[1], and Sangam Chatterjee[1,2]
[1]Faculty of Physics, Philipps-Universität Marburg, Germany
[2]Institute of Experimental Physics I, Justus-Liebig University Giessen, Germany
e-mail: sangam.chatterjee@physik.uni-giessen.de

Organic molecular solids feature various properties considered advantageous for next-generation photovoltaic devices such as mechanical flexibility and ease of fabrication by, e.g., large-scale printing. Additionally, they may feature Singlet-Exciton Fission, which allows surpassing the Shockley-Queisser limit. Here, one photoexcited singlet-type exciton splits into two triplet-type excitons doubling the number of extractable charge carriers; for example, pentacene (PEN) –C_{60} heterojunctions may yield above-unity quantum efficiencies [1].

Here, we study the carrier dynamics at well-defined PEN-C_{60} interface model samples by time-resolved photoluminescence spectroscopy experiments for different excitation photon energies. Thereby, we disentangle charge transfer and excitation dynamics, i.e., injection, transport, dissociation, and extraction.

The photoluminescence spectra reveal two distinct transition energies associated with charge-transfer states expected from photoelectron spectroscopy experiments [2]. Additionally, the C_{60} photoluminescence efficiency strongly quenches for increasing PEN coverage while the lifetime is drastically enhanced yielding strong evidence for an electron transfer between the PEN ground and C_{60} when only the latter is photoexcited.

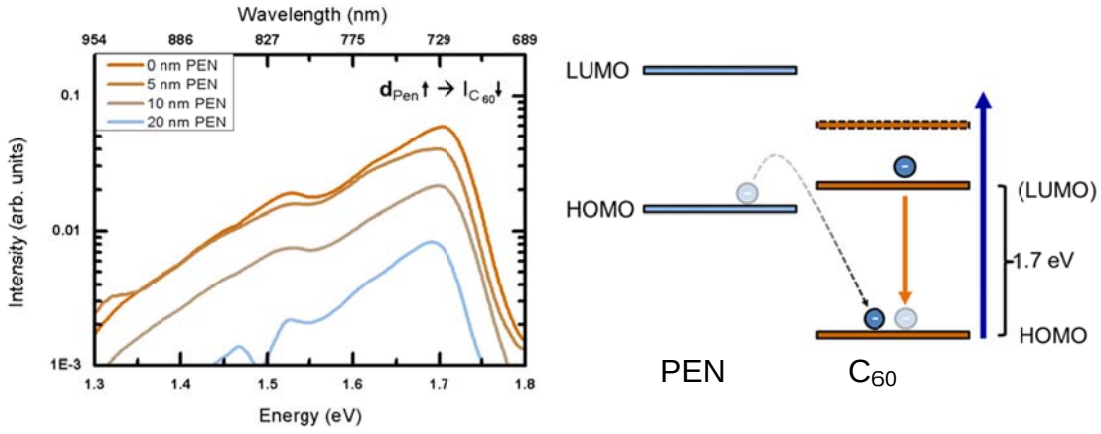


Fig. 1: Photoluminescence efficiencies for different pen coverages of bulk crystalline C_{60} (l.h.s.) and proposed electron-transfer mechanism at the PEN-C_{60} interface.

[1] D. N. Congreve et al., Science **340**, 334–337 (2013).
[2] I. Salzmann et al., J. Appl. Phys. **104**, 114518 (2008).

Unoccupied electronic structures of rubrene: from evaporated films to single crystals

T. Yamada and T. Munakata
Department of Chemistry, Osaka University, Japan
e-mail: munakata@chem.sci.osaka-u.ac.jp

Two-photon photoemission (2PPE) spectroscopy and ultraviolet photoemission spectroscopy (UPS) have been performed for rubrene single crystals and evaporated thin films on highly oriented pyrolytic graphite (HOPG). The 2PPE intensity from the single crystals changes by the polarization of the light and by the angle of the light incident plane against the crystalline axes. The changes indicate that the molecular arrangement on the surface is similar to that in the bulk crystal. On the other hand, in the case of evaporated films, the polarization dependence of 2PPE indicates that the tetracene backbone becomes standing upright as the thickness increases. In spite of the alignment of molecules, the broadened 2PPE spectral features for thick films suggest that the films are amorphous and molecules are in largely different environments. The film structures are confirmed by scanning tunneling microscopy (STM). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) derived levels of the single crystal are shifted by +0.18 and -0.20 eV, respectively, from those of the 0.8 ML film. The shifts are attributed to the packing density of molecules. It is shown that the unoccupied electronic structure is more sensitively affected by the film structure than the occupied electronic structure.

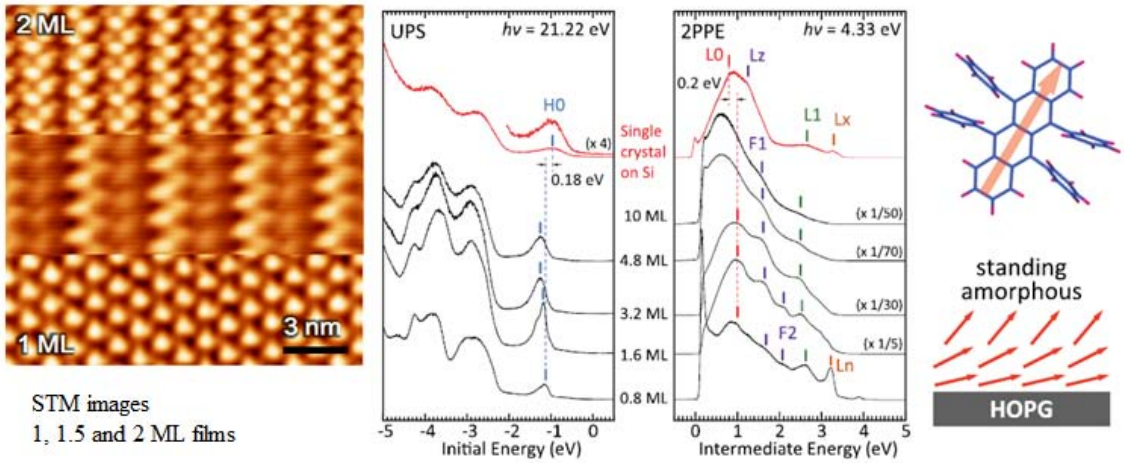


Fig.1 STM images (left), UPS and 2PPE spectra for films and crystals (middle). Schematics of the molecular arrangement (right).

Electron and exciton dynamics in sexithiophene on Au(111)

Cornelius Gahl[1], Wibke Bronsch[1], Sebastian Baum[1], Malte Wansleben[1,2], Kristof Zielke[1], and Martin Weinelt[1]
[1] Department of Physics, Freie Universität Berlin, Germany
[2] Present address: Physikalische Technische Bundesanstalt Institut Berlin, Germany
e-mail: c.gahl@fu-berlin.de

Sexithiophene (6T)/Gold is a model system for an organic semiconductor/metal interface. Exciton formation and relaxation as well as charge transfer processes across those interfaces are of high relevance in molecular electronics. The morphology of 6T films on Au(111) depends strongly on the preparation conditions. Adsorption at room temperature results in the formation of crystallites on top of a wetting layer. Starting from the optical properties of 1 to 10 monolayers 6T on Au(111) investigated by differential reflectance spectroscopy (DRS), we used time-resolved two-photon photoelectron spectroscopy (2PPE) to study the electron and exciton dynamics upon excitation at photon energies in the range of the S1 absorption band. For the wetting layer and the 6T crystallites different excitation and relaxation pathways can be distinguished.

Influence of the interface state on charge transfer processes at well-defined metal/organic interfaces

A. Lerch[1], J. Zimmermann[1], A. Namgalies[1], F. Schiller[1,2], U. Höfer[1]
[1] *Department of Physics, Philipps-Universität Marburg, Germany*
[2] *Centro de Física de Materiales San Sebastian, Spain*
e-mail: alexander.lerch@physik.uni-marburg.de

The charge carrier transport across metal/organic and organic heterointerfaces was investigated by means of time-resolved two-photon photoemission (2PPE). We deposited thin layers of controlled thickness of titanylphthalocyanine (TiOPc), copper(II)phthalocyanine (CuPc) and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on an Ag(111) substrate as well-defined model systems for organic semiconductor heterolayer interfaces. An optical parametric oscillator (OPO) provided tuneable pump pulses with photon energies ranging from 1.6 to 2.5 eV while at the same time the probe photon energy stays constant.

The Shockley-type interface states of a monolayer of PTCDA/Ag(111) and TiOPc/Ag(111), located 0.6 eV and 0.3 eV above the Fermi level, are usually populated from the metal and show little dependence on excitation energy. For the heterosystems CuPc/PTCDA/Ag(111) and PTCDA/TiOPc/Ag(111) we find a strong resonant enhancement at 1.8 eV and 2.3 eV, respectively. Time-resolved measurements show a delayed filling of the interface states on the time scale of 50 fs for CuPc/PTCDA and 200 fs for PTCDA/TiOPc under these conditions, before the population relaxes by electron-hole-pair decay into the metal. Comparison with a bilayer of pure PTCDA/Ag(111) and TiOPc/Ag(111) reveal that these resonances are the result of a HOMO-LUMO excitation in the second or third layer followed by a fast electron transfer to the interface state. Our results highlight that metal/organic interface states, located between Fermi level and LUMO, directly contribute to charge separation and transfer between metals and organic semiconductors.

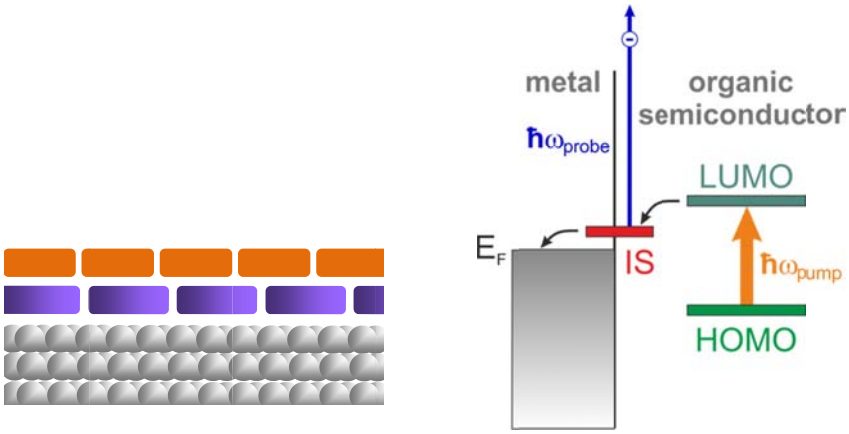


Fig. 1 Schematic illustration of a heterostructure (left) and selective excitation of the organic overlayer followed by charge transfer to the interface state and relaxation into the metal (right).

First-principles study of anthracene and pentacene adsorbed on coinage metal surfaces: the effects of the van der Waals interactions

Juliana M. Morbec and Peter Kratzer
Faculty of Physics, University of Duisburg-Essen, Germany
e-mail: juliana.morbec@uni-due.de

The adsorption of conjugated organic molecules on metal surfaces is a subject of intense interest because of the potential of such hybrid interfaces for a wide range of applications, including photovoltaics, field effect transistors and light emitting diodes. Although several works have been performed in the past years to investigate the adsorption of oligoacenes (particularly pentacene) on coinage metals, the effects of the van der Waals (vdW) interactions on the structural and electronic properties of those interfaces are not yet completely understood. In this work we carried out first-principles calculations based on density functional theory to study the adsorption of anthracene and pentacene on Ag(111). We employed both Tkatchenko-Scheffler (vdW-TS) [1] and many-body dispersion (vdW-MBD) [2,3] van der Waals methods, as well as the recently proposed self-consistent interatomic van der Waals functional [4], in order to investigate the anthacene/Ag(111) and pentacene/Ag(111) interfaces. Our results show that the adsorption energy is roughly proportional to the number of C atoms in these aromatic molecules. We also found that the vdW-MBD method renders a reduced adsorption energy (by about one third) compared to the vdW-TS method, while the adsorption height in vdW-MBD is slightly (by 0.05 Å) shorter. The agreement of the absorption energy in vdW-MBD with experiment is within 0.15 eV.

[1] Alexandre Tkatchenko and Matthias Scheffler, Phys. Rev. Lett. 102, 073005 (2009).
[2] Alexandre Tkatchenko, Robert A. DiStasio, Jr., Roberto Car, and Matthias Scheffler, Phys. Rev. Lett. 108, 236402 (2012).
[3] Alberto Ambrosetti, Anthony M. Reilly, Robert A. DiStasio Jr. and Alexandre Tkatchenko, J. Chem. Phys. 140, 18A508 (2014).
[4] Nicola Ferri, Robert A. DiStasio, Jr., Alberto Ambrosetti, Roberto Car, and Alexandre Tkatchenko, Phys. Rev. Lett. 114, 176802 (2015).

Spin filtering at a Bi superstructure on Au(111) interface

Sebastian Jakobs[1], Dominik Jungkenn[1], Christian Tusche[2], Jürgen Kirschner[2], Benjamin Stadtmüller[1], Mirko Cinchetti[1], and Martin Aeschlimann[1], Stefan Mathias[3]

[1] Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern, Germany
[2]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 062120 Halle/Saale, Germany
[3]I. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
e-mail: smathias@uni-goettingen.de

Spin-dependent scattering of electrons at interfaces is one of the most relevant microscopic processes that determine for instance the performance of spintronics devices. However, the scattering process itself is hard to address experimentally. Here, we use spin-resolved momentum microscopy to investigate the scattering of photoelectrons at a Bi superstructure on Au(111). We find that photoelectrons, originating from a resonant bulk transition in the Au(111) substrate, experience a spin-dependent scattering in the Bi while travelling to the surface. These elastic scattering processes are induced by the reduced Brillouin zone size of the Bi superstructure. Using a scattering model based on spin-orbit coupling, we are able to model the observed spin texture and find that the Bi overlayer acts as a spin filter for the photoelectrons stemming from Au(111). Moreover, the observed spin texture depends strongly on the direction and even on the number of scattering events in the Bi superstructure (see Fig. 1). Hence, the Bi/Au(111) interface constitutes a simple model system to understand spin-dependent electron scattering processes on a microscopic level.

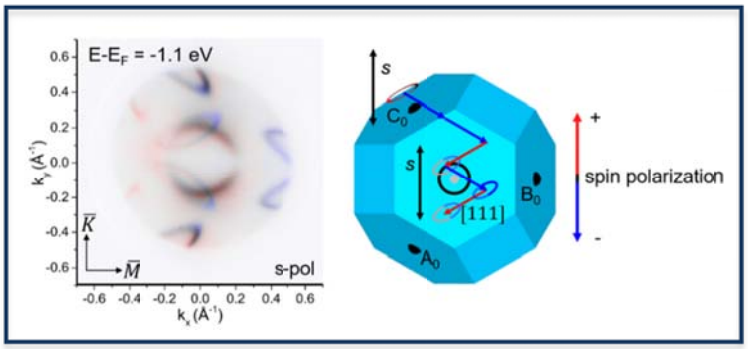


Fig. 1: Spin-resolved constant binding energy map (left) and corresponding schematic of the scattering model (right).

Oral Abstracts Friday

Dynamic transport of quantum clusters

M. Kira[1], U. Huttner[1], J. T. Steiner[1], M. Mootz[1], O. Vänskä[1], S.W. Koch[1], F. Langer[2], M. Hohenleutner[2], C. Schmid[2], C. Poellmann[2], P. Nagler[2], T. Korn[2], C. Schüller[2], O. Schubert[2], M. Knorr[2], M.S. Sherwin[3], C. Lange[2], and R. Huber[2]

[1] *Department of Physics & Material Sciences Center, University of Marburg, Germany*

[2] *Department of Physics, University of Regensburg, Germany*

[3] *Department of Physics and the Institute for Terahertz Science and Technology, University of California at Santa Barbara, USA*

e-mail: mackillo.kira@physik.uni-marburg.de

Most dramatic advancements in nanoscience can be realized by optimizing individual quantum processes and by adding new processes to the design repertoire. We briefly overview a realistic first-principles many-body theory [1] that includes interactions by rigorously identifying particle clusters participating in diverse quantum processes. The approach can be applied to study a great variety of experimentally relevant phenomena.

As an illustration, we discuss how electrons, excitons, and correlations [2] can be transported through semiconductor interfaces using well-designed sequences of terahertz (THz) pulses. In a two-dimensional electron gas, magnetic field creates Landau levels which, according to the Kohn's theorem, behave linearly even under strong electron-electron interaction. Nevertheless, we demonstrate that a combination of electron-ion and electron-electron interaction yields strong nonlinear THz wave-mixing signatures [3]. We also consider how strong THz fields induce an interplay of interband polarization and intraband currents during high-harmonic generation [4] (HHG) and electronic quantum interference yielding a massive reshaping of the time-resolved harmonic emission [5]. We also discuss how a combination of optical and THz pulses can be applied to realize a quasiparticle collider [6]. Besides these semiconductor examples, our approach works extremely well also in other many-body systems, as shown by a quantitative analysis of strongly interacting Bose-Einstein condensates [7].

[1] M. Kira and S. W. Koch, *Semiconductor Quantum Optics*, (Cambridge, 2011).

[2] O. Vänskä, I. Tittonen, S.W. Koch, and M. Kira, *Coherent terahertz control of vertical transport in semiconductor heterostructures*, PRL **114**, 116802 (2015).

[3] T. Maag *et al., Coherent cyclotron motion beyond Kohn's theorem*, Nat. Phys. **12**, 119 (2016).

[4] O. Schubert *et al., Sub-cycle control of terahertz high-harmonic generation by dynamical Bloch oscillations*, Nat. Photon. **8**, 119 (2014).

[5] M. Hohenleutner *et al., Real-time observation of interfering crystal electrons in high-harmonic generation*, Nature **523**, 572 (2015).

[6] F. Langer, M. Hohenleutner, C. Schmid, C.Poellmann, P. Nagler, T. Korn, C. Schüller, M. S. Sherwin, U. Huttner, J. T. Steiner, S. W. Koch, M. Kira, and R. Huber, *Lightwave-driven quasiparticle collisions on a sub-cycle timescale*, accepted for publication.

[7] M. Kira, *Coherent quantum depletion of an interacting atom condensate*, Nat. Comm. **6**, 6624 (2015).

GaP-on-Si(100) heterointerfaces studied *in situ*

O. Supplie[1-3], S. Brückner[1,2], MM. May[1-3], P. Kleinschmidt[1], A. Nägelein[1], A. Paszuk[1], O. Romanyuk[4], F. Grosse[5], and T. Hannappel[1,2]

[1] *TU Ilmenau, Institute of Physics, Department of Photovoltaics, Ilmenau, Germany*
[2] *Helmholtz-Zentrum Berlin, Institute for Solar Fuels, Berlin, Germany*
[3] *Humboldt-Universität zu Berlin, Institute of Physics, Berlin, Germany*
[4] *Institute of Physics, Academy of Sciences of the Czech Republic, Prague*
[5] *Paul-Drude Institut für Festkörperelektronik, Berlin, Germany*
e-mail: thomas.hannappel@tu-ilmenau.de

Pseudomorphic GaP/Si(100) is considered as generic quasisubstrate for high-efficiency III/V-on-Si devices desired in optoelectronics and energy conversion [1]. The entire growth process—Si(100) surface preparation, initial GaP nucleation, GaP epilayer growth, GaP/Si(100) surface preparation—must be controlled precisely, preferably at the atomic scale, in order to get high-grade material. Here, we give an overview on how we combine optical *in situ* spectroscopy (reflection anisotropy spectroscopy, RAS) during industrially scalable growth processes by metalorganic vapor phase epitaxy (MOVPE) with electron-based *in vacuo* surface science analytics via a contamination-free MOVPE-to-UHV transfer [2] in order to study the GaP/Si(100) heterointerface formation and its atomic structure. We revealed a kinetically driven Si(100) surface formation and *in situ* control enabled the preparation of almost single-domain, monohydride-terminated Si(100) surfaces [3], which are essential to avoid antiphase disorder in subsequently grown GaP epilayers [4]. Time-resolved RA measurements enable to monitor the nucleation process *in situ* and a characteristic RA spectrum can be attributed to a dielectric anisotropy arising at the heterointerface [5]. With X-ray photoelectron spectroscopy (XPS), we estimate that the heterointerface constitutes of roughly one monolayer of Si-P bonds [5]. The measured GaP sublattice orientation agrees with the one expected for abrupt Si-P interfaces, which are (according to DFT) energetically favored over abrupt Si-Ga interfaces [6]. The GaP sublattice can be inverted by a ‘rotation’ of the Si dimers prior nucleation or more Ga-rich reactor conditions [6]. Regarding further III/V integration, the impact of As on the Si surface as well as GaP nucleation is investigated and single-domain GaP/Si(100):As surfaces are demonstrated [7]. The presence of As causes a more complex structure of the heterointerface and enables control over the GaP sublattice orientation both on Si(100) [7] and on Si(111) [8].

[1] Hu et al., *EES* **6**:2984, 2013; May et al., *Nat. Commun.* **6**:8286, 2015.
[2] Hannappel et al., *RSI* **75**:1297, 2004; Aspnes and Studna, *PRL* **54**:1956, 1985.
[3] Brückner et al., *PRB* **86**:195310, 2012; *NJP* **15**:113049, 2013.
[4] Döscher et al. *APL* **93**:172110, 2008; Krömer, *JCG* **81**:193, 1987.
[5] Supplie et al. *JPC Lett.* **6**:464, 2015; *PRB* **86**:035308, 2012.
[6] Supplie et al. *PRB* **90**:235301, 2014; *ACS Appl. Mater. Interfaces* **7**:9323, 2015.
[7] Supplie et al. *APL Mater.* **3**:126110, 2015.
[8] Paszuk et al. *APL* **106**:231601, 2015.

Ultrashort acoustic pulses generated at buried GaP/Si interfaces

K. Ishioka[1], A. Rustagi[2], A. Beyer[3], W. Stolz[3], K. Volz[3], U. Höfer[3], H. Petek[4], C. J. Stanton[2]
[1]*National Institute for Materials Science, Tsukuba, Japan*
[2]*Department of Physics, University of Florida, Gainesville, USA*
[3]*Material Sciences Center and Faculty of Physics, Philipps-University, Germany*
[4]*Department of Physics and Astronomy, University of Pittsburgh, USA*
e-mail: ISHIOKA.Kunie@nims.go.jp

Absorption of an ultrashort laser pulse at a solid surface can lead to the generation of coherent acoustic phonons in the form of a ballistically propagating strain pulse. Coherent acoustic phonons in semiconductor heterostructures are of particular interest because one can design the heterostructures to generate intense phonons with high frequencies (> 1 THz). In the present study we investigate the coherent acoustic phonons at a buried GaP/Si(001) interface. Lattice-matched GaP layers of different thicknesses L are grown on the Si(001) substrates by metal organic vapor phase epitaxy. Pump-probe reflectivity measurements are performed in near back-reflection configuration using laser pulses with 10 fs duration and 3.1-eV photon energy. The pump laser pulse creates strain pulses at the GaP/Si interface, one of which propagates into the GaP film and the other into the Si substrate [Fig. 1]. The reflectivity changes ΔR/R exhibit ultrashort (< 1ps) kinks indicated by arrows in Fig. 2. These kinks correspond to the arrival of one of the strain pulses at the GaP/air surface. The observations indicate the sensitivity of our reflectivity measurements to the surface, despite the optical penetration depth being larger than the GaP film thicknesses L. ΔR/R also shows a quasi-periodic modulation on a picosecond time scale [Fig. 2] due to the Fabry-Perot-type interference from the propagating strain pulses in the GaP film and Si substrate.

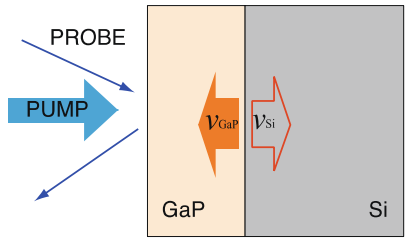


Fig. 1 Schematic of the pump-probe experiments. The pump pulse creates acoustic phonons at the GaP/Si interface propagating in both GaP and Si directions. Phonons arriving at GaP surface give rise to pulse-like response in the reflectivity change ΔR/R.

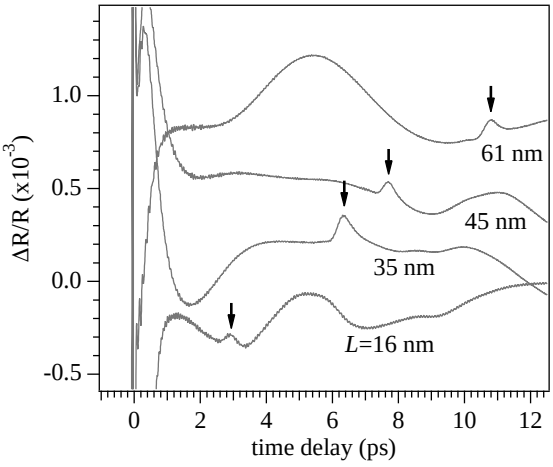


Fig. 2 Reflectivity changes of the GaP films of different thicknesses L on Si(001) substrates.

Ultrafast coherent optical phonon probing of electronic properties of surfaces and interfaces

Avinash Rustagi[1], Christopher J. Stanton[1], Kunie Ishioka[2], Andreas Beyer[3], Wolfgang Stolz[3], Kerstin Volz[3], Ulrich Höfer[3], and Hrvoje Petek[4]
[1]Department of Physics, University of Florida, Gainesville, FL 32611, USA
[2]National Institute for Materials Science, Tsukuba, 305-0047 Japan
[3]Material Sciences Center and Faculty of Physics, Philipps-University, Germany
[4]Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh,
e-mail: stanton@phys.ufl.edu

The coherent many-body interaction between the lattice vibrations and the nonequilibrium electron-hole plasma can provide a detailed understanding of the fundamental electronic, optical and transport properties of polar semiconductors and their devices. Coherent phonon spectroscopy allows one to *all-optically* probe the surface and interface *electronic fields* and *band structures*. We present a joint experimental and theoretical study on the coupled plasmon-phonon modes in bulk GaAs [1], GaP [2] as well as GaP films grown on a Si(001) substrate [3]. We perform pump-probe reflectivity measurements using laser pulses with 10-fs width and 400-nm wavelength to photoexcite and probe within 100 nm from the surface. The laser pulses excite electrons predominately in the L valley in GaAs and in the X valley in GaP, both of which are heavily damped. The nonuniform carrier distribution within the laser spot leads to a time-dependent phonon frequency (Fig. 1). For the GaP films on Si(001), we find that the coherent phonon *amplitude* critically depends on the film growth conditions, particularly on the presence or absence of antiphase domains. The phonon amplitude can be interpreted in terms of the magnitude of internal electric fields, which vary with the morphology of the antiphase boundaries within the nominally undoped GaP films.

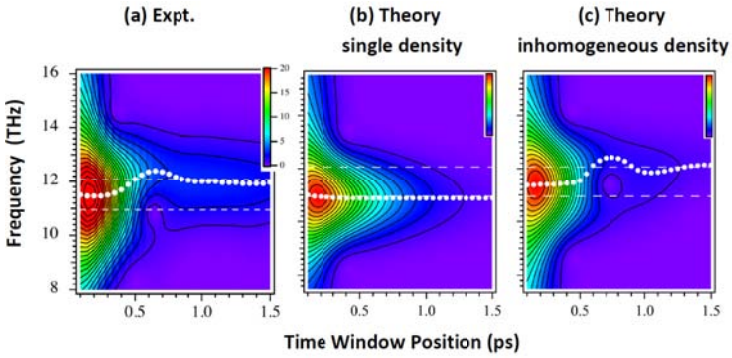


Fig. 1: Time-windowed FT amplitudes of the reflectivity oscillations of GaP as functions of time window position and frequency for (a) experimentally measured signal, (b) theoretical calculation for a homogeneous density within the laser spot and (c) theoretical calculation for a laterally inhomogeneous density.

Supported by the National Science Foundation through DMR- 1311845, and DMR-1311849.

[1] *Phys. Rev. B* 91, 125201 (2015).
[2] *Phys. Rev. B* 92, 205203 (2015).
[3] *Appl. Phys. Lett.* 108, 051607 (2016).

Realization of interface-dominated type-II-(GaIn)As/Ga(AsSb)/(GaIn)As "W"-quantum well lasers in the near infrared emission wavelength range on (001) GaAs-substrate

C. Fuchs[1], C. Berger[1], C. Möller[1], M. Weseloh[1], S. Reinhard[1], A. Ruiz Perez[2], J. Hader[3], J.V. Moloney[3], A. Beyer[1], K. Volz[1], S.W. Koch[1], W. Stolz[1]

[1] Material Sciences Center & Faculty of Physics, Philipps-University, 35032 Marburg, Germany
[2] NAsP III/V GmbH, D-35041 Marburg, Germany
[3] Nonlinear Control Strategies Inc., Tucson, Arizona 85704, USA
e-mail: wolfgang.stolz@physik.uni-marburg.de

Highly efficient interface-dominated lasers in the near-infrared regime based on the type-II band alignment in (GaIn)As/Ga(AsSb)/(GaIn)As single "W"-quantum wells on (001) GaAs-substrate are verified. The structure is designed by applying a full microscopic theory, realized by employing metal organic vapor phase epitaxy, and characterized using electroluminescence measurements as well as broad-area and vertical external cavity surface-emitting laser (VECSEL) studies.

The characteristic blue shift with increasing charge carrier density of type-II material systems is observed and compared to theoretical investigations. Low threshold current densities of 0.4 kA/cm^2, high differential efficiencies of 66 %, pump-power limited optical output pulse powers of 1.4 W per facet, and internal losses of only 1.7 cm^{-2} are observed at a wavelength of 1.16 μm for broad-area lasers under pulsed operation at room temperature. No indication for type-I-related transitions for injection current densities up to 4.5 kA/cm^2 is observed. In addition, the first successful realization of multi-Watt output power type-II-VECSEL structures with maximum output power of 4 W clearly point to the potential for applications of this novel laser structures with optimized design of the active (GaIn)As/Ga(AsSb)/(GaIn)As "W"-quantum wells.

Detailed quantitative atomic-scale chemical analysis of the actually grown laser structures in particular of the interface configurations applying sophisticated high-angle annular dark field scanning transmission electron microscopy (HAADF)-STEM techniques forms the basis for additional future improvements in these novel interface-dominated laser structures.

Electron diffusion in Ni studied with time-resolved X-ray diffraction

Anna I. H. Persson[1], Amélie Jarnac[1], Xiaocui Wang[1], Henrik Enquist[2], Andrius Jurgilaitis[2], Jörgen Larsson[1,2]
[1] Department of Physics, Lund University, Lund, Sweden
[2] MAX IV Laboratory, Lund University, Lund, Sweden
e-mail: anna.persson@fysik.lth.se

We present a novel method for studying electron diffusion by probing the strain transmitted from a metal film. A 150 nm thick Ni-film was coated on a bulk InSb sample. It was laser-excited with an 800 nm, 50 fs laser pulse. This lead to heating of the top layer of the metal, which leads thermal expansion, stress and finally generation of a propagating strain pulse [1]. The strain pulse travels through the film into the InSb, where it is detected with time-resolved x-ray diffraction. The shape of the strain pulse is sensitive to how far the electrons diffuse into the film before the electron-phonon system reaches equilibrium. The laser radiation only excites the first tens of nanometres of the metal film, so all strain measured in InSb originates from Ni. The first change in x-ray intensity is related to the shape of the strain pulse. By comparing to simulations carried out with the two-temperature model the electron diffusion properties of Ni could be accessed. It was found out that the electron-phonon coupling constant was lower than the previously known value for the bulk. Data is seen in Fig. 1.

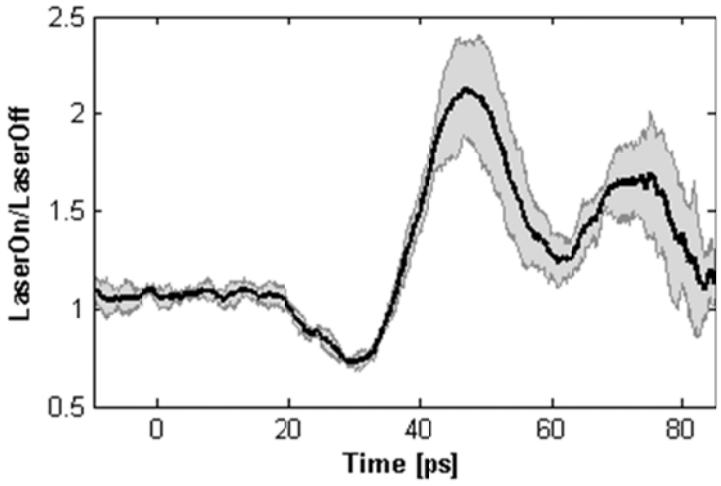


Fig. 1 X-ray intensity variations in InSb due to strain generated in an overlying Ni-film.

[1] C. Thomsen, H. T. Grahn, H. J. Maris, and J. Tauc, 'Surface Generation and Detection of Phonons by Picosecond Light Pulses', *Physical Review B*, 34 (1986), 4129-38.

Topological states at semiconductor interfaces: a view from first principles

Friedhelm Bechstedt
Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Germany
e-mail: bechsted@ifto.physik.uni-jena.de

By means of modern electronic structure calculation methods we investigate topological states at interfaces between topological and trivial insulators. Combinations of the zero-gap semiconductors HgTe and grey tin with the wide-gap semiconductor CdTe to quantum-well structures with (001) and (110) interfaces are studied [1,2]. The localization at interfaces, symmetry protection, linear k-dispersion, and spin polarization of the topological interface states are studied (see Fig.1). We demonstrate the central role of spin-orbit interaction and resulting band inversion in HgTe and alpha-tin for the occurrence of the quantum spin Hall phase by topological invariants [3] and band crossing versus the thickness of quantum wells [1, 2]. Critical distances between the two interfaces of about 5 nm for the topological transition in the HgTe case are increased in the Sn case [1, 4]. Above the critical film thickness Dirac cones and topological states appear for all interfaces, except the Sn/CdTe(110) one [4]. The reasons are the strong ionic interface bonds resulting in strong in-plane electric fields. We discuss the detection and the dimensionality of the topological interface states [1] observed in recent experiments [5].

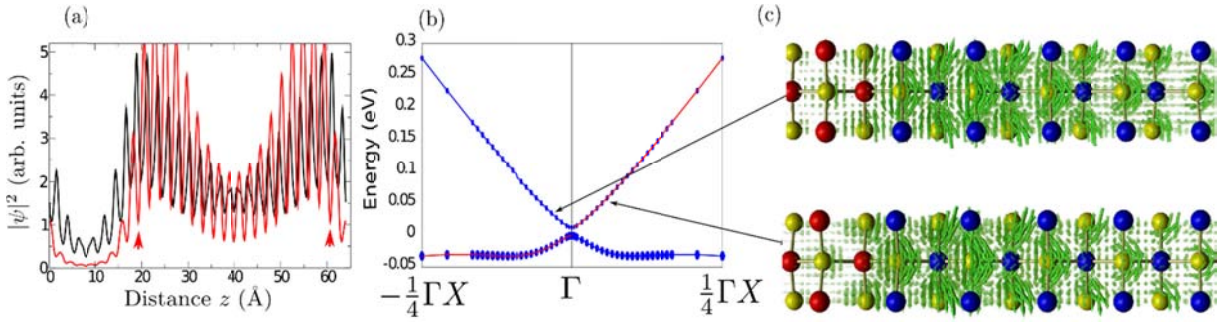


Fig. 1 (a) Wave-function localization, (b) band dispersion, and (c) spin polarization of topological states at HgTe/CdTe interface

[1] S. Küfner and F. Bechstedt, Phys. Rev. B 89, 195312 (2014); 93, 045304 (2016).
[2] S. Küfner et al., Phys. Rev. B 90, 125312 (2014).
[3] L. Matthes et al., Phys. Rev. B 93, 121106(R) (2016).
[4] S. Küfner et al., Phys. Rev. B 91, 035311 (2015).
[5] M. König et al., Science 318, 766 (2007); A. Roth et al., Science 325, 294 (2009).

Poster abstracts – Session I

Band offsets in cubic GaN/$Al_xGa_{1-x}N$ heterostructures

M. Landmann, E. Rauls, and W.G. Schmidt
Theoretische Physik, Universität Paderborn, Paderborn, Germany
e-mail: landmann@mail.uni-paderborn.de

The band offsets in cubic GaN/$Al_xGa_{1-x}N$ heterostructures are determined by hybrid functional based density functional theory within the whole composition range extending preceding studies on binary cubic GaN/AlN superlattices [1] towards the band alignment with ternary cubic $Al_xGa_{1-x}N$ alloys. [2]

The band alignment at cubic GaN/$Al_xGa_{1-x}N$ heterojunctions shows a type-I alignment with a valence band offset (VBO) changing almost linear with increasing composition parameter x. The fundamental conduction band offset (CBO) exhibits a discontinuity due to the direct-indirect band gap crossing in cubic $Al_xGa_{1-x}N$ alloys (see Ref. [2]). Below the critical crossover composition, the fundamental CBO increases continuously with Al content. Within the Al-rich composition regime the quasi-indirect alloy-band gap slightly reduces the fundamental CBO.

Upper and lower boundaries for band discontinuities in strained cubic GaN/$Al_xGa_{1-x}N$ quantum-well heterostructures are determined.

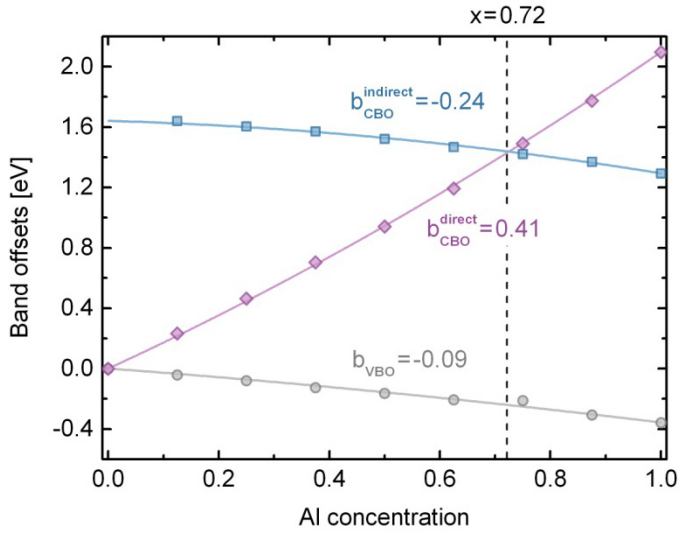


Fig. 1 Valence and conduction band offsets in cubic GaN/$Al_xGa_{1-x}N$ heterostructures

[1] M. Landmann et al., *Band offsets in cubic GaN/AlN superlattices*, Phys. Rev. B **83**, 195301 (2011)
[2] M. Landmann et al., *Transition energies and direct-indirect band gap crossing in zinc-blende $Al_xGa_{1-x}N$*, Phys. Rev. B **87**, 195210 (2013)

3D investigation of InGaN nanodisks in GaN nanowires

Katharina I. Gries[1], Julian Schlechtweg[1], Andreas Beyer[1], Pascal Hille[2], Jörg Schörmann[2], Martin Eickhoff[2], Kerstin Volz[1]

[1] *Faculty of Physics and Materials Science Center, Philipps-Universität Marburg, Germany*
[2] *I. Physikalisches Institut, Justus-Liebig-Universität Gießen, Germany*
e-mail: katharina.gries@physik.uni-marburg.de

Nanoscaled structures like nanowires (NWs) can influence device characteristics (e.g. higher internal efficiency [1]), making them very suitable for the application in optoelectronic devices. Complex structures like InGaN nanodisks (NDs) embedded in GaN NWs can for example be used as active regions of tunable color and white light LEDs [2,3]. Transmission electron microscopy (TEM) analyses of such InGaN/GaN NWs were reported in [4]. There it was shown that the ~4nm thick InGaN NDs exhibit a truncated pyramidal shape consisting of a (0001) central facet that is delimited by declining sixfold {10-1*l*} facets, where *l* can be -1, -2 or -3. In addition to this declined facets a continuation of the (0001) central facet towards the m-plane sidewalls of the NWs could be observed but is not described in the published scanning TEM (STEM) images [4]. Since these images contain projected information they do not deliver knowledge on the real shape of the NDs.

To obtain a deeper insight into the three dimensional geometry of the embedded InGaN NDs electron tomography is the method of choice. To overcome the effect of missing wedge artifacts [5] and to improve the resolution the NWs were prepared in a special way that enables a tilt of +/-90° in TEM. A section through the middle of the reconstruction of a NW running parallel to the (11-20) plane (a-plane) shows two features. First the faceting of the InGaN NDs with an increased steepness of the inclination angle of the side facets for higher lying NDs can be observed. The inclination angle fits well to the above mentioned {10-1*l*} planes. Second the afore-noted split of NDs is visible. This is particularly interesting since the tomography reconstruction proved that this structure, which could be easily attributed to projection artifacts in conventional STEM images, is a real feature of the sample.

This example shows, that selecting a sample geometry which allows a tilt angle range as high as possible, is essential for obtaining the required resolution.

[1] D.J. Sirbuly et al., *J. Phys. Chem. B* **109** (2005) 15190-15213
[2] R. Armitage and K. Tsubaki, *Nanotechnology* **21** (2010) 195202-1-195202-7
[3] W. Guo et al., *Appl. Phys. Lett.* **98** (2011) 193102-1-193102-3
[4] Th. Kehagias et al., *Nanotechnology* **24** (2013) 435702-1-435702-14
[5] I. Arslan et al., *Ultramicroscopy* **106** (11-12) (2006) 994-1000

We acknowledge support of the German Science Foundation (DFG) in the framework of the Collaborative Research Centre “Structure and Dynamics of Internal Interfaces” (SFB 1083)

Correlation of interface morphology and composition in GaInP/GaAs with growth conditions

Han Han[1], Andreas Beyer[1], Jürgen Belz[1], Alexander König[1,2], Wolfgang Stolz[1], Kerstin Volz[1]

[1] Philipps-Universität Marburg, Faculty of Physics and Materials Science Center, Hans-Meerwein-Str. 6, 35032 Marburg, Germany

[2] present address: Center for Tumor Biology and Immunology, Philipps-Universität Marburg, Germany

e-mail: han.han@physik.uni-marburg.de

Ternary (GaIn)P materials systems grown on GaAs have attracted a lot of attention for laser applications, especially due to the low recombination velocities at the interface [1]. The physical properties of the interface are greatly influenced by the interface morphology, which can be controlled by either the growth temperature or growth interruptions or the introduction of interlayers, consisting e.g. of GaP. The interface morphologies of the semiconductor quantum wells (QW) can be characterized by the quantitative evaluation of high resolution high angle annular dark field (HAADF) images in scanning transmission electron microscopy (STEM). In the present work, quantitative evaluation of HAADF imaging in STEM is used to correlate the interface morphology and composition in (GaIn)P grown on GaAs with the growth conditions.

The (GaIn)P/GaAs QWs were grown with metal organic vapor phase epitaxy (MOVPE) on GaAs (001) substrate at temperatures of 525°C and 625 °C, respectively, with different growth interruption times with or without GaP interlayer. In order to be able to compare different samples, a carefully applied method to gain reliable results from high resolution STEM micrographs was used. Also, to derive the chemical composition maps, the chemical sensitive background intensity is subtracted after image normalization. From the composition maps, the interface features are revealed and then correlated with the growth conditions. The growth interruptions can significantly affect the composition fluctuation and the interface morphology. At higher temperature of 625 °C, with the two GaP monolayers between (GaIn)P and GaAs substrate, shorter growth interruption time leads to intermixing at the interface while a longer growth interruption results in a sharp interface. Also, without the GaP buffer layer, platelet islands can be observed at the interface. At lower temperature of 525 °C the GaP buffer layer has less influence. Hence, the quantitative evaluation of HAADF STEM images can reveal the interface morphologies, which also have important influence on the optoelectronic properties.

[1] J.M. Olson, R.K. Ahrenkiel, D.J. Dunlavy, B. Keyes and A.E. Kibbler, Appl. Phys. Letters 55 (1989)

GaP-interlayer formation on epitaxial GaAs(100) surfaces in MOVPE ambient

Henning Döscher, Philip Hens, Andreas Beyer, Kerstin Volz, and Wolfgang Stolz
Materials Science Center and Department of Physics, Philipps-Universität Marburg, Germany
e-mail: henning.doescher@physik.uni-marburg.de

Thinnest gallium phosphide (GaP) layers embedded in GaAs-based epitaxial films may influence the interface formation in heterostructures or act as effective diffusion barriers (for dopants etc.) protecting crucial layers integral to the function of complex device structures. Ideal interlayers might consist of just a singular monolayer (ML) of the embedded material abruptly confined within the host matrix, but in practice these interlayers will smear out with the host material. This disorder is driven by a multitude of fundamental and practical factors limiting the sharpness of epitaxial III-V hetero-interfaces such as (a) roughness of the growth surface, (b) vertical extent of the present surface reconstruction, (c) finite exchange rate of process and precursor gases, (d) background ambient of the growth environment, and (e) thermal inter-diffusion. In this study, we investigate preparation strategies for different GaAs(100) surface reconstructions and their stability in MOVPE ambient with respect to the formation of sharp functional hetero interfaces and interlayers.

We deposited thinnest GaP-interlayers periodically in a GaAs matrix and determined the effective layer thickness and the actual ternary compositions based on high-resolution X-ray diffraction (HR-XRD) and scanning transmission electron microscopy (STEM) analysis in dependence of different gas-source switching sequences in an MOVPE reactor ambient. *In situ* reflection anisotropy spectroscopy (RAS) monitored the GaAs surface reconstruction preceding the GaP interlayer deposition and provided important insight for sharper interface preparation strategies. In effect, we obtain ternary Ga(AsP) interlayers with peak concentrations way below unity P-content, extending over several ML instead. In particular, the c(4x4) GaAs standard growth surface terminates with two ML of As usually maintained by an explicit overpressure in the gas phase at elevated temperature. Better preconditions to embed sharp interlayers of another group V species such as P might be obtained by a growth interruption also avoiding any group-V-stabilization. Our *in situ* results indicate that obtaining explicitly Ga-rich surface reconstructions requires thermal annealing at significantly higher temperature to induce the required removal of As from the surface. We also investigated an alternative preparation approach by a group III prepulse. Remarkably, transient RAS measurements shows rather quick decay of the Ga-rich (4x2) surface reconstruction towards the more As-rich (2x4) surface in the absence of intentional As flow indicating significant supply of As_4 from the MOVPE ambient. In close correlation between *in situ* surface analysis (by RAS) and *ex situ* structural characterization on both global (by HR-XRD) and microscopic scale by (STEM), we obtained quantitative insight into GaP or Ga(PAs)-interlayer characteristics in dependence of different MOVPE preparation strategies.

Interface analysis on MOVPE grown InP-GaInAs-InP double hetero structures for application in infrared solar cells

Anja Dobrich[1], K. Schwarzburg[2], T. Hannappel[1]
[1] *Department of Physics, Technische Universität Ilmenau, Germany*
[2] *Nano-architectures for Energy Conversion, Helmholtz-Zentrum Berlin, Germany*
e-mail: anja.dobrich@tu-ilmenau.de

We investigate the $Ga_{0.47}In_{0.53}As$ to InP interface with respect to their charge carrier lifetimes, interface recombination velocity and lateral interface homogeneity. Therefore we test different metal organic vapor phase epitaxy (MOVPE) preparation routes for the critical GaInAs/InP interface, which is a crucial part of the tunnel junction in an InP-based GaInAs/GaInAsP tandem solar cell in order to grow it as sharp as possible. Especially group III- and group V-rich variations of the interface preparation have been applied. A specific, III-rich GaInAs termination was found to be the most favorable starting point for the GaInAs/InP interface formation [1]. Since both the lifetime of the minority carriers within the absorber layers and the recombination at the interface have a fundamental impact on the allover performance of the solar cell, we studied the minority carrier lifetime with spatially resolved and time resolved photoluminescence (TRPL) in a corresponding lattice matched InP/GaInAs/InP double hetero structure using a confocal single photon counting setup. This is significant because the minority carrier lifetime is considered the most critical and variable parameter in photovoltaic (PV) materials, and is a key determining factor of a device's open-circuit voltage. Accurately measuring the bulk minority carrier lifetime is one of the greatest challenges in evaluating photoactive materials used in photovoltaic cells. Hence, TRPL is a smart approach to address layer- and interface quality without any sample post processing.

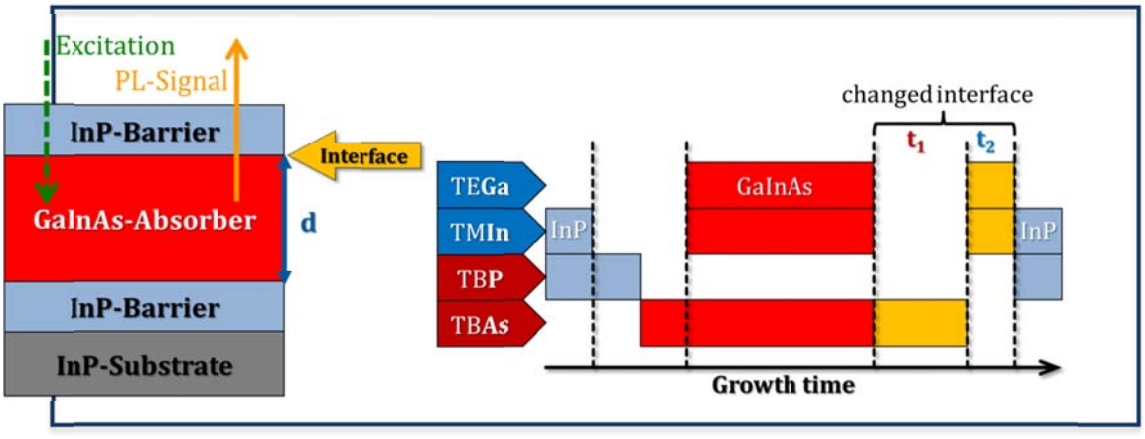


Fig. 1: DH-structure design (left). Gas switching sequences used for DH-structure growth (right).

[1] A. Dobrich; K. Schwarzburg, T. Hannappel; Solar Energy Materials & Solar Cells 148 (2016) 25.

Growth and characterization of (GaIn)As/Ga(AsSb)/(GaIn)As "W"-quantum well heterostructures for laser applications

C. Fuchs[1], C. Berger[1], C. Möller[1], M. Weseloh[1], S. Reinhard[1], A. Ruiz Perez[2], J. Hader[3], J. V. Moloney[3], S. W. Koch[1], and W. Stolz[1,2]

[1] *Material Sciences Center and Department of Physics, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany*

[2] *NAsP$_{III/V}$ GmbH, Hans-Meerwein-Straße, 35032 Marburg, Germany*

[3] *Nonlinear Control Strategies, Inc., 7040 N Montecatina Drive, Tucson, Arizona 85704, USA*

e-mail: christian.fuchs@physik.uni-marburg.de

GaAs-based semiconductor laser technology has enabled the realization of highly efficient semiconductor lasers at important wavelengths such as 808nm and 980nm. However, its application in telecommunication systems has proven to be challenging. Even though novel GaAs-based material systems such as (GaIn)(NAs) and Ga(AsSb) were suggested as gain media for 1.3 µm emitters, current systems mostly employ InP-based technology. As a consequence, type-II band alignments were suggested in order to suppress Auger losses and to expand the wavelength regime that can be accessed using GaAs substrate.

The present work discusses the MOVPE growth of (GaIn)As/Ga(AsSb)/(GaIn)As/GaAs "W"-quantum well heterostructures ("W"-QWH) on GaAs substrate specifically designed for type-II heterostructure laser applications. Triethylgallium (TEGa) and trimethylindium (TMIn) are used as group-III precursors and triethylantimony (TESb) and tertiarybutylarsine (TBAs) as group-V precursors, respectively. The "W"-QWHs are grown under various growth conditions at 550 °C, systematically varying V/III- and V/V-ratios. High-resolution X-ray diffraction (HR-XRD) and photoluminescence (PL) spectroscopy are applied to identify the efficient Sb-incorporation up to 40 %, high quality interface formation and high luminescence efficiency.

Type-II (GaIn)As/Ga(AsSb)/(GaIn)As "W"-QWHs, specifically designed for high material gain, with PL emission wavelengths in the range of 1.2 µm to 1.47 µm have successfully been realized. First broad-area lasers at 1.2 µm exhibit threshold current densities down to 0.4 kA/cm² with slope efficiencies up to 70 % and output powers up to 1.4 W under pulsed electrical injection. The spectral emission analysis verifies the type-II-transition as the laser transition for the entire emission power range. These characteristics clearly point out the high potential for applications of these novel type-II laser structures.

Type-II quantum well structures for interface-dominated lasers

C. Berger[1], M. Weseloh[1], C. Möller[1], C. Fuchs[1], A. Ruiz Perez[2], J. Hader[3], J. V. Moloney[3], N. W. Rosemann[1], J. Veletas[1], S. Chatterjee[1,4], W. Heimbrodt[1], W. Stolz[1,2], and S. W. Koch[1]

[1] *Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany*

[2] *NAsP$_{III/V}$ GmbH, Hans-Meerwein-Straße, 35032 Marburg, Germany*

[3] *Nonlinear Control Strategies, Inc., 7040 N Montecatina Drive, Tucson, Arizona 85704, USA*

[4] *I. Physikalisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 16, 35392 Gießen, Germany*

e-mail: christian.berger@physik.uni-marburg.de

e-mail: maria.weseloh@physik.uni-marburg.de

We present design, realization, and analysis of "W'-aligned type-II multi-quantum well heterostructures for use as active medium in lasers. Type-II systems are characterized by a spatial separation of electrons and holes in their respective quantum wells and therefore show emission caused by recombinations across an interface.

For our studies, we combine two semiconductor alloys with rather large band gap to achieve an emission wavelength in the near infrared. We arrange (GaIn)As/Ga(AsSb)/(GaIn)As in a "W" configuration of the conduction band on GaAs substrate as presented in Fig. 1. In our recent work we analyze experimental photoluminescence spectra to show type-II signatures and predict gain for this material system. A more thorough investigation comparing experiment and theory for photomodulated reflectance spectra confirms this results and emphasizes the recombination path through the interface between (GaIn)As and Ga(AsSb).

It is shown that the microscopic features of the interface strongly influence the material gain properties. The gain can be optimized by deliberate grading of the interfaces.

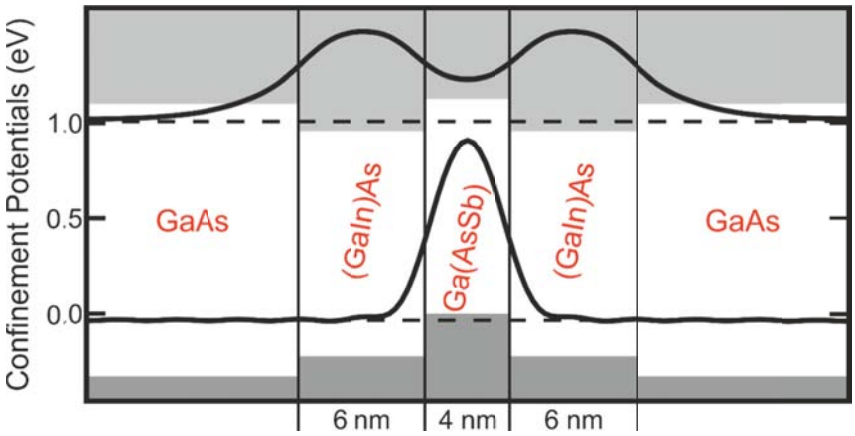


Fig. 1 Spatial confinement potential (shaded area) with energy levels (dashed lines) and wave functions (solid lines) for the first electronic state in valence and conduction band at 300 K.

Charge transfer luminescence in (GaIn)As/Ga(AsSb) and (GaIn)As/Ga(NAs) quantum wells

Sebastian Gies[1], Christian Berger[1], Phillip Springer[1], Christian Fuchs[1], Han Han[1], Antje Ruiz Perez[2], Nils W. Rosemann[1], Julian Veletas[1], Sangam Chatterjee[1], Wolfgang Stolz[1], Kerstin Volz[1], Stephan W. Koch[1], Jörg Hader[3], Jerome V. Moloney[3], and Wolfram Heimbrodt[1]

[1] Department of Physics and Materials Sciences Center, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

[2] NAsP$_{III/V}$ GmbH, Am Knechtacker 19, 35041 Marburg, Germany

[3]College of Optical Sciences, University of Arizona, Tucson, Arizona 85721, USA

e-mail: Sebastian.gies@physik.uni-marburg.de

Semiconductors with a type-II band alignment are a very important class of materials with a wide variety of applications ranging from optoelectronics to photonic devices. Especially for IR-lasers type-II heterostructures not only suppress the Auger losses, but also offer more freedom in device design. To achieve efficient device operation it is necessary to have exact knowledge of the band structure and the hetero-offsets between the different materials and the interface between the different materials. We present a comprehensive analysis of the luminescence of (GaIn)As/Ga(NAs) and (GaIn)As/Ga(AsSb) by means of experiment and fully microscopic theory in order to reveal the materials' band alignment and interface properties. The quantum wells under investigation were grown epitaxially via metal-organic vapor-phase epitaxy on GaAs-substrates. For interface modification a GaAs-interlayer between the electron- and the hole-confining material has been introduced. Using photoluminescence (PL) spectroscopy we can clerly identify the type-II transition. Furthermore, we used photomodulated reflectance spectroscopy to determine the energetic positions of ground and excited states in the respective quantum wells. The conjunction of experiment and theory enables us to precisely determine the hetero-offset between Ga(NAs) and GaAs and Ga(AsSb) and GaAs, respectively. This allows to produce an exact picture of the band structure and the wave functions responsible for the type-II luminescence. For the Ga(InAs)/Ga(NAs) material system the band structure resulting from our analysis is depicted in Fig. 1. The conduction band offset of the Ga(NAs)/GaAs-interface is 0.56 eV and the light hole valence band offset is 0.04 eV. Furthermore, it can be seen that the type-II PL results from the (e1-hh1) transition with the electron being confined in the Ga(NAs), while the first type-I luminescence is due to the e3-hh1 transition in the Ga(InAs).

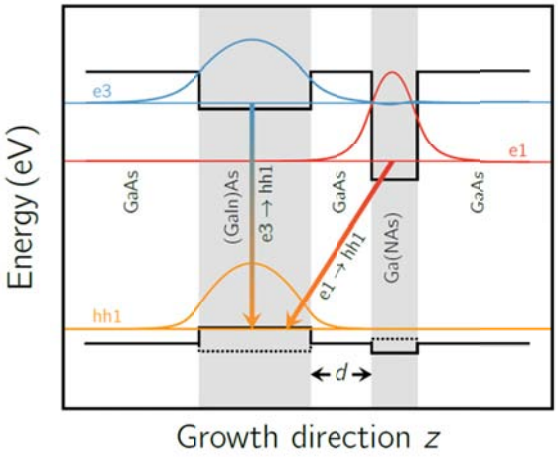


Fig. 2: Schematic depiction of the conduction band and valence band edge of the Ga(InAs)/Ga(NAs)-type-II material system. Also shown are the most important electron and hole wave functions and the resulting type-I and type-II transitions.

Excitonic transitions in type-II heterostructures

J. Veletas[1], S. Gies[1], C. Berger[1], N. W. Rosemann[1], C. Fuchs[1], P. Hens[1], A. Ruiz Perez[2], S. W. Koch[1], W. Stolz[1,2], W. Heimbrodt[1], and S. Chatterjee[1,3]

[1] *Department of Physics, Philipps-Universität Marburg, Germany*

[2] *NAsP$_{III/V}$ GmbH, Marburg, Germany*

[3] *I. Physikalisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 16, 35392 Gießen, Germany*

e-mail: julian.veletas@physik.uni-marburg.de

Heterostructures composed by inorganic semiconductor layers are the heart of today's advanced opto-electronic devices. Commonly, a type-I band alignment for direct-gap material are considered optimal for active devices such as semiconductor lasers. However, pushing the emission wavelength further into the infrared causes significant challenges regarding inherent loss mechanism such as intersubband absorption or enhanced Auger losses. An alternate extreme promising concept to circumvent many of these challenges the combination of multiple type-II transitions to form a structure called "W"-laser structure. The individual layers have large band gaps suppressing the loss channels; nevertheless, such structures offer significant oscillator strength and hence gain at energies below all fundamental band gap of the individual layers high despite the local type-II character. Here, the overall band alignment of the complex heterostructures needs to be considered. While the prototypical type-II heterointerfaces are GaAs/(Al,Ga)As superlattices, advanced combinations of inorganic III-V semiconductor compounds allow pushing the emission wavelength towards the mid-infrared.

Here, we study a series of (Ga,In)As/Ga(As,Sb) "W-structures" targeted as gain media in future laser applications. The multiple quantum well heterostructures are investigated by modulation spectroscopy to characterize the electronic transitions and explain the complex structure of electron and hole states.

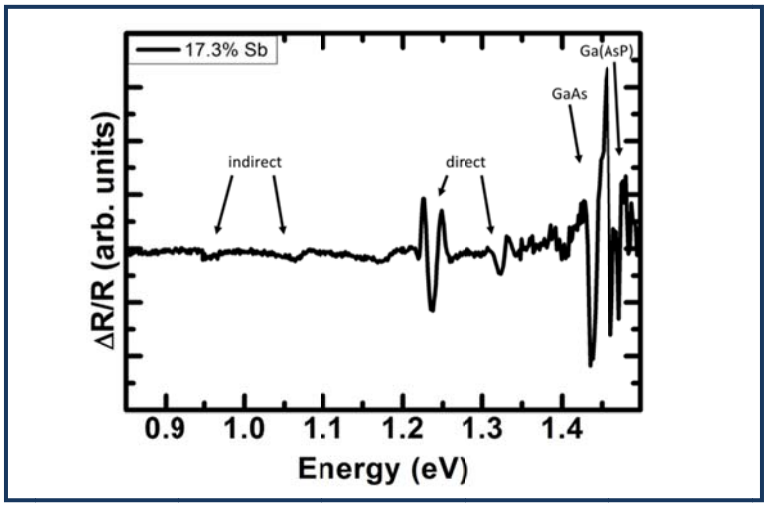


Fig. 1: Modulation spectra of the sample containing 17.3% Sb. Type-I and type-II transitions can be observed.

Time-resolved gain spectroscopy on type-I and type-II VECSEL chips

C. Lammers[1], M. Stein[1], M. Fey[1], C. Fuchs[1], C. Möller[1], A. Ruiz-Perez[2], C. Berger[1], A. Rahimi-Iman[1], J. Hader[3], J. Moloney[3], S.W. Koch[1], W. Stolz[1], and M. Koch[1]

[1] *Department of Physics, Philipps-Universität Marburg, Germany*

[2] *NAsP$_{III/V}$ GmbH, Germany*

[3] *College of Optical Sciences, University of Arizona, USA*

e-mail: christian.lammers@physik.uni-marburg.de

Theoretical as well as experimental gain in a near-infrared emitting type-II vertical-external-cavity surface-emitting-laser (VECSEL) consisting of GaAs/(GaIn)As/Ga(AsSb)/(GaIn)As/GaAs semiconductor heterostructures are presented. Time resolved gain spectroscopy in reflection geometry is used to obtain carrier dynamics, which is necessary to determine light amplification inside the chip. The recombination takes place across the interface in this laser medium. Gain is established for a timespan of 1.5 ns. The experimental results monitoring the development of gain in the laser chip are predicted by a fully microscopic approach using the semiconductor Bloch equations. Analogous measurements of a type-I VECSEL, also emitting in the near-infrared, are compared with the gain dynamics of the type-II VECSEL. For the type-I structure, we observe a faster cooling of charge carriers and a more persistent gain.

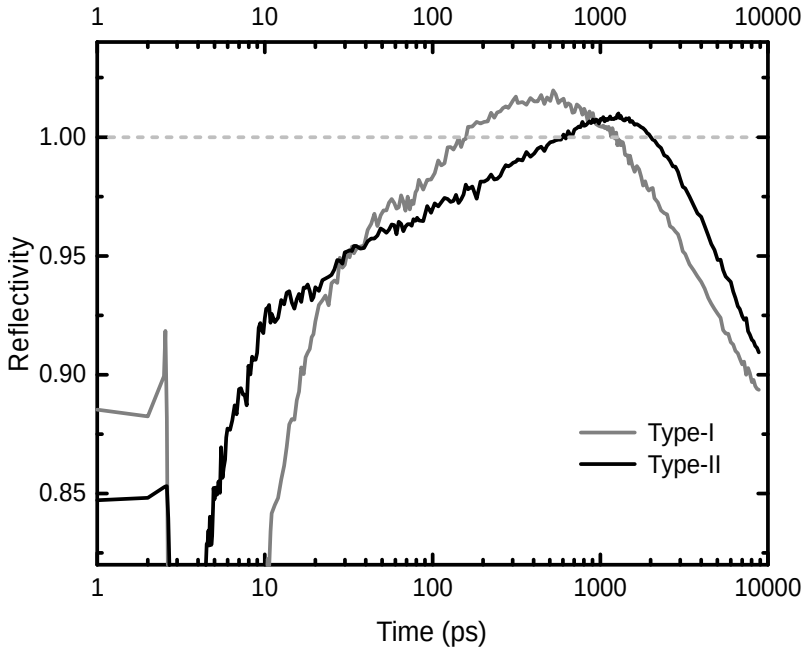


Fig. 1: Semilogarithmic plot showing the gain dynamics of the type-II ``W"-VECSEL chip (black line) in comparison to a conventional type-I chip (grey line).

1.2 µm emitting VECSEL based on type-II aligned QWs

C. Möller[1], C. Fuchs[1], C. Berger[1], A. Ruiz Perez[2], M. Koch[1], S. W. Koch[1], J. Hader[3], J. V. Moloney[3], W. Stolz[1,2]

[1]Material Sciences Center and Department of Physics, Philipps-Universität Marburg, Renthof 5, D-35032 Marburg, Germany

[2]NAsP III/V GmbH, Am Knechtacker 19, D-35041 Marburg, Germany

[3]Nonlinear Control Strategies Inc, 3542 N. Geronimo Ave., Tucson, AZ 85705, USA

e-mail: christoph.moeller@physik.uni-marburg.de

We present the first vertical-external-cavity surface-emitting laser (VECSEL) based on 10 type-II aligned quantum wells arranged in a resonant periodic gain structure. Each quantum wells consists of a (GaIn)As/Ga(AsSb)/(GaIn)As heterostructure. For such quantum well design, material gain only based on electron-hole transitions across the (GaIn)As/Ga(AsSb) interfaces has been predicted which makes this design a promising candidate for interface dominated laser systems.

A first VECSEL structure is realized for the emission at 1188 nm. Room temperature laser operation is demonstrated using an 808 nm continuous wave pump source. Output powers up to 4 W are achieved. A detailed study is performed in order to investigate the properties of the novel laser. The characteristic blue shift of the type-II material gain is observed. Furthermore, the pump density and heat sink temperature dependent wavelength shift rates are determined accurately. Consequently, the thermal resistance of the structure is measured which enables the indication of the gain temperatures for any pump density and heat sink temperature, most importantly at threshold and maximum output power. The obtained results from these studies are part of a closed-loop optimization process which includes a fully microscopic modelling, the epitaxial growth and fundamental laser anylsis.

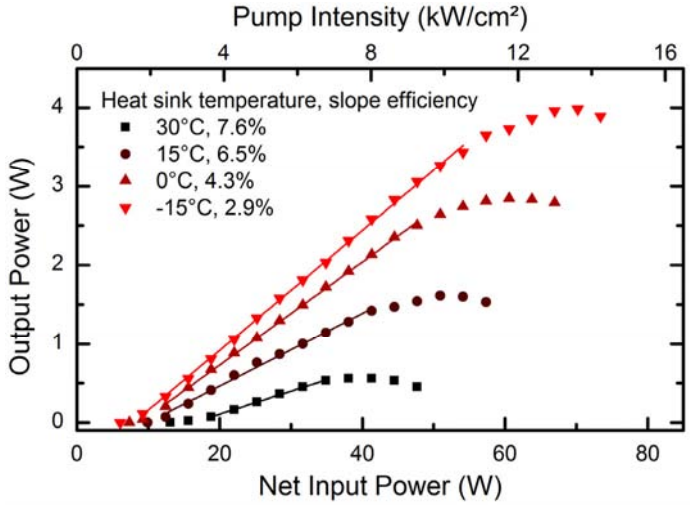


Fig. 1: Power curves of the VECSEL with type-II quantum well gain.

Coherent control of correlation transport through interface between semiconductor quantum wells

Osmo Vänskä[1,2], Ilkka Tittonen[2], Stephan W. Koch[1], Mackillo Kira[1]
[1]*Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Germany*
[2]*Department of Micro- and Nanosciences, Aalto University, Finland*
e-mail: vaenskae@staff.uni-marburg.de

Controlling transport of charge carriers through internal interfaces of semiconductor systems is essential for a wide variety of applications. For example, the efficiency of solar cells and quantum cascade lasers depends on selective transport of electrons and holes through interfaces. There are many unknown aspects in these transport phenomena, e.g., how the roughness of the interfaces affects the transport efficiency. Therefore, it is important to search for new coherent-control processes that can be used for systematic probing of the interface itself and its influence on the electronic transport.

We present the concept of a terahertz (THz) coherent-control scheme for the selective electron-hole transport of different quasi-particles through semiconductor interfaces [1]. We theoretically study the details of the introduced transport process in a double-quantum-well structure. Here, the location of the holes is fixed while the electrons can be moved through the barrier separating the wells.

We find [1] that by changing the THz frequency, we can selectively move either plasma electrons or correlated electrons through the interface. The respective transport protocols are highly efficient even in the presence of considerable dephasing. On this basis, we introduce an additional transport protocol where only pure excitonic correlations are transported between the quantum wells.

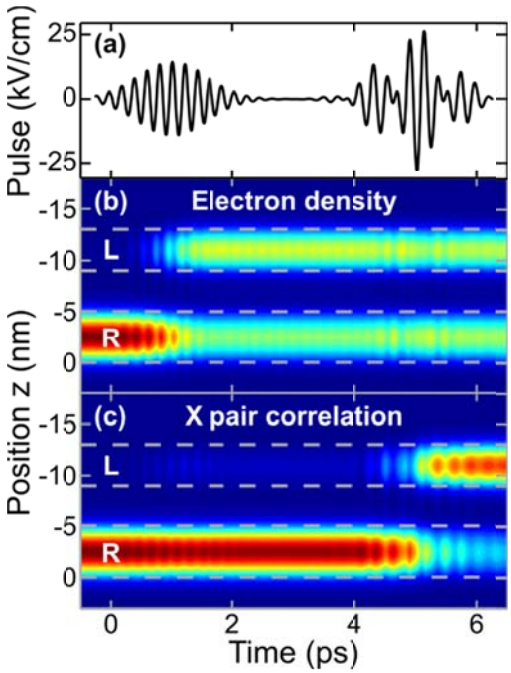


Fig. 1 Pure correlation-transport protocol. (a) Two THz pulses are applied. The first pulse separates plasma and correlated electrons to the left (L) and rigth (R) quantum wells. Transport is monitored from the distribution of (b) electrons and (c) correlations. During the second pulse, the electron density remains practically constant while correlations are moved from right to left.

[1] O. Vänskä, I. Tittonen, S. W. Koch, and M. Kira, *Phys. Rev. Lett.* **114**, 116802 (2015).

Deutsche Forschungsgemeinschaft is funding this work via SFB 1083.

Hybrid cluster-expansion and density-functional-theory scheme and its application for optical absorption in TiO_2

O. Vänskä[1], M. P. Ljungberg[1,2], P. Springer[1], D. Sánchez-Portal[3,2], M. Kira[1], S. W. Koch[1]
[1]*Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Germany*
[2]*Donostia International Physics Center, Spain*
[3]*Centro de Física de Materiales CFM-MPC, Centro Mixto CSIC-UPV/EHU, Spain*
e-mail: vaenskae@staff.uni-marburg.de

Several semiempirical methods can be used to provide parameters that are needed for methods describing many-body dynamics of a semiconductor system. However, there are several "nontrivial" systems where many of the needed parameters for this kind of modeling are not characterized well enough. These cases include, e.g., hybrid organic-inorganic materials and many types of interfaces. Thus, it is important to search for new approaches to overcome the restrictions of semiempirical schemes.

In the presented work [1], we combined density functional theory (DFT) and cluster-expansion (CE) method [2]. By using DFT, we can access the properties of electronic states with a minimal amount of experimental input. We use the electronic wave functions from DFT to compute the interaction matrix elements need for CE. The many-body dynamics can be effectively determined via CE. As a result, we achieve the hybrid CE and DFT scheme that does not require many empirical parameters for a modelling of many-body phenomena in nontrivial systems.

We apply the hybrid approach for rutile TiO_2 that seems to be a normal semiconductor material, but actually possesses many characteristics of a nontrivial system. For example, the effective mass for electrons is very poorly characterized in TiO_2 and it has a direct but dipole-forbidden band gap [3]. To demonstrate our hybrid approach, we model the near-bandgap optical absorption in TiO2. We found strong evidence that the experimentally detected [3] excitonic signature below the band gap originates from a dipole-forbidden but quadrupole-allowed 1*s* exciton.

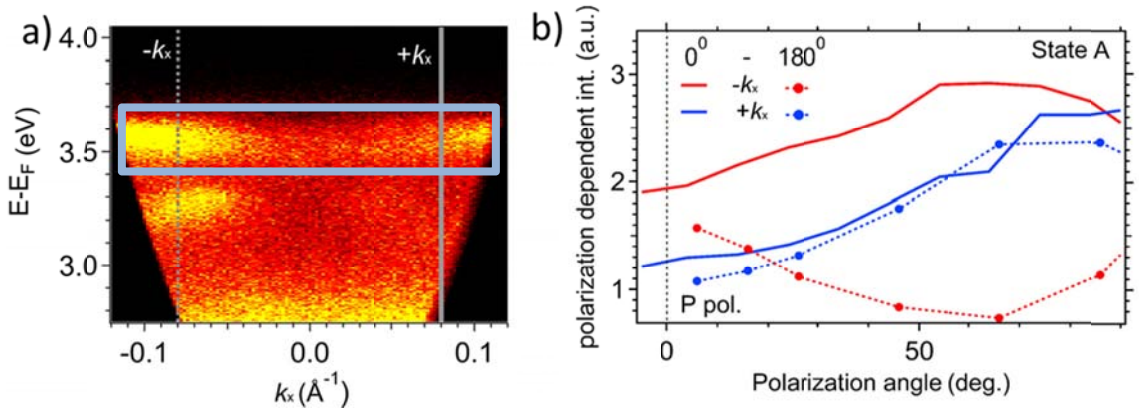
[1] O. Vänskä, M. P. Ljungberg, P. Springer, D. Sánchez-Portal, M. Kira, S. W. Koch, *J. Opt. Soc. Am. B* (to be published), (2016).
[2] M. Kira and S. W. Koch, *Semiconductor Quantum Optics* (Cambridge University Press, Cambridge, 2012).
[3] J. Pascual, J. Camassel, and H. Mathieu, *Phys. Rev. Lett.* **39**, 1490 (1977).

This work is funded by Deutsche Forschungsgemeinschaft via SFB 1083.

Polarization-dependent two-photon photoemission of unoccupied electronic states in Pb/Si(557)

Abdul Samad Syed[1], Vesna Mikšić Trontl[1], Manuel Ligges[1], Daniel Lükermann[2], Christoph Tegenkamp[2], Herbert Pfnür[2], Uwe Bovensiepen[1]
[1] *Fakultät für Physik, Universität Duisburg-Essen, Germany*
[2] *Institut für Festkörperphysik, Leibniz Universität Hannover, Germany*
e-mail: abdulsamad.syed@uni-due.de

The Pb/Si(557) surface reconstruction forms a nanowire system which is known for its temperature-dependent transition from a high temperature laterally isotropic semi-conducting to a low temperature one dimensional metallic electric conductivity [1], a finding that could so far not be confirmed by angle-resolved photoemission studies. Also the atomic structure is not completely understood. Such information is, however, required for electronic structure calculations to make contributions. Our earlier measurements using two-photon photoemission (2PPE) revealed two unoccupied electronic bands at 3.30 and 3.55 eV above the Fermi level [2]. Here, we use 2PPE to characterize the symmetry of the higher lying state by polarization-dependent measurements. The 2PPE intensity of this state exhibits an unusual dependence on light polarization. It is found to (i) be different along positive and negative momentum directions $+k_x$, $-k_x$ along the steps, respectively, see Fig. (a), and (ii) show a dependence along $-k_x$ that is inverted after rotating the surface by π around the surface normal, while it remains along $+k_x$, see Fig. (b). Given a local $\sqrt{3}\times\sqrt{3}$ surface structure [1] we conclude that our observation is consistent with a superposition of a six-fold and a three-fold symmetry of the electronic Pb-Si hybrid state, potentially due to two coexisting atomic structures at the interface.



[1] C. Tegenkamp et al., Phys. Rev. Lett. **95**, 176804 (2005).
[2] A. Samad Syed et al., Phys. Rev. B. **92**, 134301 (2015).

This work is funded by the DFG through research unit FOR 1700 *Metallic nanowires on the atomic scale: Electronic and vibrational coupling in realworld systems.*

Two-dimensional metallic Na layers in Si stacking faults

Lars Winterfeld and Erich Runge
Institut für Physik, Technische Universität Ilmenau, Germany
e-mail: lars.winterfeld@tu-ilmenau.de

Using a combination of density functional theory (DFT) and semiconductor device simulations, we report on the influence of implanted sodium (Na) ions into Si stacking faults. Unlike Na point defects in Si, two-dimensional Na layers are not yet studied in detail. Due to screening by the mobile electrons in Si, the effect of implanted ionic charges is calculated to be weak. A low Na concentration leads to a smaller band gap and induced inner-gap states lead to increased recombination. High Na concentrations above approximately 10^{18} cm^{-2} close the band gap and leads to metallic conductivity within the 2D Na layer. Such concentrations are found as contamination in silicon photovoltaic devices, where they lead to tremendous impairment of the filling factor and a decrease in external quantum efficiency.

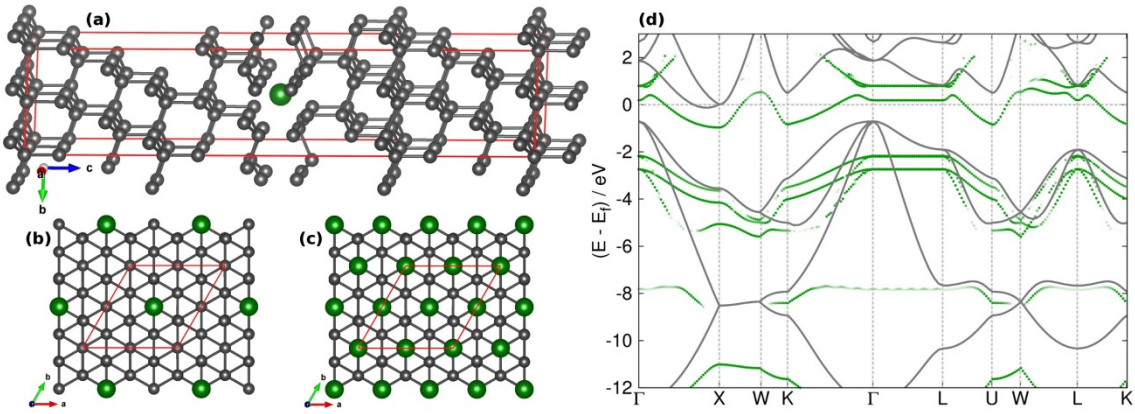


Fig. 1: Left: atomic structure of Na-contaminated, intrinsic stacking fault in (a) side and (b) top view for low 1/4 monolayer and (c) top view for 1 monolayer of Na.
Right: (d) Band structure corresponding to one Na monolayer in Si.

Strong terahertz excitations in semiconductors

U. Huttner[1], J. T. Steiner[1], S.W. Koch[1], M. Kira[1],
F. Langer[2], M. Hohenleutner[2], C. Schmid[2], C. Poellmann[2], P. Nagler[2], T. Korn[2],
C. Schüller[2], O. Schubert[2], M. Knorr[2], M.S. Sherwin[3], and R. Huber[2]
[1] Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Germany
[2] Department of Physics, University of Regensburg, Germany
[3] Department of Physics and the Institute for Terahertz Science and Technology, University of California at Santa Barbara, USA
e-mail: ulrich.huttner@physik.uni-marburg.de

The regime of ultrafast quasiparticle transport in semiconductors can be realized by applying extremely strong and ultrashort terahertz (THz) excitations. By applying this concept in different situations, we demonstrate high-harmonic generation (HHG) in GaSe [1], electronic quantum interference within HHG [2], and a general approach for a quasiparticle collider [3].

We present our microscopic theory [1, 2] based on multi-band semiconductor Bloch equations [4]. Tracing the temporal structure of high-harmonic emission in GaSe reveals that the radiation is emitted exclusively during positive crests of the driving THz field [2] due to a distinct electronic quantum interference. By applying a femtosecond optical and THz pulse simultaneously, coherent excitons are created at a well-defined phase of the THz waveform, while the underlying electrons and holes are accelerated by the THz field. Upon recollision, electrons and holes annihilate, leading to the emission of high-order sideband (HSB) radiation. Such a creation-acceleration-collision cycle yields the concept of a quasiparticle collider. We demonstrate this concept in WSe_2, and show that HSB resolves collision events with a high temporal resolution [3].

[1] O. Schubert, M. Hohenleutner, F. Langer, B. Urbanek, C. Lange, U. Huttner, D. Golde, T. Meier, M. Kira, S. W. Koch, and R. Huber, *Sub-cycle control of terahertz high-harmonic generation by dynamical Bloch oscillations*, Nature Photon **8**, 119 (2014).

[2] M. Hohenleutner, F. Langer, O. Schubert, M. Knorr, U. Huttner, S. W. Koch, M. Kira, and R. Huber. *Real-time observation of interfering crystal electrons in high-harmonic generation*, Nature **523**, 572, 2015.

[3] F. Langer, M. Hohenleutner, C. Schmid, C.Poellmann, P. Nagler, T. Korn, C. Schüller, M. S. Sherwin, U. Huttner, J. T. Steiner, S. W. Koch, M. Kira, and R. Huber, *Lightwave-driven quasiparticle collisions on a sub-cycle timescale*, accepted for publication.

[4] M. Kira and S. W. Koch, *Semiconductor Quantum Optics*, (Cambridge University Press, 2011).

This work was supported by the Deutsche Forschungsgemeinschaft through SFB 1083.

Exciton mass anisotropy revealed by THz spectroscopy

M. Stein, C. Lammers, P. Richter, P. Springer, M. Kira, S.W. Koch, M. Koch
Department of Physics, Philipps-Universität Marburg, Germany
e-mail: markus.stein@physik.uni-marburg.de

In this work, we use THz spectroscopy to study the formation dynamics of excitons with anisotropic effective masses in germanium (Ge). Our experimental observations reveal that the THz spectra show two definite resonances related to the L-valley electron-mass anisotropy. This splitting was predicted by theoretical calcultions based on a fully microscopic approach using the semiconductor Bloch equations. For examination of these excitonic transitions we use an optical-pump and THz-probe time domain spectrometer. Therefore, the output of a 1 kHz Ti:sapphire amplifier system with 35 fs-pulses is split into three parts for each THz generation, electro optical sampling (EOS) and optical pumping. The transient complex dielectric changes are then obtained by calculating the Fourier transformation of the recorded THz waveforms with and without optical excitation. As a sample we use a 500 µm thick undoped n-type Ge with a room temperature resistivity >30 Ωcm^{-1}, which is cooled down to 12 K in a continuous flow liquid-He cryostat.

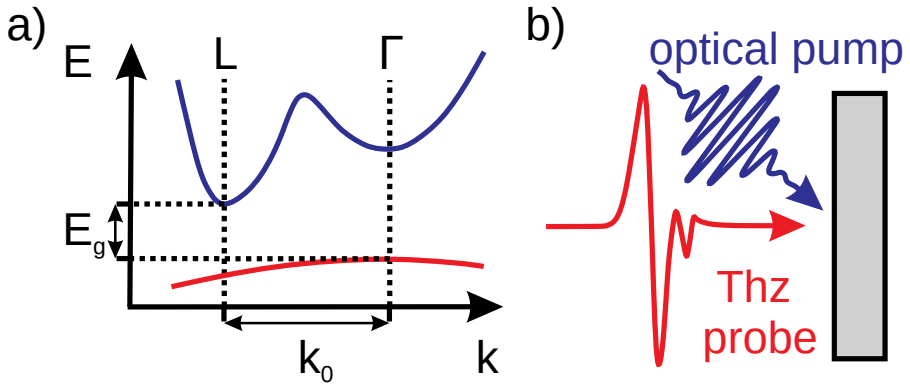


Fig. 1: Band structure of germanium (a) showing the electron mass anisotropy in the L-valley and a schematic diagramm of the optical-pump THz-probe experiment.

Ultrafast magnetization dynamics at the Co/Cu(001) interface investigated with time-resolved magnetization-induced second harmonic generation

Jinghao Chen, Andrea Eschenlohr, Jens Wieczorek, Shunhao Xiao, Alexander Tarasevitch and Uwe Bovensiepen
Fakultät für Physik, Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany
e-mail: jinghao.chen@uni-due.de

The nonlinear optical technique of Magnetization-induced Second Harmonic Generation (MSHG) is an interface-sensitive tool which has the potential to make a valuable contribution to the study of magnetic phenomena at buried interfaces [1].

In this work we measure the MSHG yield from Co/Cu(001) epitaxial films depending on the Co thickness to approach ferromagnetic material interfaces. For Co/Cu(001) films thicker than 2nm, there are two contributions from the vacuum/Co and Co/Cu interfaces, in the thickness range 2nm-4nm both contributions are nearly equal and result in strong interference effects. We analyze the magnetic part of the SHG yield, finding that the involved Fresnel factor leads to a phase difference of 180° between the vacuum/Co and Co/Cu interfaces.

Ultrafast magnetization dynamics in Co/Cu(001) system consists of local and nonlocal contributions. In order to understand the microscopic processes of local spin-flip and nonlocal spin current at interfaces, we investigate the ultrafast magnetization dynamics via the time-resolved MSHG signal from different interfaces. By pump-probe experiments on the same Co/Cu(001) system, the local spin-flip processes and spin-dependent transport effects in the bulk were recently studied by time-resolved magneto-optical Kerr effect (MOKE) [2]. Based on the static MSHG analysis above this work aims at understanding the ultrafast spin dynamics at the vaccum/Co and Co/Cu interfaces.

[1] A. Kirilyuk et al., J. Opt. Soc. Am. B **22**, 148 (2005)
[2] J. Wieczorek et al., Phys. Rev. B **92**, 174410 (2015)

Spectroscopy and dynamics of a two-dimensional electron gas on top of ultrathin helium films on Cu(111)

N. Armbrust, J. Güdde, U. Höfer
Fachbereich Physik und Zentrum für Materialwissenschaften,
Philipps-Universität Marburg, Germany
S. Kossler, P. Feulner
Physikdepartment E20, Technische Universität München
e-mail: Jens.Guedde@physik.uni-marburg.de

Electrons in image-potential states on the surface of bulk helium represent a unique model system of a two-dimensional electron gas. Here, we investigate their properties in the extreme case of reduced film thickness: a monolayer of helium physisorbed on a single-crystalline (111)-oriented Cu surface. For this purpose we have utilized a customized setup for time-resolved two-photon photoemission (2PPE) at very low temperatures under ultra-high vacuum conditions. We demonstrate that the highly polarizable metal substrate increases the binding energy of the first (n = 1) image-potential state by more than two orders of magnitude as compared to the surface of liquid helium. An electron in this state is still strongly decoupled from the metal surface due to the large negative electron affinity of helium and we find that even one monolayer of helium increases its lifetime by one order of magnitude compared to the bare Cu(111) surface.

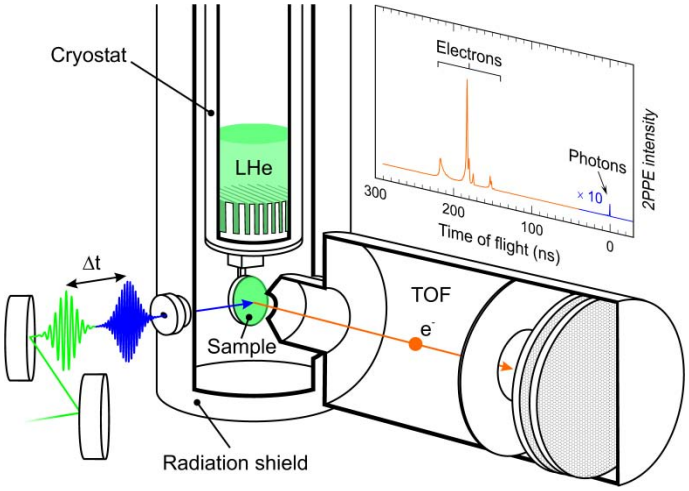


Fig. 1.Experimental setup for 2PPE at sample temperatures of less than 1.2 K. The whole time-of-flight (TOF) electron spectrometer, the cryostat, and the sample mount are enclosed by a 80 K radiation shield. The inset shows a typical TOF spectrum with the consecutive arrival of
scattered uv photons and photo-electrons.

Unoccupied band structure of MgO/Ag(100)

Rebecca Pöschel, Gianluca di Fillipo, Andrej Classen, Thomas Fauster
Solid state physics, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany
e-mail: Rebecca.Poeschel@fau.de

Magnesium oxide is used as a model system to control the charge transfer between a metallic substrate and a molecular species adsorbed on the surface.

In this work magnesium oxide thin films were grown by evaporating magnesium on a well-defined Ag(100) single-crystal kept at 440 K in $5 \cdot 10^{-7}$ mbar oxygen. Films of different thicknesses between 1 ML to 20 ML were deposited on the crystal. The samples were studied by monochromatic angle-resolved two-photon photoelectron spectroscopy (3.05 eV - 3.38 eV and 4.56 eV - 4.71 eV) and by angle-resolved vacuum ultra-violet photoelectron spectroscopy (21.2 eV). Due to the negative electron affinity of MgO the conduction band minimum is observed near the low-energy cut-off and the valence band maximum near the high energy cut-off within the same UPS spectrum. We determined the dispersion of the conduction band minimum and the valence band maximum of a 20 ML thick film. For films up to 10 ML we found two unoccupied states with a binding energy of 1.24 eV and 1.6 eV, respectively. The used photon energy is too low to pump these states from the oxide's bulk, so there has to be a charge transfer from the substrate through the oxide layer.

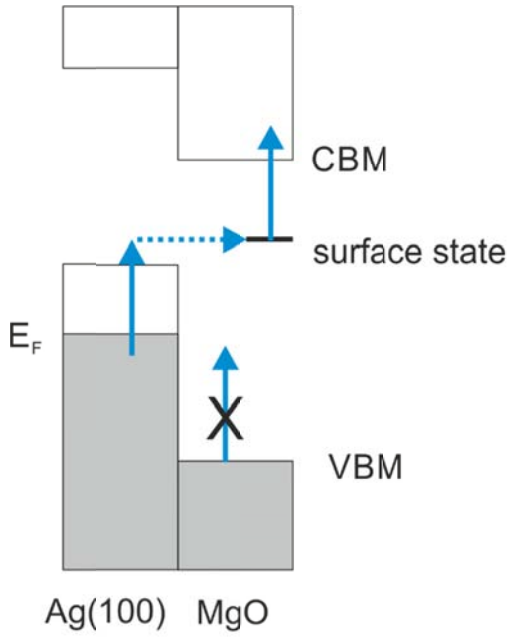


Fig. 1 Charge transfer through the the oxide layer

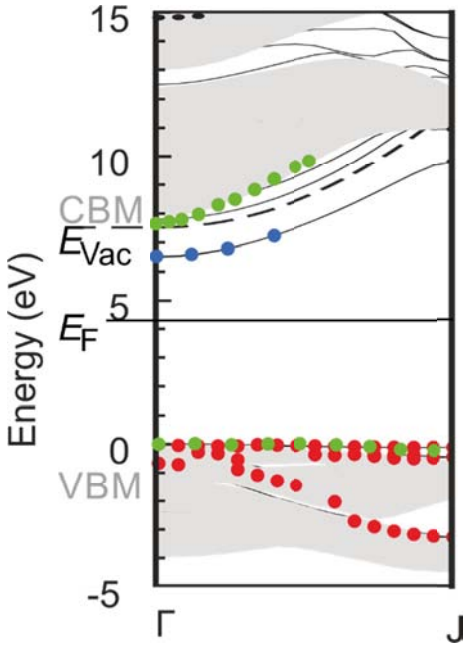


Fig. 2 Measured band structure in comparison to theory[1]

[1] B. Baumeier et al., Phys. Rev. B 76, 205404 (2007)

Ultrafast dynamics of photocurrents in the Dirac cone surface state of a topological insulator

J. Reimann, K. Kuroda, J. Güdde, U. Höfer
Fachbereich Physik und Zentrum für Materialwissenschaften
Philipps-Universität Marburg, Germany
e-mail: johannes.reimann@physik.uni-marburg.de

The Dirac-cone surface states of 3D topological insulators are characterized by a chiral spin texture in k-space with the electron spin locked to its parallel momentum. We demonstrate by means of time- and angle-resolved two-photon photoemission (2PPE) that pulsed laser excitation of such a topological surface state (TSS) in Sb_2Te_3 offers the possibility to create and control spin-polarized electrical surface currents on ultrafast timescales.

We employ mid-infrared (MIR) pulses with photon energies below the bulk band gap ($\hbar\omega$ = 0.2 - 0.4 eV) in order to directly induce electrons from the occupied into the unoccupied part of the TSS. With this pump scheme across the Dirac point, we are able to create a pronounced asymmetry of the transient TSS population in k-space which corresponds to a spin-polarized photocurrent in real space. Time-delayed photoemission out of the TSS allows for detailed investigations of the microscopic scattering processes leading to the decay of the surface currents. We observe elastic scattering times that exceed those of electrons on metal surfaces by orders of magnitude. The results provide clear experimental evidence that the TSS electrons are effectively protected from back scattering by phonons and non-magnetic impurities [1].

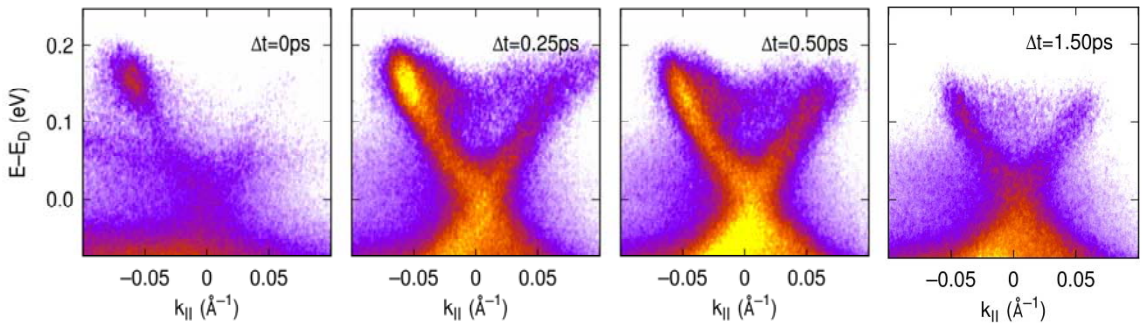


Fig. 1. Angle-resolved 2PPE spectra for Sb_2Te_3 at 80K for different time delays Δt between the MIR ($\hbar\omega$ = 0.35 eV) pump pulse and the UV ($\hbar\omega$ = 5.15 eV) probe pulse. The carrier asymmetry for small delays corresponds to an optical excited photocurrent inside the topological surface state. The energy scale is given in respect to the energy of the Dirac Point E_D.

[1] K. Kuroda, J. Reimann, J. Güdde, and U. Höfer , PRL **116**, 076801 (2016)

Charge transport at an internal interface – turning the interface into an interphase

J. Martin[1], S. Mehrwald[1], M. Schäfer[1], T. Kramer[2], C. Jooss[2], K.-M. Weitzel[1]
[1] Department of Chemistry, Philipps-Universität Marburg, Germany
[2] Department of Physics, Georg-August Universität Göttingen, Germany
e-mail: johannes-martin@chemie.uni-marburg.de

The competition of Na^+ ion versus K^+ ion transport in a mixed alkali borosilicate glass has been investigated by low energy bombardment induced ion transport employing Cs^+ ions as the foreign ion [1]. Electrodiffusion causes the replacement of Na^+ and K^+ down to about 200 nm below the surface of the glass. Beyond this electrodiffusion front (in the direction of ion transport) K^+ ions accumulate to a density above the bulk concentration while Na^+ is further depleted towards the backward platinum electrode. At the backward electrode only Na is electrodeposited since the electrical potential does not allow for K electrodeposition. A full simulation of the electrodiffusion profiles reveals the complete concentration dependence of the diffusion coefficients of the Na^+ and K^+ ions. As a consequence of the ion transport in the bulk material the former internal glas / platinum interface is turned into a Na interphase.

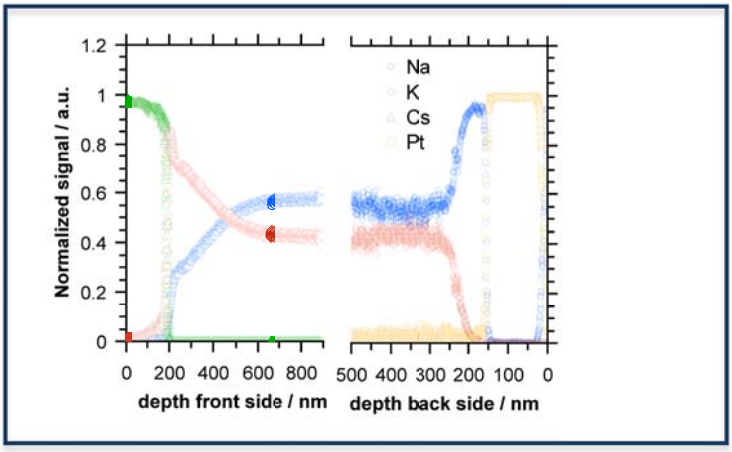


Fig. 1 Concentration profiles for Cs (green), K (red) and Na (blue) in a mixed ion conducting glass. Note, the formation of a Na interphase at the former glass / platinum interface.

[1] Johannes Martin, Sarah Mehrwald, Martin Schäfer, Thilo Kramer, Christian Jooss, Karl-Michael Weitzel, Electrochimica Acta, 191, 616-623, (2016)

Gate voltage dependency of Förster resonance energy transfer in Graphene - quantum dot photo-detection

Ruifeng Li[1,*], Lorenz Maximilian Schneider[2,*], Wolfram Heimbrodt[2], Huizhen Wu[1], Martin Koch[2] and Arash Rahimi-Iman[2]

[1] *Department of Physics and the State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou, 310058, P.R. China*

[2] *Material Science Centre and Experimental Semiconductor Physics, Philipps University, Marburg, 35032, Germany*

**these authors contributed equally*

e-mail: a.r-i@physik.uni-marburg.de

Photo-detectors comprised of a monolayer graphene functionalized by colloidal quantum dots (cQDs) have revealed effective photo detection. Howbeit the detectors are known of being based on a charge or energy transfer, the transfer from the cQDs to graphene is not sufficiently understood. This study examines a graphene field-effect transistor, which is functionalized with CdSe/ZnS core shell cQDs covering it's conductive channel. To investigate energy transfer dynamics in this system, we have measured time-resolved cQD photo-luminescence in dependency of the applied gate voltage. A pronounced increase in the photo-luminescence lifetime has been observed at increasing backgate-voltage, indicating a change of the decay channels. To support our observation, we provide data for a model based on non-radiative Förster resonance energy transfer as a function of the gating-voltage. The model reveals that by applying an external potential at the backgate, absorption of graphene can be tuned with respect to the photo-luminescence of the cQDs. From this finding a new transfer rate can be calculated.

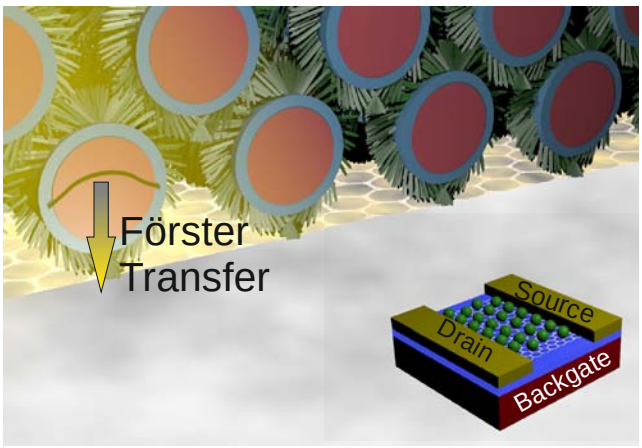
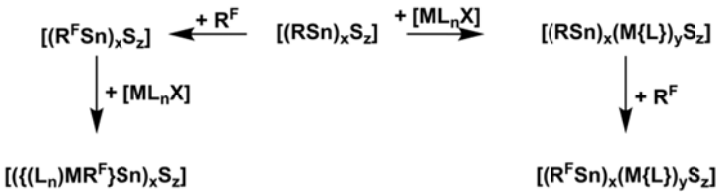


Fig. 1: Schematic representation of a cQD-graphene photo-detector. It consists of colloidal quantum dots drop-casted onto a monolayer of a graphene. The optical power absorbed can be transferred from the cQDs with long ligands to graphene by non-radiative transfer leading to a change of source-drain current. This work focuses on the influence of an applied backgate-voltage on the Förster transfer. The inset shows a schematic view of such a photo-detecting structure including its contacts.

Functional binary and ternary organotin sulfide clusters

Eugenie Geringer, Eike Dornsiepen, Stefanie Dehnen
Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: eugenie.geringer@chemie.uni-marburg.de

The last few decades have afforded a large variety of tetrelchalcogenide clusters featuring organic ligands.[1] These can be assembled as core-shell-shell clusters with an inorganic core with a semiconductor-derived composition, surrounded by an organic ligand sphere, which itself is the basis for a second comprising transition metal complexes. Another route addresses reactions of binary organotin chalcogenide clusters with coinage metal complexes to access ternary clusters that allow for fine tuning of the physical properties of the inorganic core.[2] The use of different organic ligands influences the physical properties as well as reactivities towards molecules or semiconductor surfaces. By reaction of functional binary clusters with organic molecules of complementary reactivity, hetero- and polyaromatic ligands can be attached that greatly affect the opto-electronic properties.[3] Metallocene-decorated clusters with specific electrochemical features can be synthesized in a similar fashion.[4]



Scheme 1: Access to binary and ternary organotin sulfide clusters with functional organic ligands (R = organic moiety, R^F = functional organic ligand, M = transition metal, L = ligand, X = anion).

Recent investigations additionally aim at the attachment of chelating ligands to the clusters which may then be reacted with transition metal complexes. Besides the quoted effect of π-aromatic substituents on the electronic structure of the cluster molecules, the linkage of polyaromatic ligands may enable their interaction with and deposition on surfaces. By inclusion of transition metal atoms beyond group 11 metals into the cluster core the band structure of the inorganic core can be varied.

[1] a) H. Berwe, A. Haas, *Chem. Ber.* **1987**, 120, 1175-1182; b) Z. Hassanzadeh Fard, C. Müller, T. Harmening, R. Pöttgen, S. Dehnen, *Angew. Chem.* **2009**, 121, 4507-4511; c) J. P. Eußner, B. E. K. Barth, E. Leusmann, Z. You, N. Rinn, S. Dehnen, *Chem. Eur. J.* **2013**, 19, 13792, 13802. d) L. Nicole, C. Laberty-Robert, L. Rozes, C. Sanchez, *Nanoscale* **2014**, 6, 6267-6292.

[2] a) R. Hauser, K. Merzweiler, *Z. Anorg. Allg. Chem.* **2002**, 628, 905-906; b) J. P. Eußner, S. Dehnen, *Chem. Commun.* **2014**, 50, 11385-11388.

[3] a) J. P. Eußner, *Dissertation*, Philipps-Universität Marburg **2015**; b) E. Leusmann, F. Schneck, S. Dehnen, *Organometallics* **2015**, 34, 3264-327.

[4] E. Leusmann, M. Wagner, N. W. Rosemann, S. Chatterjee, S. Dehnen, *Inorg Chem.* **2014**, 53, 4228-4233.

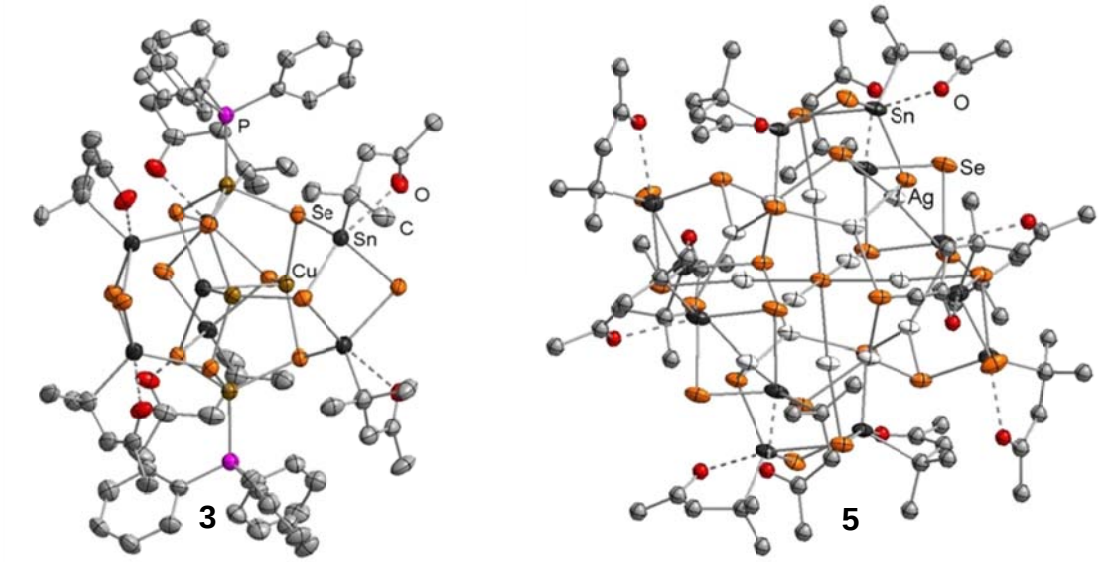
Chemistry of organofunctionalized Sn/Se clusters

Niklas Rinn, Stefanie Dehnen
Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: rinn@students.uni-marburg.de

Although Sn/S-based compounds have shown the greatest variety in the literature, recent work in our group have showcased the chemistry of Sn/Se-based clusters utilizing R^1SnCl_3 ($R^1 = CMe_2CH_2C(O)Me$) and $Se(SiMe_3)_2$ as precursors.[1] The products can be subject to further derivatizations – both at the organic ligand and in reactions with transition metal compounds that lead to ternary M/Sn/Se cluster architectures.[2]

We investigated the chemistry of $[(SnR^1)_3Se_4Cl]$ (**1**) and the "double decker" type cluster $[(SnR^1)_4Se_6]$ (**2**) towards phosphine salts of Cu, Ag and Pd and hydrazine derivatives. Reactions with $[Cu(PPh_3)_3Cl]$ and an excess of $Se(SiMe_3)_2$ lead to the mixed-valence cluster $[\{(R^1Sn^{IV})_2Se_2\}_3\{Cu(PPh_3)\}_2\{Cu_2Sn^{II}\}(\mu_3\text{-}Se)_6]$ (**3**) in the presence of **1** and $[\{(R^1Sn^{IV})_2Se_2\}_2\{Cu(PPh_3)\}_2(Sn^{II}Cl)_2(\mu_3\text{-}Se)_2]$ (**4**) after addition to **2**, showcasing the different chemistry of the clusters. An analogous reaction of **1** with $[Ag(PPh_3)Cl]$ yielded $[\{(Se@Ag_6)\}@Ag_8(\mu\text{-}Se)_{12}\{(R^1Sn)_2Se_2\}_6]$ (**5**). Functionalizations using $[Pd(PPh_3)_2Cl_2]$ yield smaller clusters with a trigonal bipyramidal Se_2Pd_3 base.

The copper derivatives have been treated with hydrazine hydrate, leading to a rearrangement of the inorganic core in case of **3** to $[\{(R^2Sn^{IV})_2Se_2\}_2\{Cu(PPh_3)\}_2Sn^{II}(\mu_3\text{-}Se)_4]$ (**6,** $R^2 = CMe_2CH_2C(N_2H_2)Me$) while a reaction with (**4**) lead to the simple condensation product $[\{(R^2Sn^{IV})_2Se_2\}_2\{Cu(PPh_3)\}_2(Sn^{II}Cl)_2(\mu_3\text{-}Se)_2]$.



[1] J. P. Eußner, B. E. K. Barth, E. Leusmann, Z. You, N. Rinn, S. Dehnen, *Chem. Eur. J.* **2013**, *19*, 13792−13802.
[2] N. Rinn, J. P. Eußner, W. Kaschuba, X. Xie, S. Dehnen, *Chem. Eur. J.* **2016**, *22*, 3094–3104.

Organic–inorganic hybrid materials based on porphyrin dicacids and halogenidobismuthates

Bettina Wagner, Johanna Heine
Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: johanna.heine@chemie.uni-marburg.de

Hybrid organic-inorganic materials have seen a rise in research interest in diverse areas, from gas storage to solar applications. It has been our goal to investigate, understand and engineer the interactions between the organic and inorganic components in a specific subclass of materials. In these, organic cations are combined with halogenidometalate anions, such as in methyl ammonium lead iodide, a material used in the recently developed perovskite solar cells. We have chosen porphyrin diacid cations and halogenidobismuthate anions to prepare our materials, as these combine easy modification of electronic properties in the organic component with a structurally diverse and non-toxic inorganic one. First results of this approach are presented here.

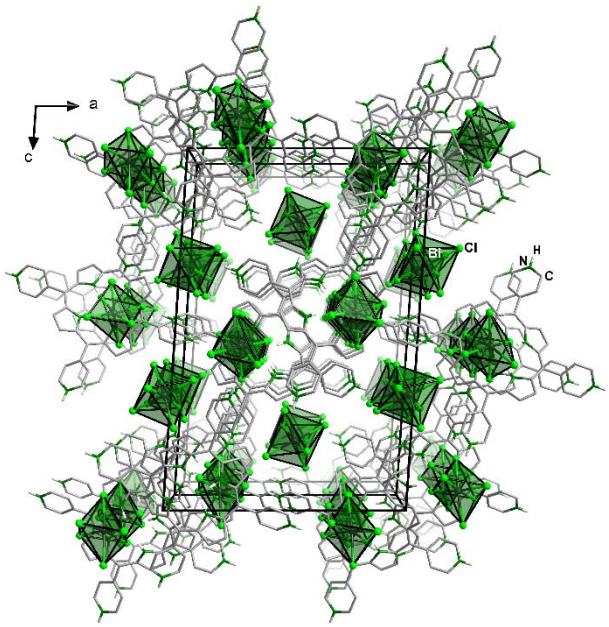


Fig. 1 Excerpt of the crystal structure of a hybrid material containing a porphyrin diacid cation and halogenidobismuthate anions.

Time-resolved SHG-microscopy of 2D monolayer structures

Jonas Zimmermann, Gerson Mette, Ulrich Höfer
Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, 35032 Marburg, Germany
e-mail: jonas.zimmermann@physik.uni-marburg.de

Van-der-Waals coupled 2D materials span the whole range from metallic over semiconducting up to isolating materials and their combination leads to fascinating opportunities for designing stacked heterostructures. The huge variety of possibilities calls for experimental methods which can effectively probe the structure as well as the electron dynamics of these heterostructures.

Here, we present first results of our new experimental setup for time-resolved studies on interfaces between 2D heterostructures. Our SHG microscopy technique allows us to quantify the crystal structure via polarization dependent measurements and gives us access to the electron dynamics via time-resolved pump-probe measurements. We demonstrate the capabilities of our setup with measurements done on CVD grown polycrystalline WS_2 monolayer flakes. The spatial resolution of the experiment is diffraction limited to about 2µm. The relative orientation of several crystal domains can be determined with an error of a few degrees. Because the setup is designed to exclude any dispersion afflicted components, high temporal resolution by the use of ultra-short laser pulses in a pump-probe measurement is achieved. This combination of high temporal and spatial resolution can be applied to 2D heterostructures to study the effects of relative crystal orientation on time-dependent charge transfer processes between different materials.

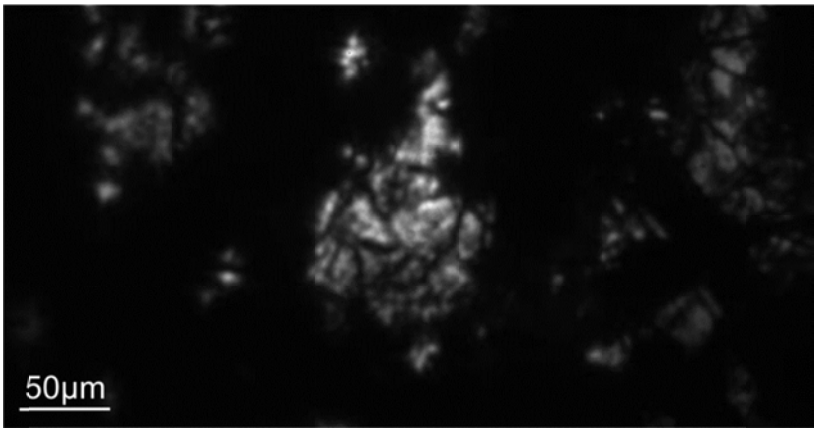


Fig. 1 SHG microscopy image of a CVD grown WS_2 flake.
Clearly visible are the domain boundaries between different crystal orientations.

Time- and angle-resolved photoemission from MoS_2

Robert Wallauer, Nico Armbrust, Johannes Reimann, Jens Güdde, Ulrich Höfer
Fachbereich Physik, Philipps-Universität Marburg, Germany
e-mail: robert.wallauer@physik.uni-marburg.de

Transition metal chalcogenides have attracted a large interest in recent years due to their rich phase diagram which includes phenomena like superconductivity, metal-insulator transitions and charge-density waves. Reducing the sample thickness has shown to change these properties significantly and revealed features like layer dependent bandgaps, tunable superconductivity or valley-selective optical excitation. One of the prototypical examples is MoS_2, which has an indirect band gap as a bulk material and turns into a direct semiconductor in a single layer sheet.

With the availability of ultrafast laser sources in the XUV by means of high-harmonic generation (HHG), a time-resolved extension of angle-resolved photoemission (ARPES) at large parallel electron momenta has become possible. It makes the $\bar{K}$ -point in MoS_2 accessible where a strong enhancement in the photoluminescence has been observed in the monolayer system. We will present first results of time-resolved ARPES of bulk MoS_2 at the $\bar{K}$ -point using our recently developed time-resolved HHG setup that combines pump pulses in the visible range and probe pulses of the 15th harmonic of 800nm (23.2 eV).

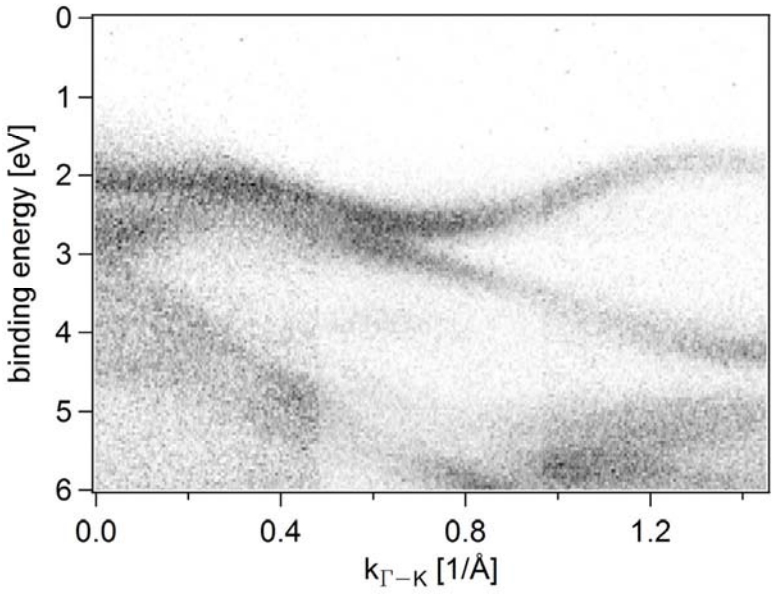


Fig. 1. ARPES bandstructure map of MoS_2 recorded with the 15th harmonic of 800nm (23.2 eV) along the $\bar{\Gamma}$ -$\bar{K}$ direction.

Photoluminescence measurements of MoS_2 and WS_2 monolayers in magnetic fields up to 7 Tesla

Jan Kuhnert, Arash Rahimi-Iman, and Wolfram Heimbrodt
Department of Physics, Philipps-Universität Marburg, Germany
e-mail: jan.kuhnert@physik.uni-marburg.de

Layered transition-metal dichalcogenides have attracted great interest in the last few years. Thinned down to the monolayer limit they change from an indirect band structure to a direct band gap in the visible region. Due to the monolayer thickness the inversion symmetry of the crystal is broken and spin and valley are coupled to each other. The degeneracy between the two equivalent K and K' valleys can be lifted by applying an external magnetic field. Here we present photoluminescence measurements at temperatures down to 4 Kelvin of CVD-grown MoS_2 and WS_2 monolayer samples. By applying magnetic fields up to 7 Tesla in Faraday geometry a splitting of the photoluminescence peaks can be observed. The temperature- and magnetic field dependence of this splitting is discussed for both materials MoS_2 and WS_2.

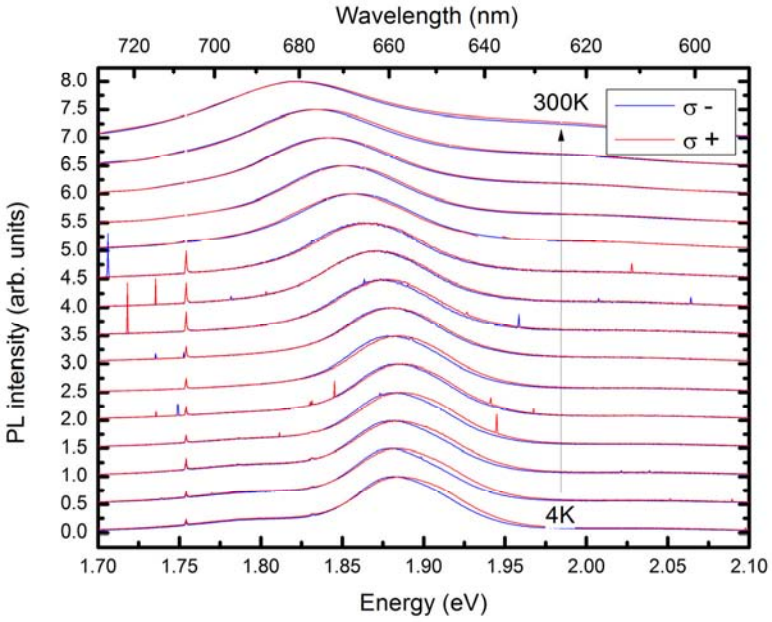


Fig. 1: Photoluminescence spectra of MoS_2 monolayers with an applied magnetic field of 7 Tesla. The photoluminescence is measured in σ+ and σ- polarization for temperatures ranging from 4 Kelvin to room temperature (300K). The Spectra are normalized and shifted for clarity.

A combined *in situ* RAS, *in vacuo* XPS and *ab initio* DFT study of the GaP/Si(100) heterointerface

O. Supplie[1-3], M. M. May[1-3], O. Romanyuk[4], F. Grosse[5], C. Höhn[2], G. Steinbach[6], H. Stange[2], A. Nägelein[1], A. Müller[1], P. Kleinschmidt[1], S. Brückner[1,2], and T. Hannappel[1,2]

[1] *TU Ilmenau, Institute of Physics, Department of Photovoltaics, Ilmenau, Germany*
[2] *Helmholtz-Zentrum Berlin, Institute for Solar Fuels, Berlin, Germany*
[3] *Humboldt-Universität zu Berlin, Institute of Physics, Berlin, Germany*
[4] *Institute of Physics, Academy of Sciences of the Czech Republic, Prague*
[5] *Paul-Drude Institut für Festkörperelektronik, Berlin, Germany*
[6] *Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany*
e-mail: oliver.supplie@tu-ilmenau.de

One of the key challenges towards a sustainable society being independent from fossil fuels is the renewable and efficient generation of hydrogen. Tandem absorber structures based on III/V-on-Si are promising candidates for hydrogen evolution by direct solar water splitting [1]. Challenges are rooted in the complexity of growth processes in metalorganic vapor phase epitaxy (MOVPE) ambient and in the material system itself, particularly regarding specific preparation of the heterointerface. Here, we study the preparation and atomic order of the buried GaP/Si(100) heterointerface *in situ* with reflection anisotropy spectroscopy (RAS). A detailed understanding of the RA spectra enables *in situ* control of the formation of atomically differently ordered Si(100) surfaces and thereby of the desired structure of the GaP epilayer. Therefore, we correlate RAS studies with complementary surface science techniques in ultrahigh vacuum (UHV), such as X-ray photoelectron spectroscopy (XPS), as well as with *ab initio* density functional theory (DFT). We demonstrate that preparation of almost single-domain dimerized Si(100) surfaces succeeds in MOVPE ambient containing (Ga, P) background residuals [2]. Antiphase disorder in III-V epilayers thus can be reliably suppressed. We obtain atomically ordered, single-domain GaP/Si(100) surfaces by pulsed GaP nucleation of a roughly 2 nm thin epilayer and subsequent annealing with phosphorus stabilization [3]. A characteristic, terrace-related dielectric anisotropy evolves during pulsed GaP nucleation and remains during further growth [3]. By optical model calculations, we attribute this anisotropy to the GaP/Si(100) heterointerface. Charge compensation at the GaP/Si(100) heterointerface can be achieved by atomic intermixture with an equal number of Si–P and Si–Ga bonds [2]. However, XPS measurements suggest a kinetically limited formation of a rather abrupt interface consisting of about one monolayer of Si–P bonds [3]. The amount of sub-monolayer coverage of the substrate prior to nucleation strongly affects the formation of the interface and the structure of the GaP epilayer [4].

[1] S. Hu et al., *EES* **6**:2984 (2013); O. Supplie et al., *JAP* **115**:113509 (2014).
[2] O. Supplie et al., *PRB* **90**:235301 (2014).
[3] O. Supplie et al., *JPC Lett.* **6**:464 (2015).
[4] O. Supplie et al., *ACS AMI* **7**:9323 (2015).

Time-resolved nonlinear spectroscopy at the buried GaP/Si interface

A. Lerch, K. Brixius, A. Beyer, K. Volz, W. Stolz, and Ulrich Höfer
[1] *Department of Physics, Philipps-Universität Marburg, Germany*
e-mail: hoefer@physik.uni-marburg.de

Epitaxially grown GaP on Si(001) has been proven as a promising candidate to combine III/V-semiconductors with silicon based technology. For this reason, GaP on Si is a structurally well characterized and technologically important model system for a polar/nonpolar semiconductor interface. The ultrafast dynamics of electronic excitations and charge transfer processes at the GaP on Si(001) interface were investigated by means of optical second-harmonic generation (SHG).

The experiments were conducted using 800-nm 45-fs pump and probe pulses in a non-collinear geometry where the SHG response of bulk GaP is suppressed. A strong static second-harmonic signal originating at the GaP/Si-interface was observed. Furthermore, this signal is shown to be correlated with a distinct dynamical response on a 10-picosecond timescale. Two different dynamical interface components could be separated phase-sensitively by utilizing the interference between SHG from GaP bulk and the transients. The first component possesses a rising-time faster than 30-fs and decays in approximately 500 femtoseconds.

From the linear dependence of the transients on the pump fluence we exclude direct excitation of both GaP and Si bulk with direct band gaps of 2.8 eV and 3.4 eV, respectively. Instead we propose a direct excitation of electronic states at the interface by the 1.55-eV pump pulses which is consistent with the fast rising-time of the first component. Subsequently the excited carriers can diffuse into the silicon bulk and build up an electric field which will give rise to electric field induced second-harmonic generation. This charge transfer is suggested to be responsible for the second interface component which rises on the timescale of several picoseconds. In addition, the discussed and confirms this assignment.

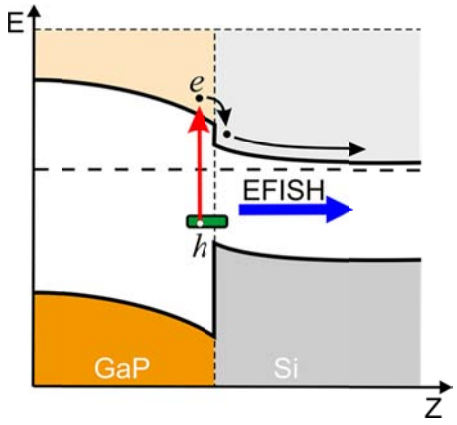


Fig. 1: Proposed excitation scheme and transfer dynamics at the GaP/Si interface.

Computer simulation of anti phase domain formation at the GaP/Si interface

Jan Oliver Oelerich[1,2], Jürgen Belz[1,2], Andreas Beyer[1,2], Kerstin Volz[1,2]
[1] *Department of Physics, Philipps-Universität Marburg, Germany*
[2] *Materials Science Center, Philipps-Universität Marburg, Germany*
e-mail: jan.oliver.oelerich@physik.uni-marburg.de

Gallium phosphide (GaP) buffer layers on silicon (Si) substrates gained considerable attention in the research of functionalized III/V semiconductors integrated monolithically on Si, as the two materials are almost lattice matched and strain at the interface is negligible. An important source of defects of this interface, however, are GaP domains with reversed lattice polarity, so-called anti phase domains (APDs) [1]. Such APDs grow preferably on imperfect (i.e., single-stepped or faceted) Si substrate surfaces, and are therefore unavoidable for the GaP/Si interface. Metal organic vapor phase epitaxy (MOVPE) and scanning transmission electron microscopy (STEM) studies of said material system showed that size, morphology, and boundary orientation of the APDs depend decisively on MOVPE parameters, especially the growth temperature [2].

To systematically investigate the formation of APDs at the GaP/Si interface, a bond-counting kinetic Monte Carlo (KMC) package was used to simulate epitaxial growth of GaP on stepped Si substrates. Formation of APDs was observed successfully (see Fig. 1), resulting in similar shapes as observed experimentally. The formation mechanisms and properties of the APDs were then studied in dependence on substrate morphology and growth temperatures. The results suggest that growth kinetics (i.e., adatom diffusion) alone can be responsible for APD formation, and that size and boundary orientation of the APDs depend primarily on growth temperature.

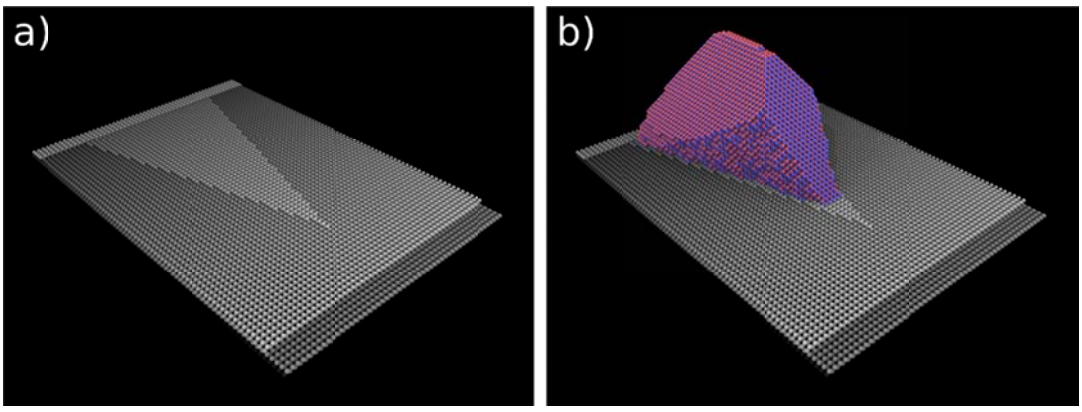


Fig. 3: The system prior to a) and after b) simulated growth of GaP layer. The Si substrate prior to growth contains two double layer steps that form a terrace on which a triangular single-layer step is set up. After growth, an APD becomes visible when the surrounding GaP material (with correct polarity) is hidden. Blue and red spheres represent Ga and P atoms.

[1]: H. Kroemer, J. Cryst. Growth **81**, 193 (1987).
[2]: A. Beyer, I. Németh, S. Liebich, J. Ohlmann, W. Stolz, and K. Volz, J. Appl. Phys. **109**, 8 (2011).

Control over the GaP sublattice orientation on Si(111) and Si(100) by As-modifications of the heterointerface

A. Paszuk[1], O. Supplie[1-3], S. Brückner[1,2], M. M. May[1-3], M. Steidl[1], C. Koppka[1], A. Nägelein[1], W. Zhao[1], A. Dobrich[1], P. Kleinschmidt[1], W. Prost[4], T. Hannappel[1,2]

[1] TU Ilmenau, Institute of Physics, Department of Photovoltaics, Ilmenau, Germany

[2] Helmholtz-Zentrum Berlin, Institute for Solar Fuels, Berlin, Germany

[3] Humboldt-Universität zu Berlin, Institute of Physics, Berlin, Germany

[4] University of Duisburg-Essen, Duisburg, Germany

e-mail: agnieszka.paszuk@tu-ilmenau.de

GaP-on-Si quasisubstrates are desired for further III/V integration. While GaP/Si(100) substrates enables planar tandem absorber structures [1], nanowire-based devices favor growth along <111> directions. In particular, growth of upright nanowires by metalorganic vapor phase epitaxy requires (-1-1-1) faces, i.e. a III/V(111) substrate with so-called B-type polarity [2]. Regarding GaP-on-Si(111) quasisubtrates, the polarity is defined by the atomic structure of the heterointerface and therefore can be tuned by control over Si surface preparation and GaP nucleation. Low-energy electron diffraction (LEED) patterns enable the distinction between GaP(111)A and GaP(111)B, since their surface reconstruction is (2×2) and (1×1), respectively. GaP epilayers grown on Si(111) terminated with hydrogen exhibit A-type polarity. In contrast, Si(111) surfaces terminated with arsenic lead to GaP/Si(111) surfaces with a (1×1) LEED pattern, indicating B-type polarity. Indeed, we obtained vertical GaAs nanowire growth on heteroepitaxial GaP with (1×1) surface reconstruction only, in agreement with growth experiments on homoepitaxially grown GaP(111)B. The As-modification of the GaP/Si(111) heterointerface thus is essential for nanowire growth. In case of Si(100) substrates, we are able to study the formation of atomically well-ordered, As-modified Si(100) surfaces and subsequent growth of GaP/Si(100) quasisubstrates *in situ* with reflection anisotropy spectroscopy [3]. Surface symmetry and chemical composition are measured by LEED and X-ray photoelectron spectroscopy (XPS), respectively. A two-step annealing procedure of initially monohydride-terminated, (1 × 2) reconstructed Si(100) in As leads to a predominantly (1 × 2) reconstructed surface. GaP nucleation succeeds analogously to As-free systems and epilayers free of antiphase disorder may be grown subsequently. The GaP sublattice orientation, however, is inverted with respect to GaP growth on monohydride-terminated Si(100), similar to what we observe for Si(111). XPS also indicates inter-diffusion in case of As being present and the atomic structure of the buried GaP/Si(100):As heterointerface is more complex compared to the As-free case [4].

[1] O. Supplie et al., *JAP* **115**:113509, 2014.

[2] A. Paszuk et al. *APL* **106**:231601, 2015.

[3] O. Supplie et al. *APL Mater.* **3**:126110, 2015.

[4] O. Supplie et al., *JPC Lett.* **6**:464, 2015.

Suppressing rotational defects in GaP/Si(111) hetero-substrates for improved III-V nanowire growth

C. Koppka, L. Winterfeld, A. Paszuk, M. Steidl, P. Kleinschmidt, T. Hannappel
[1] *Department of Physics, Ilmenau Technical University, Germany*
e-mail: christian.koppka@tu-ilmenau.de

The integration of III-V nanowire structures with Si(111) substrates is an exciting route to develop novel optoelectronic device structures. The use of a buffer layer prevents defect evolution in the Si substrates induced by the (Au-)catalyst and carryover of un-desirable Si doping into the nanowires. Due to the small lattice mismatch, GaP/Si(111) is a suitable quasi-substrate to link non-polar silicon substrates and polar III/V epilayers [1-2]. However, epitaxially grown III-V layers on (111) oriented substrates tend to form rotational twin domains (RTDs) resulting in multicrystalline layers with a high density of grain boundaries [3]. RTDs in such heteroepitaxial layers are found to strongly impede vertical nanowire growth. In order to suppress the formation of GaP-RTDs, the impact of substrate properties as well as MOVPE preparation details were investigated. The epilayer properties are significantly improved by a low temperature nucleation prior the growth. DFT calculations addressing the energetic regime of the atomic configuration at the GaP-Si interface between twinned and non-twinned domains suggest a better understanding of the RTD formation during the preparation. Utilizing Si(111) substrates with specific misorientation as well as improved nucleation procedures secure the suppression of twinned GaP domains below 5%. We directly demonstrate that these quasi-substrates are suitable for significantly improved vertical GaP nanowire growth.

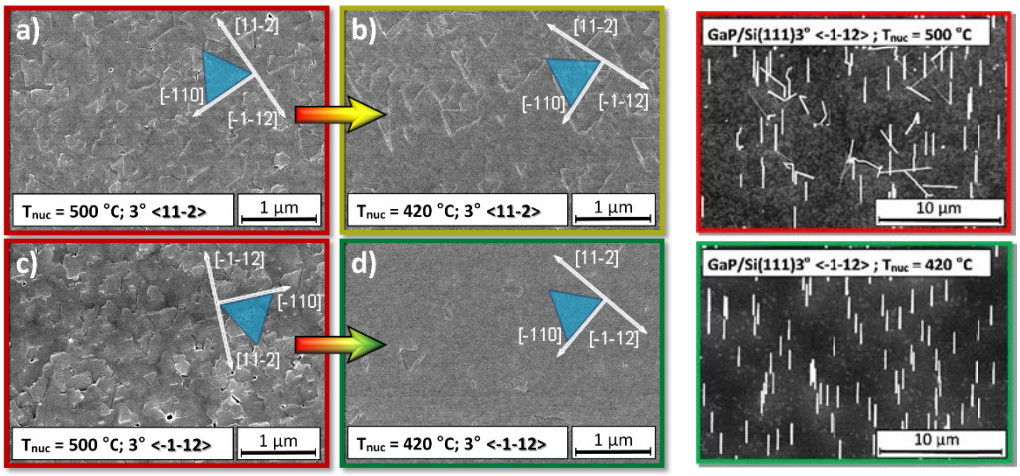


Fig. 1: SEM images of rotational twin domains in GaP epilayers and their influence on GaP nanowire growth

[1] H. Kroemer, J. Cryst. Growth, Vol. 81, (1987)
[2] O. Supplie et al., J. Phys. Chem. Letters, Vol. 6, (2015)
[3] I. Miccoli et al., Cryst. Res.Technol., Vol. 46, 795 (2011)

Diethyl ether on Si(001) – an experimental study on adsorption configurations and energy barriers

Marcel Reutzel[1], Gerson Mette[1], Marcus Lipponer[1], Michael Dürr[1,2], Ulrich Höfer[1]
[1] Department of Physics, Philipps-Universität Marburg, Germany
[2] Institute of Applied Physics, Justus Liebig University Giessen, Germany
e-mail: marcel.reutzel@physik.uni-marburg.de

The functionalization of semiconductor surfaces with organic molecules has attracted much interest, especially with respect to the challenges arising from the miniaturization in semiconductor device physics. The high reactivity of these surfaces, in particular of Si(001), can lead to complex adsorption schemes of organic molecules with different functional groups. In order to build well-defined inorganic-organic interfaces, it is thus important to understand the basic adsorption processes on a microscopic level.

Here, we present an experimental study of the adsorption configurations and the underlying potential energy curve of the ether group on Si(001): At low temperature, diethyl ether adsorbs in a datively bonded intermediate state, as observed by means of STM and XPS experiments. By thermal activation, the ether is cleaved; covalently attached Si-C_2H_5 and Si-O-C_2H_5 fragments are observed on two neighboring dimer rows [1]. Using optical second-harmonic generation (SHG), the surface mediated ether cleavage reaction was followed in realtime. Conversion rates were measured as a function of surface temperature; the conversion barrier ε_a was determined [see Fig. 1 (right)]. The respective binding energy ε_d was extracted by measuring the temperature dependence of the initial sticking coefficient using molecular beam techniques [2].

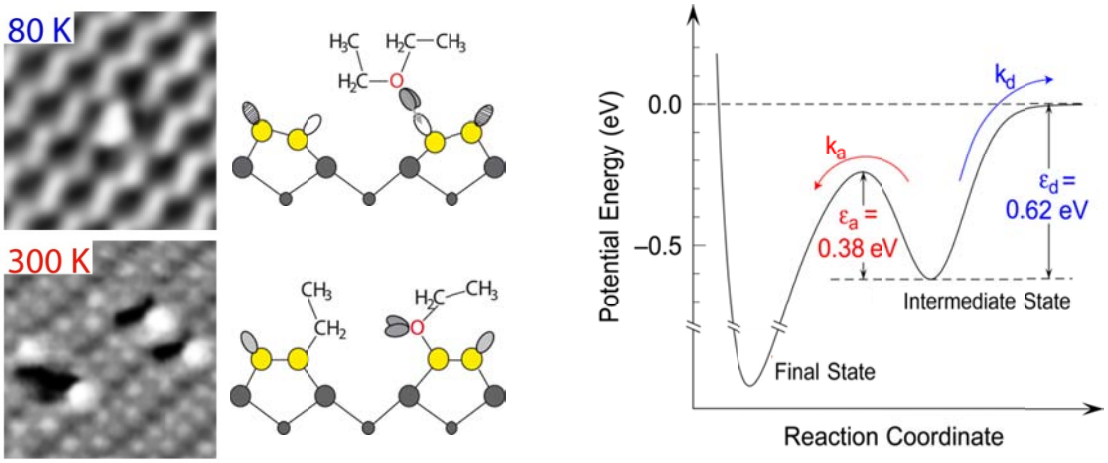


Fig. 1 (Left) Empty state STM images of diethyl ether on the Si(001) surface. At 80 K, diethyl ether adsorbs datively in a kinetically stabilized intermediate state. At 300 K, the ether is cleaved and covalent Si-C and Si-O bonds are formed on two neighboring dimer rows. (Right) Sketch of the corresponding potential energy curve with the experimentally extracted barriers for conversion ε_a and desorption ε_d.

[1] M. Reutzel *et al.*, *J. Phys. Chem. C* **119**, 6018 (2015).
[2] M. Reutzel *et al.*, *J. Phys. Chem. Lett.* **6**, 3971 (2015).

STM tip-induced manipulation of diethyl ether and tetrahydrofuran on Si(001)

T. Bohamud[1], M. Reutzel[1], G. Mette[1], M. Dürr[1,2], U. Höfer[1]
[1]*Department of Physics, Philipps-University Marburg, Germany*
[2]*Institute of Applied Physics, Justus Liebig University Giessen, Germany*
e-mail: tamam.bohamud@physik.uni-marburg.de

In the last decades, the adsorption of organic molecules on silicon surfaces has been subject of intense research. The recent interest in such inorganic-organic interfaces originates from their potential applications in microelectronics. In most cases, the respective adsorbate reactions are thermally induced; however, electronically induced processes may open additional reaction pathways and/or better control of single reaction channels. In this study, we investigate both lateral movement as well as chemical conversion of ether molecules on Si(001) induced by tunneling electrons from an STM tip.

The adsorption mechanism of ether molecules on Si(001) is well understood: At low temperature, a dative bond between the oxygen atom of the intact ether molecule and the D_{down} state of the buckled silicon dimer is established. At room temperature, ether cleavage leads to covalent $Si-O$ and $Si-C$ bonds [1,2]. For diethyl ether, a tip-induced hopping of a $-C_2H_5$ fragment is observed at positive sample bias. Depending on bias voltage, the process is either restricted to a single dimer (Fig. 1, low voltage) or proceeds along the dimer rows (higher voltage). For tetrahydrofuran, the tunneling electrons can induce the transition from the datively bonded intermediate state to the covalently bonded final state. In all cases, we observe a dependence both on tunneling voltage and current which is discussed in terms of the underlying excitation mechanisms.

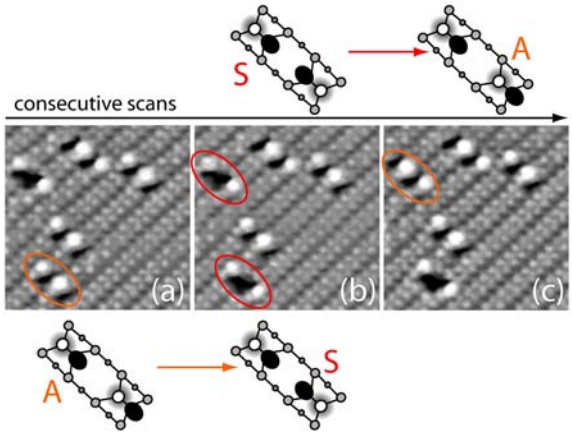


Fig 1. Consecutively scanned empty state STM images of diethyl ether adsorbed on the Si(001) surface. The sketches illustrate the hopping processes from the asymmetric (A) to the symmetric (S) configurations and vice versa.

[1] G. Mette, M. Reutzel, R. Bartholomäus, S. Laref, R. Tonner, M. Dürr, U. Koert, U. Höfer, *ChemPhysChem* **15**, 3725 (2014).
[2] M. Reutzel, G. Mette, P. Stromberger, U. Koert, M. Dürr, U. Höfer, *J. Phys. Chem. C* **119**, 6018 (2015).

Effects of surface modification with self-assembled monolayers on perylene thin film growth

Franziska Maercks, Cathy Jodocy, Matthias Wuttig
I. Institute of Physics (IA), RWTH Aachen, Germany.
Email: maercks@physik.rwth-aachen.de

The performance of organic devices such as Organic Light Emitting Diodes (OLED) or Organic Thin Film Transistors (OTFT) depends on the morphology and crystallinity of the active organic layer. Since the thin film properties are affected by the choice of substrate it is important to investigate the organic-inorganic interface with respect to the influence of substrate modifications on organic thin film growth.

A unique class of modifications is provided by Self-Assembled Monolayers (SAMs). They form the thinnest possible modification layer which leads to a small change in substrate morphology. A SAM molecule consist of three parts, anchor, spacer and head group. The overall dipole of the molecule is created from the anchor group-substrate bond and the intrinsic dipole moment of the head group. This nano-dipole results in an energy level alignment. The head group also crucially influences the organic thin film growth by changing the Surface Free Energy (SFE). It gets evident that crystallinity, coverage, size and number of perylene islands on the surface are affected by SFE and substrate morphology due to the change in diffusion length of the perylene molecules.

In this study we use silicon (001) substrates modified by Self-Assembled Monolayers to investigate the influence of SFE and substrate morphology on the growth of perylene. To confirm the substrate impact on morphology and crystallinity, perylene thin films on bare and modified substrates were characterized by Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD).

Computational study on the suitability of a bifunctional cyclooctyne molecule as a building block for growing interfaces on Si(001)

Josua Pecher, Fabian Pieck, Ralf Tonner
Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: josua.pecher@chemie.uni-marburg.de

Creating organic/silicon interfaces is an important aspect in extending the application range of semiconductors and in the development of new materials and devices. Since cyclooctyne has been shown to form dense and ordered structures in adsorption on silicon(001),[1] the use of its bifunctional derivatives is of particular interest for the construction of such interfaces. One promising candidate for this is 9-ethynyl-9-methylbicyclo[6.1.0]non-4-yne (Fig. 1, left), which would ideally see the ring triple bond attaching to the surface and the terminal triple bond being available for further functionalization.

We use reaction path determination methods in periodic density functional theory to identify adsorption pathways, structures and reactivity of this molecule on Si(001). This allows us to predict under which conditions wanted and unwanted binding motifs (Fig. 2) will occur. Additionally, simulation of STM topograhies as well as vibrational and XPS spectra will help experimentalist interpret their data once the molecule is deposited on the surface in the laboratory.

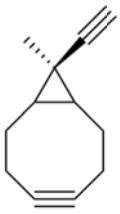


Fig. 1 Lewis structure of 9-ethynyl-9-methylbicyclo[6.1.0]non-4-yne

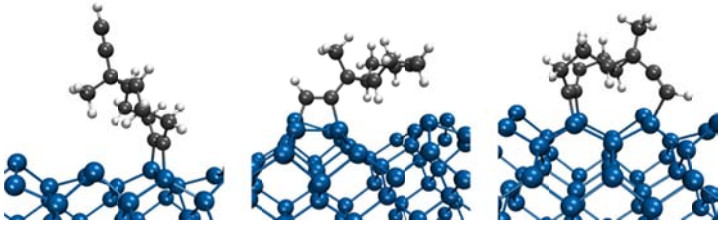


Fig. 2 Wanted (left) and unwanted (center,right) binding motifs of the bifunctional cyclooctyne to the Si(001) surface

[1] G. Mette, M. Dürr, R. Bartholomäus, U. Koert, U. Höfer, *Chem. Phys. Lett.* **2013**, *556*, 70.

This work is funded and supported by the DFG as part of SFB 1083 *Structure and Dynamics of Internal Interfaces.*

Functionalized cycloocytnes: potential building blocks for layer-by-layer synthesis in solution

M. Reutzel[1], M. A. Lipponer[1], C. Länger[3], N. Münster[2], P. Nikodemiak[2], U. Höfer,[1] U. Koert[2*], M. Dürr[3]

[1] Department of Physics, Philipps-Universität Marburg, Germany
[2] Department of Chemistry, Philipps-Universität Marburg, Germany
[3] Institute of Applied Physics, Justus-Liebig-Universität Gießen, Germany
e-mail: paul.nikodemiak@chemie.uni-marburg.de

The predictable synthesis of structurally defined interfaces is an important goal to regulate their physical, electronic, photophysical, and chemical properties. For constructing well-defined thin films of controlled thickness and composition on semiconductor surfaces[1], the layer-by-layer (LbL) assembly has turned out to be a versatile and efficient method.[2] Here, an Cyclooctyne **1** with an strained alkyne reacts with an azid-functionalised substrate **2** to the cycloadduct creating the first layer **3**. The alkyne terminated layer **3** reacts with an bis-azide **4** generating the second layer with an azid terminated surface **5** for alkynes to react with. Following this basic idea, the approach can be extended to multilayers of small molecules and dendrimers in solution.

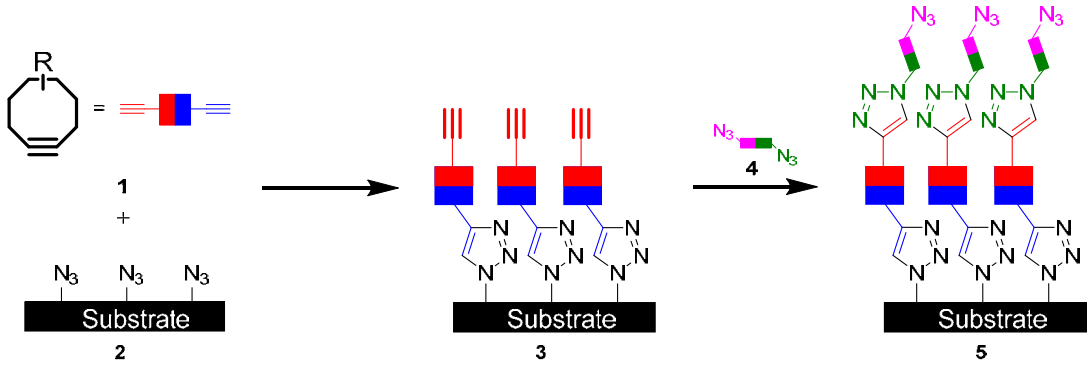


Fig. 1 Schema for the LbL assembly of well-defined thin films.

[1] G. Mette, M. Dürr, R. Bartholomäus, U. Koert, U. Höfer, *Chem. Phys. Lett.* **2013**, *556*, 70.
[2] N. J. Agard, J. M. Baskin, J. A. Prescher, A. Lo, C. R. Bertozzi, *ACS Chem. Biol.* **2006**, *1*, 644–648.

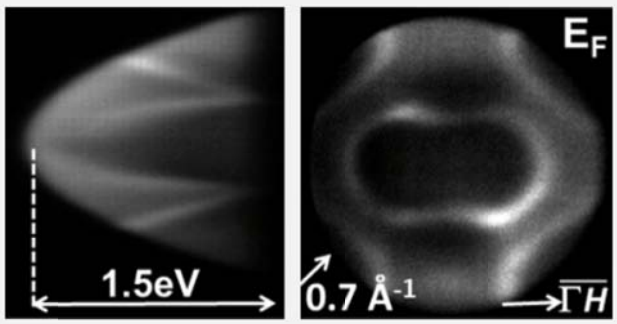
Spin-resolved time-of-flight momentum microscopy

Michael Meyer[1], Thorsten U. Kampen[1], Andreas Oelsner[2], C. Tusche[3], Gerd Schönhense[4]
[1]*SPECS Surface Nano Analysis GmbH, Voltastrasse 5, 13355 Berlin, Germany*
[2]*Surface Concept GmbH, Am Sägewerk 23a, 55124 Mainz, Germany*
[3]*Max Planck Institute for Microstructure Physics, Weinberg 2, 06120 Halle, Germany.*
[4]*Institut für Physik, Johannes Gutenberg-Universität, Staudingerweg 7, 55099 Mainz, Germany*
e-mail: Michael.Meyer@specs.com

Our newly developed time-of-flight momentum uses an optimized lens design which provides simultaneously highest energy, angular and lateral resolution. The lens provides a full 2π solid acceptance angle with highest angular resolution. In contrast to standard ARPES measurements with a conventional hemispherical analyzer, electronic structure data from and beyond the 1st Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. the design is compact with a straight optical axis. Operation modes are (k_x,k_y,E_k) data acquisition by operation in energy filtered k-space imaging, ToF-PEEM mode, energy-filtered real space imaging and micro-spectroscopy mode.

The 3D (k_x, k_y, E_k) data recording is done with a 2-dimensional delayline detector, with a time resolution of 150 ps and count rates up to 8 Mcps. It uses channelplates with 40 µm spatial resolution. While the x,y position of an incoming electron is converted into k_x,k_y wave vector, the kinetic energy E_k is determined from the flight time t. Spin-resolved imaging is achieved by electron reflection at a W(100) spin-filter crystal prior to the 2-dimensional delayline detector. Electrons are reflected in the [010] azimuth at 45° reflection angle. Varying the scattering energy one can choose positive, negative, or vanishing reflection asymmetry.

We will present data taken on different materials like Mo(110) and ferroelectric α-GeTe(111) films.



The k-space sections show the bands in an E-k∥ plane (left picture) and a cut through the Fermi surface (right picture) of Mo(110), taken with 2PPE excitation by 3.3eV photons from a Ti:Sa laser.

Poster abstracts – Session II

Characterization of charge transfer in weakly interacting organic-organic heterostructures

Paul Beyer[1], Valentina Belova[2], Eduard Meister[3], Theresa Linderl[3], Stefan Schmidt[3], Thomas Zechel[3], Tino Meisel[1], Alexander Generalov[4], Ana Sofia Anselmo[5], Reinhard Scholz[6], Alexander Hinderhofer[2], Alexander Gerlach[2], Wolfgang Brütting[3], Frank Schreiber[2], Andreas Opitz[1]

[1] Department of Physics, Humboldt-Universität zu Berlin, Germany
[2] Institut für Angewandte Physik, Universität Tübingen, Germany
[3] Institute of Physics, Experimental Physics IV, University of Augsburg, Germany
[4] Maxlab, Lund University, Sweden
[5] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany
[6] Institut für Angewandte Photophysik, Technische Universität, Dresden, Germany
e-mail: pbeyer@physik.hu-berlin.de

The relative orientation of molecules and the resulting frontier orbital overlap together with the energy level alignment at donor/acceptor (D/A) interfaces are important for charge transfer (CT) states and therefore for electrical doping via charge transfer complexes [1] and charge separation in photovoltaic cells [2]. In this contribution, perylene derivatives are used due to their high charge carrier mobilities, intense light absorption, stability and chemical tunability. We combined diindenoperylene (DIP) as donor with a dicyanoperylene-3,4:9,10-bis(dicarboxyimide) derivative (PDIR-CN_2) as acceptor, and investigated their structural properties, mixing behavior, optical, and (photo)electrical properties in planar and planar-mixed heterojunctions.

Mixed-crystal formation was found in co-deposited films with X-ray scattering. The energy levels result in a type II interface with a staggered gap as confirmed by photoelectron spectroscopy. Charge transfer transitions were observed with optical absorption, photo- and electroluminescence. In contrast to typical photovoltaic systems, a broad absorption band is present here, which also affects decisively the performance of solar cells based on this D/A system. While the open circuit voltage is equivalent for planar and planar-mixed heterojunctions, unexpectedly, the photocurrent is reduced in the case of blended films.

A combined experimental approach shows the ground state interaction between these two molecules and the effects of CT transitions on charge carrier transport and photovoltaic properties. The energy levels of the ground state will be related to the CT energies and discussed. In this system, the limited transport in blended films overcompensates the improved absorption due to CT transitions.

[1] Salzmann, I., Heimel, G., Oehzelt, M., Winkler, S. & Koch, N. Molecular Electrical Doping of Organic Semiconductors: Fundamental Mechanisms and Emerging Dopant Design Rules. *Acc. Chem. Res.* **49,** 370–378 (2016).

[2] Vandewal, K. *et al.* Efficient charge generation by relaxed charge-transfer states at organic interfaces. *Nat. Mater.* **13,** 63–68 (2014).

Electronic properties of optically switchable photochromic diarylethene molecules at interface with organic semiconductors

Qiankun Wang[1], Johannes Frisch[1], Björn Kobin[2], Stefan Hecht[2], Norbert Koch[1]
[1] *Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 6, 12489 Berlin, Germany*
[2] *Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany*
e-mail: qiankun@physik.hu-berlin.de

Photochromic molecules are those which could reversibly be switched from one state, or isomer, into another with light. Diarylethenes (DAE), which are among the most interesting photochromes, show promising application potentials due to their high fatigue resistance and thermal bistability. The photoisomerization of DAE molecules has a huge influence on the energy position of the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level of the individual isomers, which results in a difference of the ionization energy (IE) and optical gap between the open and closed-ring isomers of hundreds of meV. An important issue for all current-related applications is the position of the frontier energy levels of both open- and closed-ring forms with respect to the Fermi level (E_F) of the electrodes and the transport levels of the organic semiconductor. Therefore, the experimental determination of interface energetics of DAE-based (bulk and planar) heterojunction is of high importance for understanding the effects on charge transport and for optimizing it in photoswitchable devices.

Here, the valence electronic structure upon switching of a photochromic diarylethene derivative, 1,2-bis (2-methyl-5-p-tolylthiophen-3-yl) cyclopent- 1-ene (DAE1) was measured by ultraviolet photoelectron spectroscopy (UPS). Switching between open and closed forms was followed *in situ* upon appropriate illumination with ultraviolet and visible light, respectively. The energy level alignment at interfaces between DAE1 and organic hole (electron) transport materials was observed to be affected by the photoisomerization process, which resulted in different charge transport energy barriers for holes (electrons) before and after light irradiation. Our experimental findings provide a rationale for photo-control of charge transport in organic electronic devices.

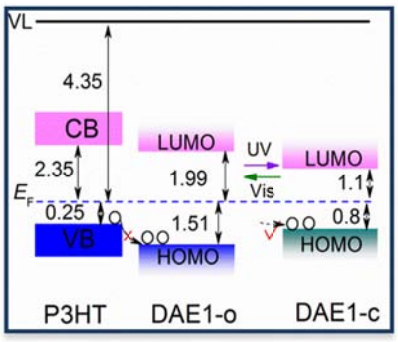


Fig. 1 Schematic energy level diagrams of P3HT/DAE1 interface.

Efficient dissociation of excitons at donor/acceptor interfaces in organic solar cells

Marina Gerhard[1], Andreas P. Arndt[2], Ian A. Howard[3], Arash Rahimi-Iman[1], Uli Lemmer[2] and Martin Koch[1]

[1] *Department of Physics, Philipps-Universität Marburg, Germany*

[2] *Light Technology Institute, Karlsruhe Institute of Technology, Germany*

[3] *Institute of Microstructure Technology, Karlsruhe Institute of Technology, Germany*

e-mail: marina.gerhard@physik.uni-marburg.de

The power conversion efficiencies of organic solar cells (OSCs) have been significantly improved during the last decade but the underlying mechanisms of charge separation are still a matter of controversy. The primary photoexcitations in OSCs are Frenkel-type excitons with binding energies on the order of several 100 meV. Dissociation of these strongly bound electron-hole pairs is, however, found to be efficient in organic donor/acceptor (D/A) heterojunctions. At the D/A interface, one of the charges is transferred to the opposite domain, thereby forming an intermediate charge transfer (CT) state with the other charge remaining in the original domain. The energetics of the CT states thus plays a decisive role in the dissociation process. It is often considered that excess energy is important to drive charge generation. On the other hand it has been argued that also thermally relaxed CT states can dissociate efficiently, when the mutual Coulomb potential is sufficiently screened at the interface. By means of time-resolved photoluminescence (PL), we are able to access the subset of thermally relaxed CT states undergoing radiative recombination at the interface. The temperature dependence of the CT intensity[1] and recent field-induced PL quenching studies of the high-performance D/A system PTB7/PCBM indicate that the emissive CT states in this material are only weakly bound, thus enabling efficient charge generation from energetically *relaxed* CT states at room temperature. Our findings suggest that both screening of the interfacial potential and disorder phenomena are essential to describe the observed field- and temperature dependencies. We further analyze our results employing a kinetic model based on a hopping mechanism for exciton dissociation[2] to quantify the underlying scales of disorder and binding energies.

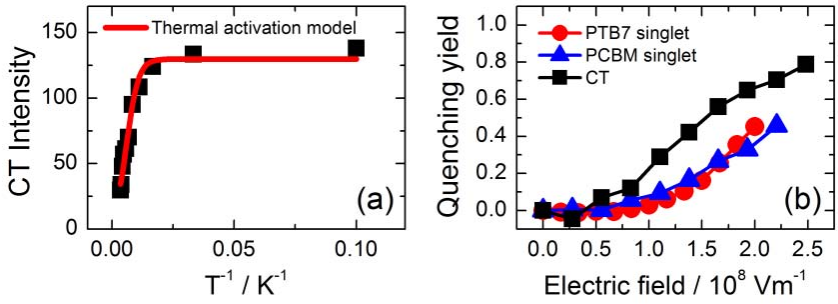


Fig. 1: (a) CT intensity in PTB7/PCBM as a function of inverse temperature. The activation energy for CT quenching obtained by the fit is 35 meV. (b) Field-dependent PL quenching yield at 10 K

[1] M. Gerhard et al, J. Phys. Chem. C 119, 28309, 2015.

[2] O. Rubel et al, Phys. Rev. Lett. 100, 196602, 2008.

Investigation of the PEDOT:PSS/silicon interface for hybrid heterojunction solar cells

Sara Jäckle[1,2], Martin Liebhaber[1], Jens Niederhausen[1], Roberto Félix[1], Regan G. Wilks[1], Marcus Bär[1], Klaus Lips[1], Silke Christiansen[2,1]

[1] *Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany*

[2] *Max Planck Institute for the Science of Light, Erlangen, Germany*

e-mail: sara.jaeckle@helmholtz-berlin.de

High efficiency inorganic solar cells rely on heterojunction contacts, providing strong charge carrier selectivity with well passivated interfaces. As organic conductive materials appeal with a wide tunability of electronic structure, we suggest a hybrid heterojunction solar cells with silicon as the absorber featuring perfect organic charge selective contacts.

We investigated the highly conductive polymer blend poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) as a hole selective contact for crystalline silicon. Photoelectron and impedance spectroscopy reveal a junction formation, without Fermi level pinning showing strong inversion of silicon at the interface [1]. In contrast to earlier literature we can prove the dark current in long-base solar cells featuring this hybrid junction is not limited by rapid thermionic emission of majority carriers at the junction but by minority carrier diffusion in the silicon bulk, leading to open circuit voltages up to 640 mV and efficiencies above 13 % [1]. The chemical structure at the buried hybrid interface is investigated by synchrotron based hard X-ray photoelectron spectroscopy (HAXPES), enabled by removal excess material through a solution post-treatment thinning the polymer without affecting the performance of the corresponding hybrid solar cells [2]. The HAXPES data unveils that the silicon at the interface to PEDOT:PSS is already oxidized immediately after preparation. The n-Si/SiOx/PEDOT:PSS junction should therefore be treated as a SIS-heterojunction. The potential of this junction in high efficiency solar cells and possible electron selective contacts are discussed.

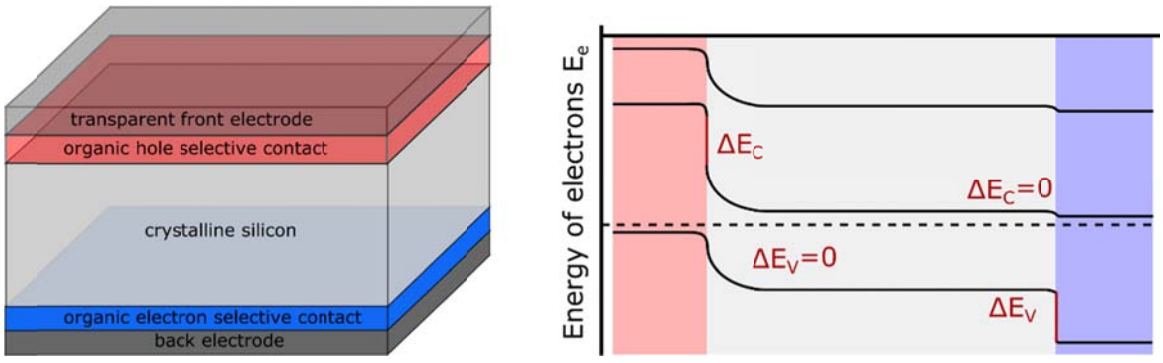


Fig. 1 Suggested hybrid heterojunction silicon solar cell featuring ideal charge selective contacts

[1] Jäckle, Mattiza, Liebhaber, Brönstrup, Rommel, Lips & Christiansen, Sci. Rep. 5 13008 (2015)

[2] Jäckle, Liebhaber, Niederhausen, Büchele, Félix, Wilks, Marcus Bär, Lips & Christiansen. ACS Appl. Mater. Interfaces 8(13), 8841-8848 (2016)

Optical spectroscopy on organic-inorganic hybrids – charge transfer in type-II level systems

Ingo Meyenburg[1], Benjamin Heidelmeier[1], Nils Rosemann[1], Christian Prinzisky[2], Martin Liebold[2], Jan Tinz[3], Jane Falgenhauer[3], Jörg Sundermeyer[2], Derck Schlettwein[3], Wolfram Heimbrodt[1]

[1] *Department of Physics, Philipps-Universität Marburg, Germany*

[2] *Department of Chemistry, Philipps-Universität Marburg, Germany*

[3] *Institute of Applied Physics, Justus-Liebig-Universität Marburg, Germany*

e-mail: ingo.meyenburg@physik.uni-marburg.de

Understanding interface processes is crucial for improvements of existing and new functional materials based on organic-inorganic hybrid semiconductor structures.

We investigated the effective radiative lifetime of various dyes (Indoline, Anthraquinone derivates, modified Zinc-Phthalocyanines) on different inorganic semiconductor substrates (ZnO, TiO_2, ZnSe) in dependence on the anchoring group and on the anchor length to reveal the influence on the charge transfer from the dye into the semiconductor. In Fig.1 the transients are depicted for Indoline dyes with different anchor groups on ZnO as example.

Kinetic model calculations enable the determination of effective charge transfer times. The influence of the anchoring chain on the charge transfer at the interface has been revealed.
The depletion of excited organic states by charge transfer into the inorganic semiconductor helps to determine the level alignment at the interface.

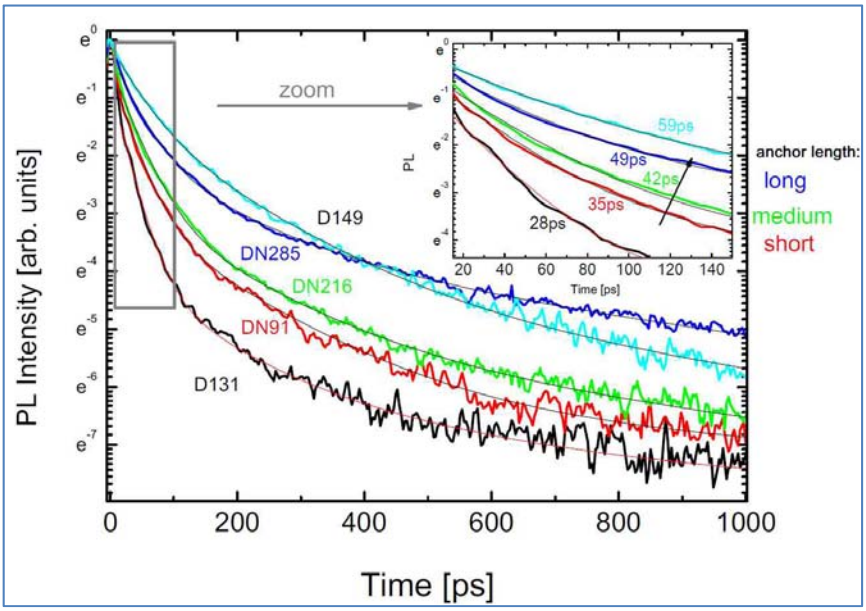


Fig. 1 Photoluminescence transients of Indoline dyes with different anchor groups.

Hybrid charge transfer excitons and interface energetics at ZnMgO/P3HT heterojunctions

Moritz Eyer[1], Johannes Frisch[2], Sergey Sadofev[1], Joachim Puls[1], Emil List-Kratochvil[2], Norbert Koch[1], and Sylke Blumstengel[2]

[1]Department of Physics, Humboldt-Universität zu Berlin, Germany

[2]Department of Physics, Department of Chemistry, and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

e-mail: moritz.eyer@physik.hu-berlin.de

The performance of hybrid inorganic/organic solar cells is governed by the efficiency of charge separation at the interface. It is suggested that an intermediate charge transfer state is involved hereby. If an exciton produced either in the inorganic or organic part of a hybrid photovoltaic heterojunction diffuses to the interface, a hybrid charge transfer exciton (HCTE) is formed, i.e. a pair of electron and hole residing on different sides of the interface and bound by Coulomb interaction. Only if a HCTE dissociates, a contribution to a photocurrent is made.

We present experimental evidence for the formation of HCTE in diodes containing a planar heterojunction of ZnMgO and poly(3-hexylthiophene) (P3HT) by observing their radiative recombination in the near infrared in electroluminescence measurements[1].

The energy offset ΔE_{IO} between the conduction band minimum of ZnMgO and the P3HT highest occupied molecular orbital is tuned systematically by varying the Mg content. The resulting energy level configuration is studied by UV photoelectron spectroscopy. By measuring temperature-dependent current-voltage characteristics of the diodes it is shown that the activation energy for the saturation current is related to the energy offset ΔE_{IO}.

Both electroluminescence maximum and open circuit voltage V_{OC} of the devices shift analogous to ΔE_{IO} which shows that both directly depend on the HCTE transition energy.

Investigation of the properties of HCTE yields valuable input for the optimization of the charge separation process at inorganic/organic semiconductor interfaces required to fully exploit the potential of hybrid devices.

[1] M. Eyer, S. Sadofev, J. Puls, and S. Blumstengel, Appl. Phys. Lett. 107, 221602 (2015).

Tuning the work function of GaN and the influence of surface states

Thorsten Schultz[1], Raphael Schlesinger[1], Jens Niederhausen[2], Norbert Koch[1,2]
[1] *Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany*
[2] *Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin, Germany*
e-mail: tschultz@physik-.hu-berlin.de

Important processes in hybrid inorganic/organic systems (HIOS) based devices, like energy or charge transfer, are controlled by the energy level alignment (ELA) at the HIOS interface. However, an unfavorable interfacial ELA is often encountered for a given HIOS. Modifying the ELA with the help of ultrathin interlayers of organic donor / acceptor molecules has been widely studied and was recently successfully applied to ZnO in a hybrid light emitting structure [1]. The adsorption of organic acceptor molecules was found to increase the ZnO work function due to two contributions, i.e., an interface dipole at the organic-inorganic interface and band bending modification inside the inorganic semiconductor [2]. However, a quantitative description of the two contributions is still missing.

A drawback of ZnO for many envisioned devices, however, is that it is naturally n-doped and hard to p-dope. In contrast, GaN is another promising wide band gap inorganic semiconductor with both types of doping available.

In this study we investigate the achievable work function range for GaN and introduce a model to describe the measured work function contributions. Two molecular organic acceptors (F6-TCNNQ, HATCN) and one donor molecule [$(RuCp^*mes)_2$] were vacuum-deposited on non-intentionally doped GaN (0001). By means of ultraviolet photoelectron spectroscopy, a huge work function range (between 2.2 and 6 eV) was observed for monolayer coverage. The contribution of band bending within GaN (ca. 0.35 eV, as determined from X-ray photoelectron spectroscopy) was found to be significantly smaller than expected from calculations, which predict the contribution of band bending to be dominant for the present doping concentrations [3].

These calculations neglected the influence of surface states. A new model is introduced, which takes into account the presence of surface states on the inorganic semiconductors and describes the experimentally found contributions of interface dipole and band bending more accurately. Different preparation methods were investigated to verify the model qualitatively.

Our investigations show that the energy level tuning scheme via organic interlayers, already successfully employed for ZnO, holds great promise for GaN as well and that both donor concentration and surface state density of the inorganic semiconductor play an important role for the energy level modification at HIOS interfaces.

[1] Schlesinger *et al*., Nat. Commun. **6**, 6754 (2015)
[2] Schlesinger *et al*., Phys. Rev. B **87**, 155311 (2013)
[3] Xu *et al*., Phys. Rev. Lett. **111**, 226802 (2013)

Interfaces and surfaces in organic radical thin films: electronic structure and paramagnetic character

R. Kakavandi[1,2], S.-A. Savu[1], M.B. Casu[1]
[1] *Institute of Theoretical Physical Chemistry, Eberhard Karls-Universität Tübingen, Germany*
[2] *Department of Physics, Philipps-Universität Marburg, Germany*
e-mail: reza.kakavandi@physik.uni-marburg.de

The Purely organic magnetic molecules are a class of emerging materials interesting for their potential use in large variety of application. Deciphering the nature of adsorption as well as understanding their electronic structure and paramagnetic character are of great interest whether one considers possible commercial applications or fundamental physical interactions.

We devoted our efforts primarily on the growth of thin films of metal-free organic magnets on the surface of metal dioxides, i.e., technologically relevant surfaces in ultra-high vacuum (UHV). The electronic properties, chemical environment at the interfaces, the magnetic character of the molecules and morphology of the thin films have been explored by a multi technique approach. Working on metal oxides is motivated by the fact that, besides the interest on the investigation of novel organic /oxide systems, it is clear how the coupling of purely organic radicals may also lead to new developments in device engineering.

Here, by using X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, we find that the paramagnetic character is kept going from molecule to material. In particular, we evidence the transitions related to the singly unoccupied molecular orbital (SUMO), as expected in open shell materials. The results are obtained by depositing pyrene derivative of the nitronyl nitroxide radical (NitPyn) and fluorophore-nitroxide radical (PPN) on TiO_2(110) single crystals and SiO_2/Si(111).

From the photon energy dependent analysis, we suggest the occurrence of a shake-up transition consisting of a dipole excitation of a core electron into a valence orbital and a monopole ionization of a valence electron. The persistence of the paramagnetic character is explored by electron spin resonance spectroscopy. The films are characterized by a high structural order, coupled to strong vacuum and air stability that make these radicals extremely promising candidate for applications in electronics.

Electronic states of thin films of 1,3-diphenylsobenzofuran

David Nobis, Angelika Demling, Janek Rieger, Daniel Niesner,
Pedro B. Coto, Michael Thoss, Thomas Fauster
Lehrstuhl für Festkörperphysik,
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU,) Erlangen, Germany
e-mail: david.nobis@fau.de

1,3-Diphenylisobenzofuran (DPIBF) is a prototypical singlet fission molecule as the excited singlet state undergoes very efficient singlet fission in thin films as shown by spectroscopy data [1]. Singlet fission is the spin-allowed conversion of one optically excited singlet, into two optically dark triplet states. In this work we present a photoelectron spectroscopy study on films of DPIBF. We investigated films in the submonolayer regime on the Au(100) surface and films with a thickness of several nanometers on SiO_2. The films where investigated with UV-photoelectron spectroscopy (UPS), two-photon photoelectron emission (2PPE) and in situ steady-state fluorescence. The results where compared to density functional theory (DFT) calculations.

The fluorescence data show a strong dependence on the preparation temperature, in this study we focus on the low temperature phase, grown at a temperature of 80 K.
With UPS we record the position of the HOMO (6eV below the vacuum energy) and of the deeper-lying occupied molecular orbitals. The results agree excellent with DFT calculations.
2PPE gives us access to the excited states. On thick layers we can observe two features in the 2PPE spectra. They can be interpreted as the first excited singlet state S_1 and the first excited triplet state T_1 at 2.8 eV and 1.4 eV respectively [2]. The occupation of the optically dark triplet state can be explained by singlet fission. The occurring high intensity of both states fits to the long lifetime of the triplet state and to a refilling of the singlet states via triplet-triplet annihilation due to the high excitation density. The observed states S_1 and T_1 are quenched in the submonolayer films.

[1] Johnson J. C. *et al.*, J. Am. Chem. Soc. B **132** (2009) 16302
[2] Schwerin A. F. *et al.*, J. Phys. Chem. A **114** (2010) 1457

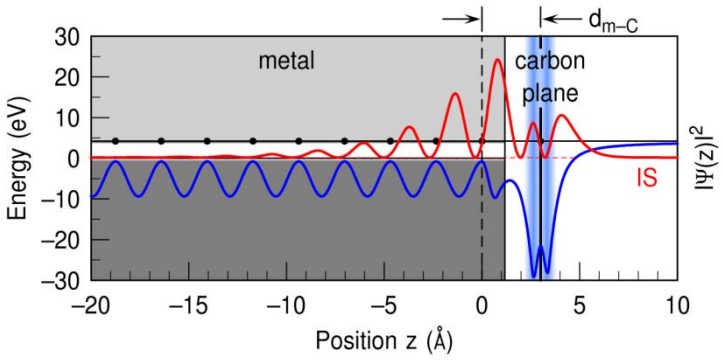
Model potential for description of metal/organic interface states

Nico Armbrust[1], Frederik Schiller[1,2], Ulrich Höfer[1]
[1] Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, 35032 Marburg, Germany
[1] Centro de Física de Materiales, CFM-CSIC, San Sebastián, Spain
e-mail: nico.armbrust@physik.uni-marburg.de

A parameter-free one-dimensional model for the description of the surface and interface potential of molecular layers on single crystal metal substrates is presented. The analytical potential utilizes a flat one-atom thick carbon layer (graphene) as a universal representation of flat-lying organic molecular adlayers. The solution of the one-dimensional Schrödinger equation for this model potential yields the energy and the wave function of the image-potential states [Armbrust *et al.* New J. Phys. **17** (2015) 103043] as well as of the interface state that emerges from the former *Shockley* state or resonance of the clean metal surface.

The energy of the interface state is highly sensitive to the bonding distance between the plane of the carbon backbone and the metal substrate. If the bonding distance is known, e.g. from X-ray standing wave experiments, the model predicts the energy position of the interface state as well as the overlap of its wave function with the bulk metal. Both parameters critically influence the charge carrier dynamics at the organic/metal interface.

Numerous experimental results for different flat-lying organic molecules on various closed-packed metal surfaces closely follow the systematic trend of the interface state's energy calculated within the range of measured bonding distances. This comparison demonstrates the applicability and robustness of the model.



Probability density $|\psi(z)|^2$ of the interface state (IS, solid red line) for a carbon layer with a typical bonding distance $d_{m\text{-}C}$ on a metal substrate as calculated using the analytical one-dimensional model potential (solid blue line)

Investigation of the potassium doping of DBP on Ag(111) by photoelectron spectroscopy

Felix Otto, Christian Udhardt, Tino Kirchhuebel, Bernd Schröter, Roman Forker, and Torsten Fritz
Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany
e-mail: felix.otto@uni-jena.de

Tetraphenyldibenzoperiflanthene (DBP, $C_{64}H_{36}$) has been explored for some years because of its possible use in organic electronics [1]. DBP consists of an aromatic backbone with four phenyl rings attached nearly perpendicular to the molecular plane. We analyzed the change of electronic properties due to the doping process of this organic dye with potassium. Special attention is paid to the possible adsorption sites of the potassium atoms and the resulting charge transfer in the organic/inorganic heterosystem. We used *in situ* differential reflectance spectroscopy (DRS) to determine changes of the optical properties due to the potassium deposition [2, 3]. These results are compared with x-ray (XPS) and angle resolved ultraviolet photoelectron spectroscopic (ARUPS) measurements to elucidate the charge transfer between the alkali metal and DBP. Furthermore effects on the electronic structure are discussed in terms of lowest unoccupied molecular orbital (LUMO) filling and the evolution of an interface dipole.

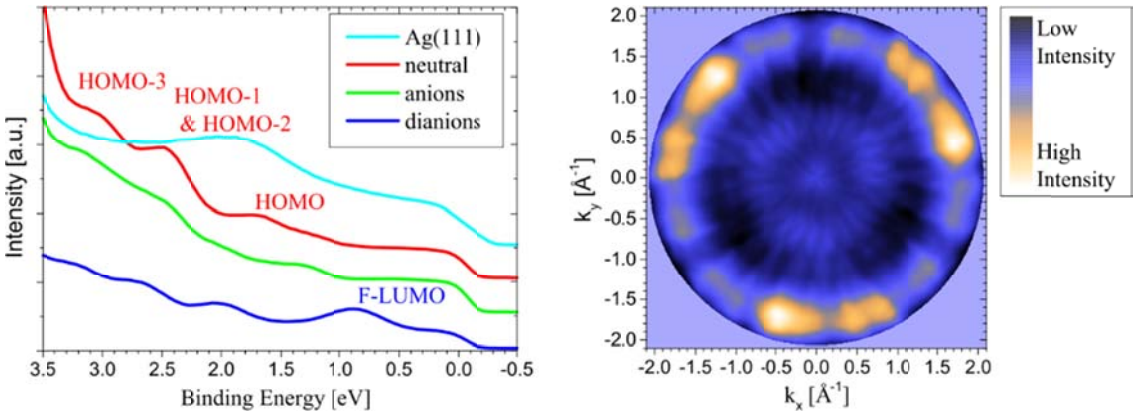


Fig. 1 UPS investigation of 0.7 ML DBP on Ag(111). *Left:* angle integrated UP spectra with an increasing potassium concentration from neutral molecules to dianions. *Right:* k-resolved intensity distribution of the filled former LUMO of the neutral molecule.

[1] J. D. Debad *et al.*, J. Am. Chem. Soc. **118**, 2374 (1996).
[2] R. Forker and T. Fritz, Phys. Chem. Chem. Phys. **11**, 2142 (2009).
[3] R. Forker *et al.*, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. **108**, 34 (2012).

Metalation reactions of corroles at metal-organic interfaces

Malte Zugermeier[1], Nicolas Bock[1], Min Chen[1], Falk Niefind[1], Jan Herritsch[1], Lukas Ruppenthal[1], Martin Schmid[1], Peter Schweyen[2], Martin Bröring[2], J. Michael Gottfried[1]

[1] Department of Chemistry, Philipps-Universität Marburg, Germany

[2] Institute for Inorganic and Analytical Chemistry, Technische Universität Braunschweig, Germany

e-mail: zugermeier@chemie.uni-marburg.de

Tetrapyrroles such as porphyrins and phthalocyanines undergo well-defined coordination reactions at interfaces. In particular, they react with atoms from a metal surface (or with co-adsorbed metal atoms) to form the corresponding metal complexes. This reaction includes oxidation of the metal to its cation. The porphyrins and phthalocyanines studied so far lead to the +2 oxidation state of the metal ion.[1] Corroles differ from porphyrins by the absence of a methin group in the macrocycle. The resulting size-reduced cavity provides a tighter coordination environment and stabilizes higher oxidation states.[1,2] In addition, the corrole contains three aminic hydrogen atoms and thus can potentially oxidize metal atoms to their +3 oxidation state. However, metallo-corroles with a +2 or even +1 oxidation state have also been observed, making it a non-trivial question which oxidation state is reached by the interfacial coordination reaction. For insight into the interfacial coordination chemistry of corroles, we have studied monolayers and multilayers of an octa-alkyl corrole and their reaction with Co and Ni by XPS, UPS, NEXAFS and STM. In the case of Co, the data unambiguously indicate the formation of a Co(III) corrole complex. At the metal/organic interface, the corrole-bound Co(III) ions interact substantially with the metal surface, but retain an electronic state that is distinctly different from that of Co(II) ions in porphyrins in the same environment. Our experiments show that the valence electronic structure of the interfacial Co(III) system is similar to the related Fe(II) system in the same environment. This remarkable result may reflect the fact that Co(III) and Fe(II) are isoelectronic. In the case of Ni, comparison of the corrole complex with a Ni(II) porphyrin shows differences in the valence electronic structure, indicating that reaction between Ni and corrole does not lead to a Ni(II) complex. As a related aspect, it was found that the corrole undergoes an interface reaction with Ag(111) from 240 K on, resulting in the loss of one aminic hydrogen atom. This is very different from the behavior of free-base porphyrins and phthalocyanines, which do not undergo N-H bond dissociation on Ag(111) even at elevated temperatures.

[1] J. M. Gottfried, *Surf. Sci. Rep.* **2015**, 70, 259-379.

[2] I. Aviv, Z. Gross, *Chem. Commun.* **2007**, 1987-1999.

Free-base 5,10,15-tris(pentafluorophenyl)corrole adsorption on Ag(111)

Hazem Aldahhak[1], Mateusz Paszkiewicz[3], Stefano Tebi[2], Eva Rauls[1], Uwe Gerstmann[1], Stefan Müllegger[2], Florian Klappenberger[3], Wolf Gero Schmidt[1]

[1] *Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, Germany*

[2] *Festkörperphysik, Universität Linz, Austria*

[3] *Physik Department E20, Technische Universität München, Germany*

e-mail: aldahhak@mail.uni-paderborn.de

Tetrapyrrole compounds such as porphyrins and corroles, are intriguing macrocycles omnipresent in diverse science fields. While corroles are structurally closely related to porphyrins, their compounds have lower symmetry and smaller cavities, which enables them to stabilize metal ions in exceptionally high oxidation states. This makes them highly interesting molecules for a variety of applications in medicine, catalysis, sensors as well as for solar cells [1, 2]. For the related higher-symmetry compounds (porphyrins and phthalocyanines), intensive studies have been carried out to disclose their interfacial properties. In contrast, only few studies on the surface-supported corroles have been performed so far.

First principles calculations have been performed to investigate the adsorption of the free-base 5,10,15-tris(pentauorophenyl)corrole on Ag(111) surface. The theoretical approach was supported by complementary scanning tunneling microscopy (STM) as well as X-ray photoelectron spectroscopy (XPS) measurements. Both single adsorbed molecules as well as monolayer thin films have been studied. Single molecules adsorb with their macrocycles tilted with respect to the surface. The tilted adsorption geometries enable the molecules to aggregate in non-trivial interwoven monolayer structures. The simulated STM data [3] as well as the simulated X-ray photoelectron spectroscopy (XPS) data for the C1s, F1s and N1s edges in conjunction with the measurements nicely confirm the site-selective single deprotonation reaction of a specific N atom as well as a ring-closing reaction taking place between a fluorophenyl ring and the macrocycle upon annealing to 430 K [4].

[1] Z. Gross and N. Galili, Angew. Chem. Int. Ed., 1999, 38, 2366.

[2] R. Paolesse, L. Jaquinod, D. J. Nurco, S. Mini, F. Sagone, T. Boschia, and K. M. Smith, Chem. Commun., 1999, 307.

[3] S. Tebi, H. Aldahhak, G. Serrano, W. Schöfberger, E. Rauls, W. G. Schmidt, R. Koch, and S. Müllegger, Nanotechnology 27, 2016, 025704.

[4] M. Paszkiewicz, H. Aldahhak, S. Tebi, E. Rauls, U. Gerstmann, P. Deimel, P. Casado Aguilar, D. A. Duncan, A. C. Papageorgiou, Y.-Q. Zhang, F. Allegretti, W. Schöfberger, S. Müllegger, R. Koch, W. G. Schmidt, J. V. Barth, F. Klappenberger. JACS (submitted, 2016).

PTCDA molecules on Terraces and at Steps Sites of the KCl(100) and NaCl Surfaces

Hazem Aldahhak, Eva Rauls and Wolf Gero Schmidt
Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, Germany
e-mail: aldahhak@mail.uni-paderborn.de

The adsorption of PTCDA ($C_{24}H_8O_6$) on metal substrates has for a long time been used as model system for understanding molecular self-assembly. Ionic crystals as substrate provide the additional possibility to study the molecular properties with little perturbation by substrate screening or strong substrate-adsorbate bonds [1].

Here, we present density-functional theory calculations on the adsorption and the adsorbate-substrate interactions between PTCDA and planar as well as stepped NaCl or KCl surfaces. The adsorption is dominated by van-der-Waals and electrostatic forces. This leads to a site-specific adsorption of the molecule on the surface, resulting in commensurate long-range ordered structures [2]. The influence of the substrate and bonding mechanism on the molecular electronic structure is investigated in detail and compared with the experimental data available [3-5]. Our calculations for different kinds of step-edge defects show the importance of these surface defects for initiating the adsorption of organic molecules on ionic surfaces. Experimental and theoretical investigations indicate the so-called vacancy sites, formed by expelling a KCl molecule from the step edge, to be a thermodynamically favored process.

[1] V. W. Henrich, P.A Cox, The surface of metal Oxides, vol.1, Cambridge University Press, 1996.
[2] H. Aldahhak, W.G. Schmidt, E. Rauls, Surf. Sci. 617, 242, 2013.
[3] Q. Guo, A. Paulheim, M. Sokolowski, H. Aldahhak, E. Rauls, W.G. Schmidt. The Journal of Physical Chemistry C 118 (51), 29911-29918, 2014.
[4] H. Karacuban, S. Koch, M. Fendrich, Th. Wagner, R. Möller, Nanotechnology, 22, 295305, 2011.
[5] A. Paulheim, M. Müller, C. Marquardt, M. Sokolowski, Phys. Chem. Chem. Phys.15, 4906, 2013.

Probing PET with fluorescence switch off-on perylene diimides

Eduard Baal[1], Robin Döring[2], Sangam Chatterjee[2], Jörg Sundermeyer[1]
[1] *Department of Chemistry, Philipps-Universität Marburg, Germany*
[2] *Department of Physics, Philipps-Universität Marburg, Germany*
e-mail: baale@staff.uni-marburg.de

Perylene-3,4,9,10-tetracarboxylic acid diimides (PDIs) are well-known pigments and high performance materials in organic electronics. We synthesized a series of *N*-amino-substituted PDIs that exhibit a strong and unusual fluorescence quenching. The distance between the amino (donor) moiety and the perylene core (acceptor) was modified to investigate the distance dependence of the quenching process. Additionally the effect of protonation was taken into account. Using time-resolved photoluminescence (TRPL) measurements an ultrafast decay of luminescence was observed for the neutral PDI compounds. The protonated PDIs on the other hand showed a significantly stronger photoluminescence and a slower decay of luminescence.
In addition DFT calculations were carried out to explain a possible intramolecular charge transfer.

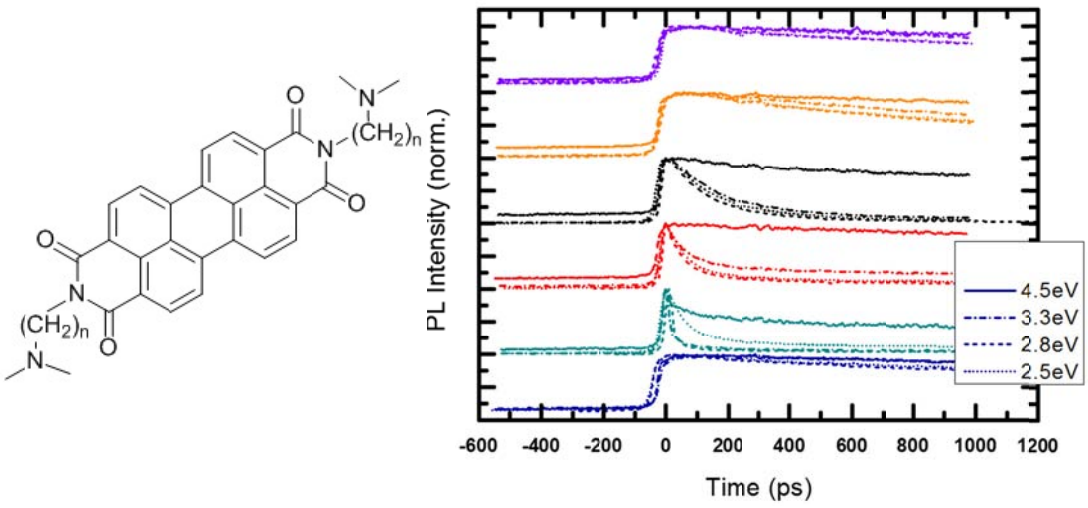


Fig. 1: Chemical structure and corresponding TRPL measurements.

Energy transfer in thin layers of PTCDA on Ag(111) and Au(111). A combined 2PPE and streak camera experiment

Andreas Namgalies, Sangam Chatterjee, Ulrich Höfer
Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, 35032 Marburg, Germany
e-mail: Andreas.Namgalies@Physik.uni-marburg.de

The energy transfer from a metal cathode into an organic semiconductor and the reverse process, the quenching of excited molecular states, is of fundamental importance for the understanding and optimization of organic electronics. We investigate thin films of PTCDA from coverages of 30 monolayers down to single layers on Ag(111) and Au(111) by combining the advantages of high resolution time-resolved photo-luminescence (PL) and two-photon photoemission spectroscopy (2PPE).

In picosecond time-resolved streak-camera measurements we analyze the decay of excited states within the organic layers and find a strong thickness dependent quenching in the vicinity of the metal. Three molecular states could be separated and their transients were compared to known quenching models. By 2PPE we detect the end result of the charge transfer, hot electrons at the metal-organic interface and expand the resolvable layer thickness down to a monolayer.

By combining both methods, we were able to identify the CT-exciton as the major component of the electron transfer. Furthermore we find, that both the direct dipole-dipole transfer and the hopping transport are required to describe the transients of the arriving charges. The different metal substrates show a particularly unequal influence on the lifetime for thin layers.

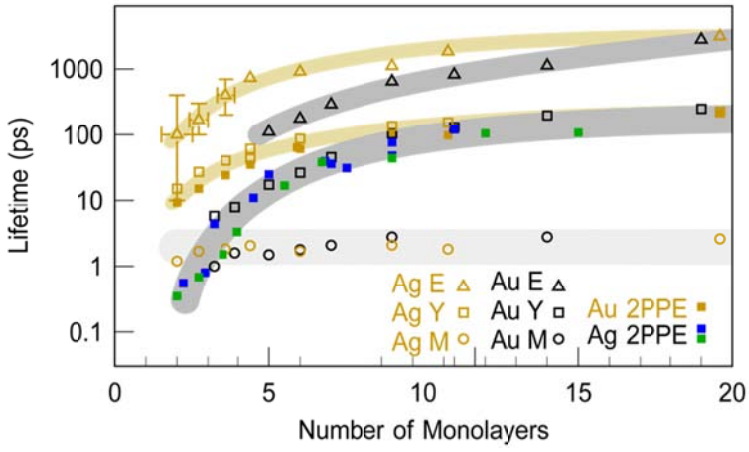


Fig. 1: Thickness dependent lifetimes of PTCDA/Ag(111) and PTCDA/Au(111), extracted from the long lived section of the PL and 2PPE transients. The CT-excitons (Y) within the organic layers show a lifetime identical to the incoming electrons (2PPE) at the metal interface. The quenching on the Au(111) substrate is significantly weaker for low coverage.

Structure and vibrational properties of the PTCDA/Ag(111) interface: Bilayer vs. monolayer

N. Zaitsev[1], P. Jakob[2] and R. Tonner[1]
[1] *Department of Chemistry, Philipps-Universität Marburg, Germany*
[2] *Department of Physics, Philipps-Universität Marburg, Germany*
e-mail: nikolay.zaitsev@chemie.uni-marburg.de

Organic molecular thin films are currently of great interest because of their possible applications in micro- and optoelectronic devices. Their performance strongly depends on the physicochemical properties of the metal-organic interface. A comprehensive description of the first organic layer on the metal substrate and the influence of the second adlayer can provide an improved understanding of the growth kinetics of organic layers with well-defined properties.

In this work, we have examined PTCDA/Ag(111) by means of density functional theory (DFT) calculation accounting for long-range dispersive forces within the vdW-DF method. The focus was on a comparative study of the vibrational properties of the monolayer and bilayer of PTCDA molecules on Ag(111). The equilibrium adsorption height of the monolayer of PTCDA/Ag(111) with the experimentally observed arrangement of the molecules was found to agree with the measurements. The vibrational modes and IR intensities of the PTCDA monolayer on silver were computed in harmonic approximation and were found to be in a good agreement with the infrared absorption spectrum.

We have examined several stable geometries of the bilayer PTCDA/Ag(111) with different position of the second layer with respect to the first one. The arrangement of the molecules in the second adlayer was kept the same as in the first layer. In case of the most favorable adsorption geometry of the bilayer, the first monolayer remains almost unchanged. The detailed analysis of the vibrational spectrum revealed the insignificant influence of the second adlayer on the structural, electronic and vibrational properties of the interface between Ag(111) and the ordered monolayer of PTCDA molecules.

These results show that already a monolayer of organic molecules creates a metal-organic interface, and the interface properties are hardly altered by increasing the thickness of the organic adlayer.

Structure and thermal stability of molecular heterolayer structures on Ag(111)

Sebastian Thussing, Laura Fernandez, Peter Jakob
Department of Physics, Philipps-Universität Marburg, Germany
e-mail: thussins@staff.uni-marburg.de

The growth of highly ordered molecular films exceeding the first few monolayers represents a challenge as these layers are inherently unstable and susceptible to dewetting processes. Understanding the kinetics of associated phase transformations and proper characterization tools are therefore crucial in such studies. We have investigated the thermal stability and intermixing of various heterolayer model systems (stacked CuPc/PTCDA and TiOPc/PTCDA layers grown on Ag(111)) by means of analyzing the characteristic vibrational modes of these molecules using IR spectroscopy. In addition, SPA-LEED provided information regarding the lateral ordering of these layers. Bilayers of TiOPc, and CuPc for comparison, have been combined with PTCDA contact primer layers or capping layers. The TiOPc bilayer exhibits exceptional thermal stability with minimal intermixing with the underlying or capping PTCDA layers up to T ≈ 450K (see fig. 1). This is in contrast to the growth of a CuPc bilayer on PTCDA/Ag(111) which shows negligible intermixing but CuPc cluster formation already at T ≈ 250K. The reversed stacking sequence, PTCDA on a bilayer CuPc/Ag(111), reveals intermixing starting at about 300K.

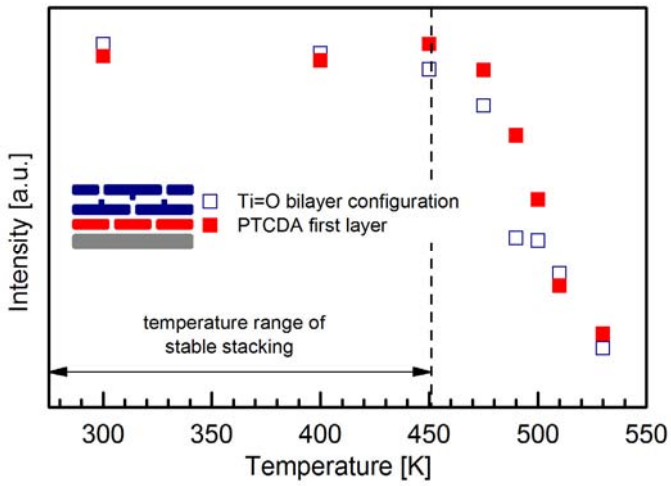


Fig. 1 Thermal evolution of stacked bilayer TiOPc grown on top of PTCDA/Ag(111). The intensity of the characteristic vibrational modes of the PTCDA monolayer and the bilayer configuration of TiOPc is shown as a function of annealing temperature.

Copper-phthalocyanine payer as contact primer for organic semiconductor films grown on coinage metals

Alexander Mänz and Gregor Witte
Faculty of Physics, Philipps-Universität Marburg, Germany
e-mail: maenz@uni-marburg.de

Functional molecular thin films have attracted significant interest in the field of organic electronics because of their ability to modify interfacial electronic properties, for instance, the work function of metal electrodes. As an alternative to SAMs, which have the disadvantage of low conductivity through their backbone and the sulfur anchor group, we propose here the use of monolayers of extended π-conjugated molecules. Promising candidates for this purpose are phthalocyanines (Pc) because they offer a large diversity of chemical functionalization and adopt planar adsorption geometry on metals which allows a large contact area. In this study we exemplarily used copper phthalocyanine (CuPc) monolayers as a contact primer for the subsequent growth of the organic semiconductor pentacene (PEN) on single crystalline surfaces of the coinage metals Au, Ag and Cu. Temperature dependent XPS und TDS measurements were employed to characterize the onset of CuPc multilayer desorption, which enables the preparation of highly ordered monolayer films by selective desorption of multilayers upon gentle heating as confirmed by STM. Afterwards PEN films were grown by means of organic molecular beam deposition and their morphology, molecular orientation and crystalline structure were investigated by means of AFM, NEXAFS and XRD. In contrast to more plate-like shaped aromatic molecules, like PTCDA, we found that PEN only initially adopts a recumbent orientation but continues to grow in an upright orientation and forms (001)-oriented poly-crystalline films for all studied metal substrates.

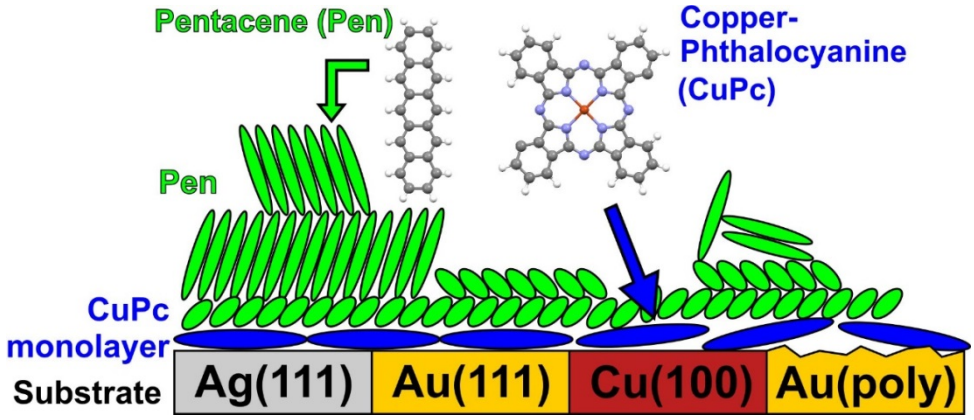


Fig. 1: CuPc monolayer as contact primer for pentacene multilayers on different metal substrates

Growth and vibrational properties of ultra-thin TiOPc films on Ag(111)

Laura Fernández, Sebastian Thussing, Alexander Mänz, Gregor Witte, Peter Jakob
Department of Physics, Philipps-Universität Marburg, Germany
e-mail: Laura.Fernandez-GR@physik.uni-marburg.de

The coverage dependent growth of titanyl-phthalocyanine (TiOPc) ultra-thin films on a Ag(111) surface has been studied using IR Spectroscopy, SPA-LEED, STM and TDS. In the monolayer regime three different phases were found (T_{growth}=300K), all of them with parallel orientation and in an "oxygen-up" configuration of the Ti=O: a 2D-gas phase in the low coverage regime ($\theta <$ 0.6 ML), a commensurate (4√3×7)rect phase for 0.8-0.9 ML, and finally, a point-on-line phase when the coverage approaches saturation (1 ML). While the IR spectra of the monolayer phases vary only slightly the vibrational modes corresponding to the monolayer and bilayers of TiOPc/Ag(111) are distinctly different, so that the transition from the monolayer to the bilayer regime is clearly defined. A microscopic model for the growth of the TiOPc bilayer, which involves specific local configurations of molecules in the first and second layer is suggested based on IR and STM data (Fig.1). Thermal desorption spectroscopy measurements reveal a high thermal stability of the TiOPc bilayer, which requires temperatures above 500K for the desorption of the second layer from the TiOPc monolayer. The unusual intrinsic stability of the TiOPc bilayer qualifies this system to be combined with other π-conjugated molecules, e.g. to design molecular heterolayer structures with a stable and well defined interface.

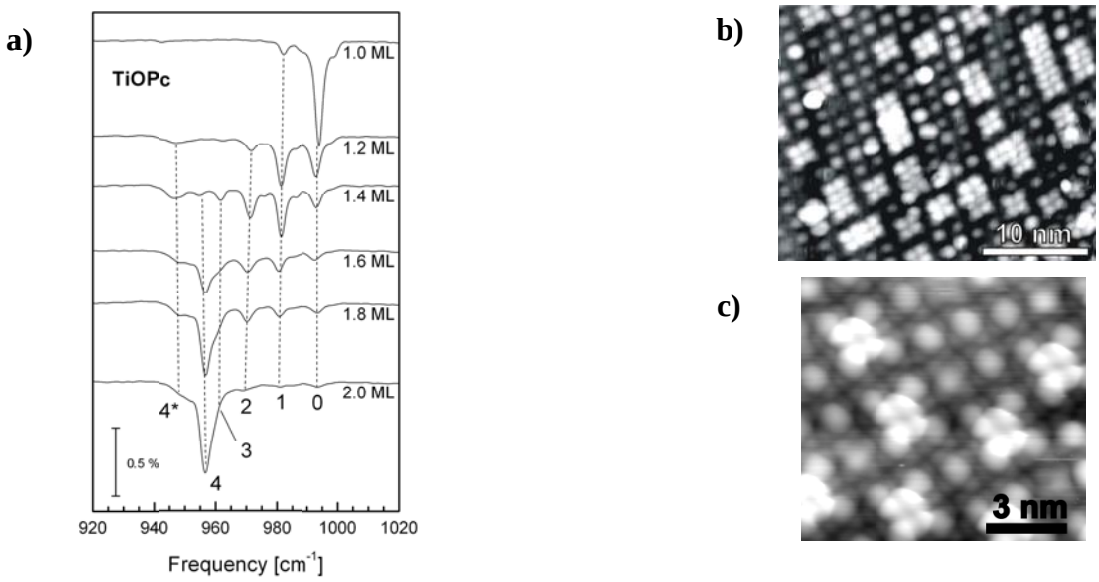


Fig. 1: (a) Evolution of IR spectra of TiOPc grown on Ag(111) with increasing film thickness. The displayed spectra focus on the frequency variation of the Ti=O stretching mode in the 1-2ML coverage regime. (b) STM measurement of 1.3 ML TiOPc/Ag(111). (c) Magnified micrograph of the sample in (c) showing the 'oxygen-up' configuration of the Ti=O group in the first layer as well as the 'oxygen-down' configuration of second layer TiOPc.

A combined 2PPE and LEED study of tin-phthalocyanine on Ag(111)

Stephan Jauernik, Petra Hein, Max Gurgel, Julian Falke and Michael Bauer
Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Germany
e-mail: jauernik@physik.uni-kiel.de

Recently, the adsorption of tin-phthalocyanine (SnPc) on Ag(111) has attracted considerable interest due to peculiarities in the adsorbate-substrate interaction and switching capabilities reported for the adsorbed SnPc [1]. In a combined Low Energy Electron Diffraction (LEED) and Photoemission/Two-Photon Photoemission (PES/2PPE) study we address in this work how structural and the electronic properties of this model system are correlated in the sub-monolayer coverage regime. Photoemission data are recorded using a widely tunable noncollinear optical parametric amplifier which offers the possibility to excite various resonant transitions from the occupied to the unoccupied electronic metal/organic structure. The study focuses on the transition regime from a gas – like phase at coverages < 0.90 monolayers (ML) to an incommensurate phase observed for coverages between 0.90 ML and 1.0 ML. The photoemission data reveal distinct changes in the occupied as well as unoccupied electronic structure of this model-type adsorption system as the coverage increases. Due to the coverage dependent reduction of the unit cell of the SnPc superstructure, molecular orbitals (MO) are pushed together in reciprocal space resulting in clear peak shifts around Γ. Furthermore, a backfolding of dispersive bands is observed due to the formation of the SnPc superstructure.

The experimental results are discussed under consideration of past LEED, STM and STS studies [1,2].

[1] C. Stadler *et al.*, Nature Physics 5, 153–158 (2009)
[2] Y. Wang *et al.*, J. Am. Chem. Soc., 2009, 131 (10), 3639–3643

The electronic structure at the TiOPc/Ag(111) interface

Frederik Schiller[1,2], Alexander Lerch[1], Antón Brión-Rios[2], Pepa Cabrera-Sanfelix[3], Daniel Sanchez-Portal[2,3], and Ulrich Höfer[1]

[1] *Department of Physics, Philipps-Universität Marburg, Germany*
[2] *Centro de Física de Materiales, CFM-CSIC, San Sebastián, Spain*
[3] *Donostia International Physics Center, San Sebastián, Spain*
e-mail: frederikmichael.schiller@ehu.es

Molecular electronics is tied to the transport properties at the molecule-metal interface. Several effects have to be considered for a proper design of that combination. On one hand side the structure and on the other hand side also the chemical bonding at the metal/molecular interfaces determines the electronic properties. Here we report on the electronic structure at the TiOPc/Ag(111) interface. For 1 and 2 monolayer (ML) thick TiOPc layers the lowest unoccupied molecular level (LUMO) is found to be situated very close to the substrate Fermi level but gets unoccupied above this thickness. The highest occupied molecular orbital (HOMO) shifts with thickness to higher binding energies, eventually establishing the bulk HOMO-LUMO gap for thickness above 2 ML. Additionally the Ag(111) substrate Shockley type surface state is transformed into an unoccupied interface state that can be observed at integer monolayer coverage. The effective mass of the interface state is relatively high compared to other phtalacyanine molecules on Ag(111). Also the lifetime of the state is shorter than previously reported [1]. Both effects are assumed to be related to a hybridization of the interface state with the LUMO levels. First principle calculations are carried out to determine the electronic structure at the interface and to compare the experimental results.

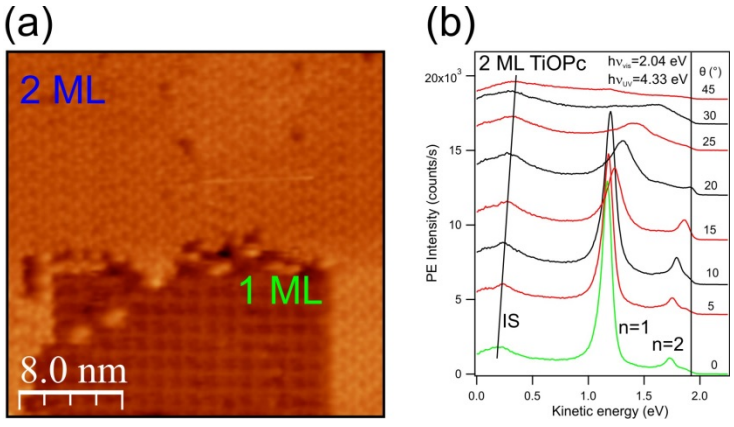


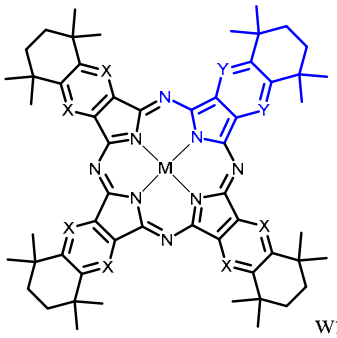
Fig. 1: (a) STM image revealing the different structure of the 1 and 2 ML thick TiOPc films at a coverage of 1.5 ML. (b) Angle-resolved two-photon photoemission of unoccupied bands: The interface state and the image potential states (n=1 and n=2) can be observed as a function of emission angle.

[1] B. W. Caplins, D. E. Suich, A. J. Shearer, and C. B. Harris; J. Phys. Chem. Lett. 5, 1679 (2014)

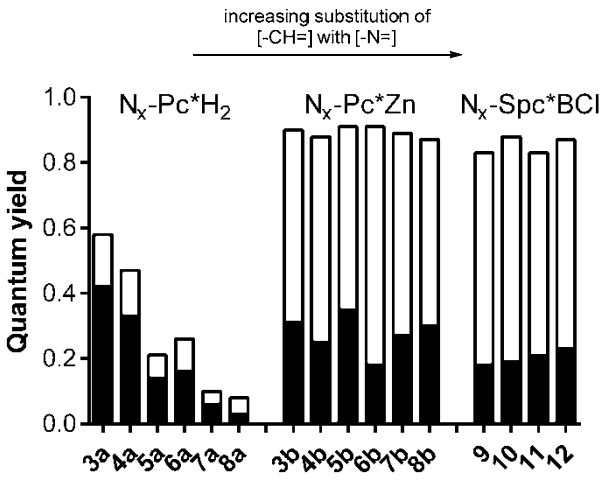
Experimental and computational study of soluble azaphthalocyanines and azasubphthalocyanines of varying number of aza units

Martin Liebold[1], **Ralf Tonner**[1], **Petr Zimicik**[2] **Jörg Sundermeyer**[1]
[1] *Department of Chemistry, Philipps-Universität Marburg, Germany*
[2] *Department of Pharmacy, Charles University of Prague, Czech Republic*
e-mail: lieboldm@staff.uni-marburg.de

The focus of the project within the DFG research cluster SFB 1083 *"Structure and Dynamics at Internal Interfaces"* is the synthesis and photophysical characterisation of new phthalocyanines (Pc), tetrapyrazinoporphyrazines (Ppz) and their hybrid compounds, so called azaphthalocyanines (N_x-Pc*H_2).



with M = Zn, or 2 H
X, Y = CH: Phthalocyanine (Pc*M)
X, Y = N: Pyrazinoporphyrazine (Ppz*M)
X = CH, Y = N: Azaphthalocyanine (N_x-Pc*M)



Measured Φ_Δ (blanc) + Φ_F (black) for N_x-[Spc*BCl] and N_x-[MPc*] series.

These compounds were synthesized in a random cocyclisation of peripheral alkyl-substituted dinitriles. These alkyl-moieties increase the solubility and minder aggregation effects whereas the symmetry of the molecule is maintained. Furthermore, this substitution makes a chromatographic separation and a systematic study of all compounds possible.

The azaphthalocyanines have been characterized by micro-CV and by correlating it with UV/Vis spectroscopy. The *Q*-bands of the azaphthalocyanines are between 655 – 710 nm. Thereby, a design of the HOMO/LUMO gap as well as the absolute HOMO/LUMO level is possible. Experimental values were compared to TD-DFT calculations.

In addition, the ability to form singlet oxygen via energy transfer from an excited triplet state after ISC (Φ_Δ) and the fluorescence quantum yield (Φ_F) was determined. The sum of $\Phi_\Delta + \Phi_F$ values is for the N_x-[Pc*Zn] series ~0.9. In comparison, N_x-Pc*H_2 shows a significant decrease of $\Phi_\Delta + \Phi_F$.

The influence of the HOMO/LUMO alignment in connection with exciton dynamics, charge transfer processes, and optical properties of heterojunction interfaces is essential for the understanding of semiconductor interfaces in physics.

Charge transfer channels between metal phthaloycanines and ferromagnetic substrates

Jing Guo[1], Volodymyr Dzhagan[1], Dmitry Smirnov[2], Georgeta Salvan[1], Dietrich R. T. Zahn[1]

[1] Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany
[2] Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin, Germany
e-mail: Jing.guo@Physik.tu-chemnitz.de

We studied the molecular orientation and the electronic structure of the phthalocyanines FePc, CoPc, and CoPc on cobalt and nickel substrates by near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The results show thickness dependent orientation of CoPc and FePc on metal substrates determined by the molecule-substrate interaction up to about 1 nm and by molecule-molecule interaction at higher film thicknesses. The suppression of the π-orbital features in the C 1s and N 1s NEXAFS spectra of FePc/Co and CoPc/Ni at the initial deposition stage indicates a charge transfer from the substrate to the pyrrole ring in the molecule. For CoPc/Co, however, C and N are far less involved in the charge transfer while the Co*3d* orbital accepts charge from the substrate which leads to the formation of an interfacial state at the Fermi level. Thus, both the center atom and the substrates play an important role in mediating the charge transfer at the interfaces.

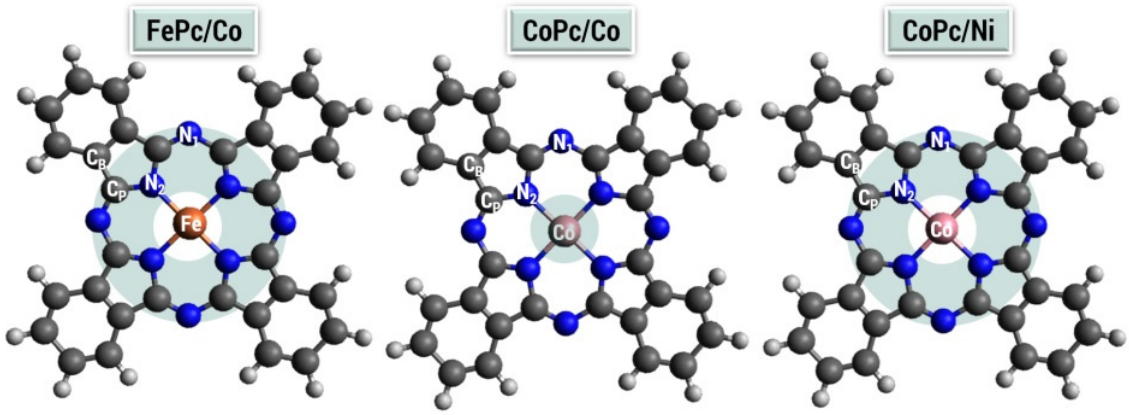


Fig. 1 Schematic diagram of different charge transfer channels for FePc/Co, CoPc/Co, and CoPc/Ni. The shaded regions represent charge transfer channels at the interfaces.

Low temperature deposition of oriented zinc phthalocyanine thin films and their optical characterization

Michael Kothe[1], Ingo Meyenburg[1], Benjamin Heidelmeier[1], Malcolm Bartlett[2], Wolfram Heimbrodt[1], Jörg Sundermeyer[2] and Gregor Witte[1]
[1] Department of Physics, Philipps-Universität Marburg, Germany
[2] Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: michael.kothe@physik.uni-marburg.de

Large radiation resistance and rich coordination chemistry distinguish phthalocyanines as robust organic semiconductors and dyes that are widely used in organic electronic devices. Though crystalline films with predefined molecular orientation can be prepared by choosing adequate templating substrates, rather higher growth temperatures are required to achieve a high degree of ordering because of the low diffusivity of such large molecules. Here, we demonstrate that addition of an anchoring unit enables a covalent fixation and thus a control of molecular orientation of thin films that can be prepared by immersion even at room temperature. For that purpose a modified zinc phthalocyanines was synthesized that comprises a thioacetat anchor group in order to enable a thiolate coupling to a gold substrate as well as butyl side groups to enhance the solubility. By means of NEXAFS measurements the molecular orientation was determined which yield an upright orientation for the anchored molecules whereas molecules without such anchoring reveal no preferential orientation. In addition to the structure also the optoelectronic properties of the differently substrate coupled films were characterized by absorption and photoluminescence spectroscopy.

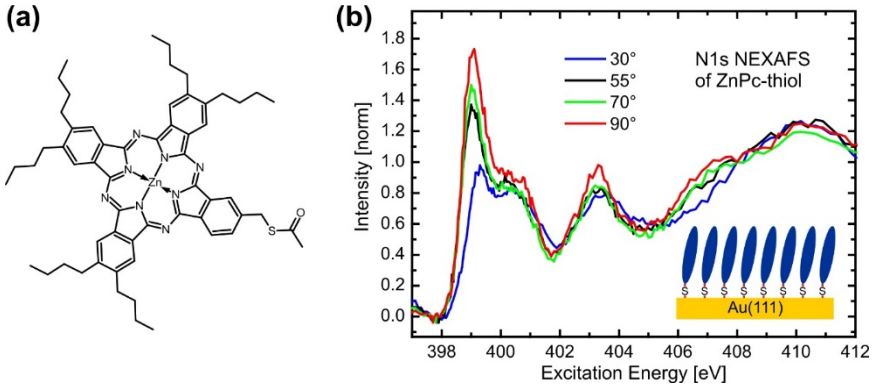


Fig. 1: (a) Scheme of the newly synthesized zinc phthalocyanine functionalized with a thioacetat anchor group and additional butyl side groups. (b) N1s NEXAFS spectra of the molecular film prepared by immersion of an Au(111) surface. The quantitative analysis of the NEXAFS dichroism yields an upright molecular orientation as shown schematically in the inset.

Two-photon photoemission from tetraphenylporphyrins on Ag(100)

Andrej Classen[1], Rebecca Pöschel[1], Gianluca Di Filippo[1], Osman Baris Malcioglu[2], Michel Bockstedte[2], Thomas Fauster[1]

[1] Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Staudtstraße 7, 91058, Erlangen, Germany

[2]Lehrstuhl für Theoretische Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Staudtstraße 7, 91058, Erlangen, Germany

e-mail: gianluca.filippo@fau.de

Porphyrins are a class of π-conjugated organic molecules of high technological interest. Their optical, electronic and chemical properties make them very suitable for energy production in solar cells, phototherapy, and catalysis [1,2]. Therefore the investigation of these systems, their excited states and their interaction with inorganic substrates is essential.

In this work ultrathin films of two different tetraphenylporphyrins (2HTPP and MgTPP) were grown in-situ under UHV-conditions on a well-defined Ag(100) single crystal. The molecules were deposited by evaporation from a home-built Knudsen-cell evaporator. The substrate was kept at room temperature and layer thicknesses range from one monolayer of molecules (1 ML) up to multilayer films (19 ML). We present an investigation of the electronic structure using ultraviolet photoelectron spectroscopy and monochromatic two-photon photoemission (2PPE). The occupied molecular orbitals of 2HTPP and MgTPP were measured using a photon energy of 21.22 eV (HeI-radiation). 2PPE probes the unoccupied molecular orbitals. The combination of both yields a HOMO-LUMO gap of 4.2 eV (MgTPP) and 4.3 eV (2HTPP) in accordance with literature [3]. Taking the measured work function into account, the ionization potential is 5.9 eV (MgTPP) and 6.1 eV (2HTPP) [4]. The electron affinity is 1.7 eV (MgTPP) and 1.8 eV (2HTPP). The obtained results are compared to GW calculations for the free molecules. Finally, the 2PPE intensity as a function of photon energy in the range from 3.08 eV to 3.38 eV follows the absorption spectrum (Soret band) of tetraphenylporphyrin.

[1] W. Auwärter *et al.*, Nature Chemistry, **7**, 105 (2015)

[2] J. M. Gottfried, Surf. Sci. Rep. **70**, 259 (2015)

[3] X. Blase *et al.*, Phys. Rev. B **83**, 115103 (2011)

[4] Y. Nakato *et al.*, Chem. Phys. Lett. **39**, 358 (1976)

Analysis of buried metal-semiconductor interfaces with Hard X-ray Photoelectron Spectroscopy (HAXPES)

Benedikt P. Klein, Malte Zugermeier, Min Chen, Martin Schmid, J. Michael Gottfried
Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: kleinbe@students.uni-marburg.de

The performance of organic-electronic devices depends on the electronic, chemical and geometric structure of interfaces between metals and organic semiconductors. Most previous model studies focused on monolayers of organic molecules on (mostly inert) single-crystal surfaces.[1] However, real devices comprise buried interfaces and often require the usage of low-work function metals, which react with the molecules, as electron-injecting electrodes. The resulting organometallic reactions are very complex and have rarely been investigated. Interdiffusion perpendicular to the interface plane leads to the formation of an extended reaction zone, an *interphase*, which influences the energy level alignment and the wave function overlap between metal and organic phase. A detailed chemical and structural understanding of this interphase is thus vital for the rational design of organic electronic devices. We have used chemical depth profiling with Hard X-ray Photoelectron Spectroscopy (HAXPES) to study diffusion and reaction processes during and after the formation of metal/organic interfaces. This requires varying the photon energy and thereby the escape depth of the resulting photoelectrons. Because of the requirements on the photon source the use of synchrotron radiation is mandatory. In our case the measurements took place at the HIKE endstation at the BESSY-II facility in Berlin.[2,3] The investigated model systems include cobalt on tetraphenylporphyrin (Co/2HTPP) as well as calcium on sexithiophene (Ca/6T). For Co/2HTPP, the N 1s XP signals of 2HTPP and the reaction product CoTPP can easily be distinguished and are used as a monitor for the diffusion depth of the Co atoms in the 2HTPP matrix. From the photon energy dependence of the XP signals, the extension of the reacted CoTPP layer between the pure metal (Co) and the pure organic phase (2HTPP) was determined to be 1.4 nm. This result is in good agreement with a Monte Carlo simulation using the SESSA program package.[4] In the Ca/6T system the sulfur 2p XP signal clearly shows the reaction and can be used to determine the reaction depth when the photon energy is varied. Of special interest with this system is the dependence of the reaction depth on the temperature of the substrate during deposition.

[1] J. M. Gottfried, *Surface chemistry of porphyrins and phthalocyanines*, Surf. Sci. Rep. **2015**, 70, 259.
[2] M. Gorgoi, S. Svensson, F. Schäfers, W. Braun, W. Eberhardt, Eur. Phys. J. Special Topics **2009**, *169*, 221.
[3] M. Gorgoi, *HIKE- High Kinetic Energy Photoelectron Spectrometer*, HZB/BESSY-II, **2012**.
[4] W. S. M. Werner, *Electron Transport in Solids for Quantitative Surface Analysis*, Surf. Interf. Anal. **2001**, *31*, 141.

The metal-organic pyrphyrin/Au(111) interface

Gerson Mette[1,*], Denys Sutter[1], Yeliz Gurdal[2], Stephan Schnidrig[2], Benjamin Probst[2], Marcella Iannuzzi[2], Jürg Hutter[2], Roger Alberto[2], and Jürg Osterwalder[1]

[1] *Physik-Institut, Universität Zürich, Schweiz*

[2] *Institut für Chemie, Universität Zürich, Schweiz*

[*] *Present address: Fachbereich Physik, Philipps-Universität Marburg, Germany*

e-mail: gerson.mette@physik.uni-marburg.de

Pyrphyrin, a tetradentate bipyridine based macrocycle, represents an interesting but widely unexplored molecular ligand. It shares some similarities with the far better known porphyrins, but it is constituted by pyridyl subunits instead of pyrroles. Metal complexes based on pyrphyrin ligands have recently shown promise as water reduction catalysts in homogeneous photochemical water splitting reactions [1]. Moreover, density functional theory calculations of Co-ligated pyrphyrin on TiO_2 indicate that the pyrphyrin molecules might be applied as molecular photosensitizer in organic photovoltaics [2].

In this study, we examined the structure of the metal-organic pyrphyrin/Au(111) interface and the metalation of the adsorbed molecules by means of low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT). Pyrphyrin coverages of approximately one monolayer and less were obtained by sublimation of the molecules on the single-crystalline substrate kept at room temperature. Depending on the coverage, the molecules self-assemble in two distinct phases of long-range molecular ordering. Cobalt deposition and subsequent annealing led to the formation of Co-ligated pyrphyrin molecules accompanied by a pronounced change of the molecular self-assembly. An intermediate state of the metalation reaction was observed and the reaction steps for the Co metalation of pyrphyrin molecules on Au(111) were established in a joint experimental and computational effort [3].

[1] E. Joliat et al., Dalton Trans., 2016, 45, 1737.

[2] Y. Gurdal et al., Phys. Chem. Chem. Phys., 2015, 17, 22846.

[3] G. Mette et al., Nanoscale, 2016, 8, 7958.

Investigation of coronene thin-films on Ag(111) using photoelectron spectroscopy

Christian Udhardt[1], Felix Otto[1], Tino Kirchhübel[1], Falko Sojka[1], Tobias Hümpfner[1], Bernd Schröter[1], Roman Forker[1], and Torsten Fritz[1]

[1] Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany

e-mail: Christian.Udhardt@uni-jena.de

Several metal-intercalated aromatic hydrocarbons, including potassium intercalated coronene, were found to have superconductive properties [Kubozono et. al, Phys. Chem. Chem. Phys. **13**, 16476 (2011)]. Preparing and investigating the organic materials as thin films on various substrates can give access to the underlying mechanisms of the observed superconductivity and make the materials available for a potential use in electronic devices. Here we characterize the electronic structure of the coronene molecules prepared as thin films in the monolayer range on Ag(111) using ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS). Comparing the results of k_x, k_y - dependent UPS measurements with those from low-energy electron diffraction (LEED) and density functional theory (DFT) calculations, we were able to reconstruct the alignment of the coronene molecules with respect to the Ag(111) surface. Results after doping the films with potassium are presented as well.

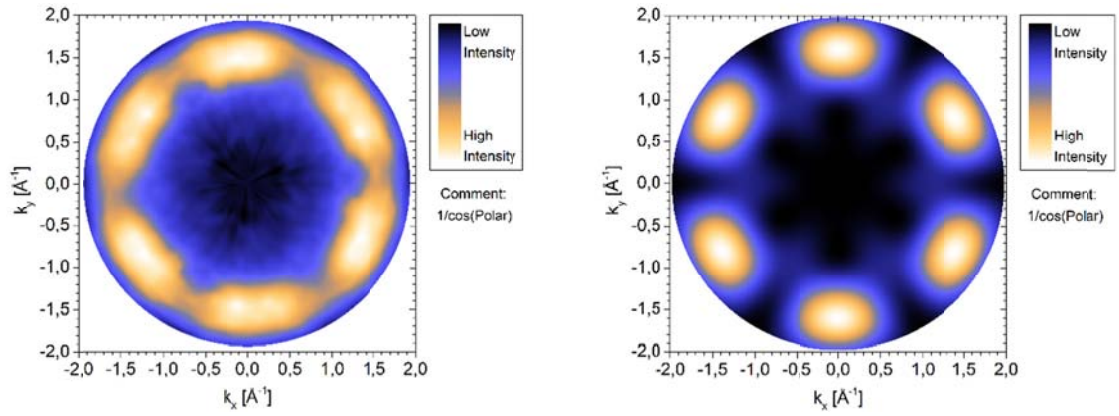


Fig. 1: k_x, k_y – dependent UPS measurement of 1 ML (left) in comparison to a simulation (right). The simulation is based on P. Puschnig et al., Science **326**, 702 (2009).

Band formation at the F_4TCNQ/Au(111) interface

David Gerbert and Petra Tegeder
Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany
e-mail: Gerbert@uni-heidelberg.de

In our ongoing efforts pointing towards a deeper understanding of the electronic properties at metal/organic interfaces a convenient approach is the characterization of well-ordered organic molecules adsorbed on single crystal noble metal surfaces. The F_4TCNQ/Au(111) interface appears to be a lucky strike for fundamental investigations of the interfacial electronic structure, providing deep insights into charge-transfer type interfacial interaction and molecule-induced band formation.

In this contribution we will present recent results from angle-resolved two-photon-photoemission (2PPE) spectroscopy of the F_4TCNQ/Au(111) interface leading to a detailed picture of the interfacial charge-transfer type interaction. Angle-resolved 2PPE measurements reveal band formation at the metal/organic interface which results in the observation of three dispersing electronic states. The former lowest unoccupied molecular orbital (LUMO), which becomes occupied due to a metal to molecule charge transfer, possesses a hole-like dispersion of $m^* \approx -0.6$ m_e. In contrast, two higher-lying unoccupied electronic states show an electron-like dispersion ($m^* > 1$ m_e).

Indium-tin-oxide (ITO) surface functionalization with organic self-assembled-monolayers

Julia Rittich, Sebastian Jung, Johannes Breuer, and Matthias Wuttig
I. Institute of Physics (IA), RWTH Aachen, Germany
Email: jrittich@physik.rwth-aachen.de

The performance of organic electronic devices such as organic thin film transistors (OTFT) or organic light emitting diodes (OLED) depends critically on the interfaces between the different layers, e.g. the organic layer and the electrodes. The alignment of the work function at the interface is a key criterion to improve charge transport in such devices.

The application of self-assembled monolayers (SAM) strongly influences the performance of such contacts. With this assembly, we have already achieved universal low work functions for noble metal contacts as well as improved device performance. Now we intend to transfer this concept to other electrodes. Therefore, we chose Tin doped Indium-Oxide (ITO), the most common material for transparent electrodes.

In this study, self-assembled monolayers with large nano-dipoles were used to tailor the work function of the ITO electrode. The used molecules are based on functional groups of carboxylic and phosphonic acids to anchor to the surface. In order to investigate the change in work function alignment to the organic layer as well as the coverage and arrangement of the surface dipoles, ultraviolet and X-ray photoelectron spectroscopy (UPS/XPS) measurements were performed.

Furthermore we could show that coating the source and drain contacts with self-assembled monolayers improved the contact resistance and overall performance of organic thin film transistors.

Optimization of charge carrier transfer in organic thin film transistors

Sebastian Jung, Julia Rittich, Dominik Meyer, Nils Norrmann, and Matthias Wuttig
I. Institute of Physics (IA), RWTH Aachen, Germany.
Email: Sebastian.Jung@physik.rwth-aachen.de

Organic devices such as light emitting diodes (OLED) and organic thin film transistors (OFET) play a crucial role in optoelectronic devices. In order to reach high efficiency in those devices it is critical to minimize energy losses at the interfaces between the different layers. We focus on tuning the work function of contact materials as a mean to enable alignment of the energy levels in a broad range. This permits even the usage of high work function materials such as Indium-Tin-Oxide in an inverted device geometry.

One way to achieve this is by applying self-assembled monolayers (SAM) between the active organic material and the device contact. We present a method to achieve a universal low work function for noble metals using self-assembled monolayers with large interface-dipoles. Furthermore, we transfer the concepts and methods learned from metal surfaces to achieve a tailored work function to transparent conductive oxides (TCOs). The alignment of the work function as well as the surface coverage were determined using ultraviolet and X-ray photoelectron spectroscopy (UPS/XPS).

We employ OFETs as test structures for the modification between electric contacts and active organic layers to demonstrate the efficiency of the concept chosen. The OFET characteristic clearly shows the potential of SAM modification in improving the device performance. Furthermore, we utilize in situ measurements of an OFET during its growth. The resulting data enable us to follow the formation of the first conductive path, showing effects which can be attributed to the closure of single layers of molecules.

Theoretical description of electronic and vibronic properties at interfaces between pentacene derivatives

Anna-Katharina Hansmann and Robert Berger
Department of Chemistry, Philipps-University Marburg, Germany
e-mail: Hansmana@students.uni-marburg.de

Organic solids consisting of π-conjugated molecules play an important role for the design of several different electronic, or optoelectronic devices. Pentacene and its perfluoro derivative are typical examples for these organic π-conjugated systems, which are used for instance as organic field-effect transistors.

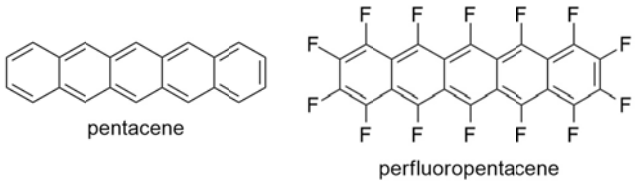


Fig. 1 Structural formula of pentacene and perfluoropentacene.

These two compounds have been chosen as model systems for quantum chemical studies of interfacial properties. To avoid computational costly calculations of extended systems, the crystals have been broken down into its molecular building units. Detailed knowledge about the properties of the involved molecules is essential, such as, electron affinity, ionization energy and electronic excitation energies are to be mentioned here. Besides electronic transitions, also vibronic effects play a crucial role for photophysical processes at internal interfaces. Selected results for pentacene and perfluoropentacene are presented and discussed with respect to their impact on interface properties.

Pentacenes and azapentacenes as building blocks for internal interfaces: syntheses, molecular and solid-state properties

P. Hofmann[2], F. Wagner[2], J. Schwaben[2], N. Münster[2], U. Koert[2], M. Klues[1], T. Breuer[1], and G. Witte[1]

[1] Department of Physics, Philipps-Universität Marburg, Germany

[2] Department of Chemistry, Philipps-Universität Marburg, Germany

e-mail: Frederic.Wagner@chemie.uni-marburg.de

Progress towards the synthesis of non-symmetrical substituted pentacenes bearing fluoro, trifluoromethyl, nitro and dimethylamino substituents is reported.[1-3] As a result of a non-symmetric substitution pattern containing electron-donating substituents in combination with electron-accepting substituents, the synthesized compounds feature distinct molecular dipoles. Azapentacenes with a variety of fluorine substituents can be prepared either via a Hartwig-Buchwald aryl amination route or by a S_NAr-strategy. All compounds are analyzed regarding their optoelectronic properties and their molecular packing in the crystal structures. The analyses of isolated molecules are complemented by thin-film studies to examine their solid-state properties.

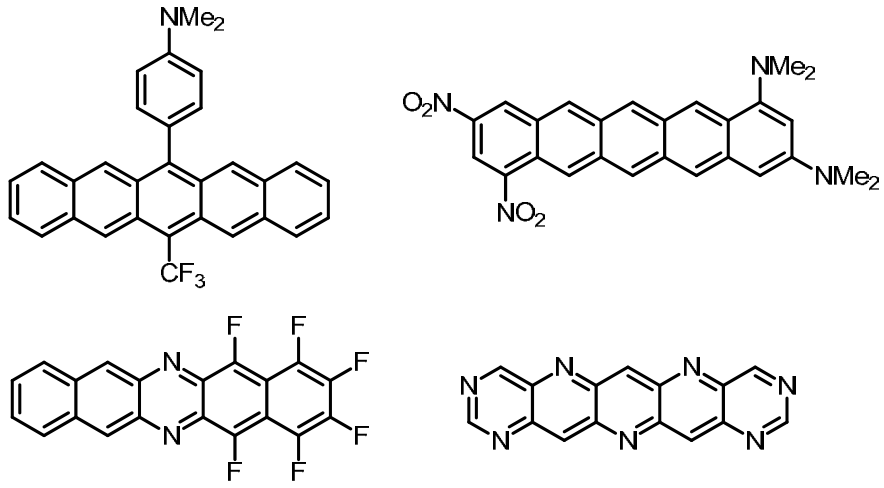


Fig. 1 Structures of substituted pentacenes and azapentacenes.

[1] J. Schwaben, N. Münster, T. Breuer, M. Klues, K. Harms, G. Witte, U. Koert, *Eur. J. Org. Chem*. **2013**, 1639.

[2] J. Schwaben, N. Münster, M. Klues, T. Breuer, P. Hofmann, K. Harms, G. Witte, U. Koert, *Chem. Eur. J.* **2015**, *21*, 13758.

[3] F. Wagner, K. Harms, U. Koert, *Org. Lett.* **2015**, *17*, 5670.

Electronic structure of fluorinated aromatic molecules

Michael Klues[1], Paul Jerabek[2], Robert Berger[2], and Gregor Witte[1]
[1] *Faculty of Physics, Philipps-Universität Marburg, Germany*
[2] *Faculty of Chemistry, Philipps-Universität Marburg, Germany*
e-mail: michael.klues@physik.uni-marburg.de

Fluorination is a widely used approach for tuning energy levels as well as packing motifs of π-conjugated molecules. Chemically this implies only the replacement of hydrogens, which seem to be a minor change. Nevertheless the impact on the molecular electronic system can be tremendous. Essentially NEXAFS is capable of probing unoccupied molecular states and therefore is a suitable technique for investigations on the influence of fluorination on the electronic structure. The comparison of previous angle resolved NEXAFS measurements at the C1s- and F1s-edge have shown that the origin of F1s-spectra is not well understood.

To elucidate this topic highly ordered crystalline films of Perfluoropentacene (PFP) were grown on HOPG and SiO_2, where molecules adopt exclusively lying or nearly upright standing orientations, respectively. This structural difference results in diverse angular dependencies of the corresponding NEXAFS resonances (dichroism), enabling an explicit assignment of underlying excitations. To gain detailed insights into the nature of these excitations the NEXAFS-signature was calculated using density functional theory as implemented in the StoBe-code. Thereby, relaxation effects turned out to be of central importance, explaining the experimentally confirmed overlay of π- and σ-type resonances. Taking these effects into account the computed results were able to reproduce not only the signature but also the experimentally observed dichroism. Combining the results of the DFT-calculations and Hückel theory the nature of π-type F1s NEXAFS resonances was identified as transition into unoccupied fluorine p_z-orbitals. This demonstrates that the π-system of fluorinated acenes also includes the fluorine atoms and thus becomes more extended than for the non-fluorinated acene which could be relevant for understanding lateral π-π-interactions between molecules in solids and interfaces, where usually only carbon-carbon distances are considered.

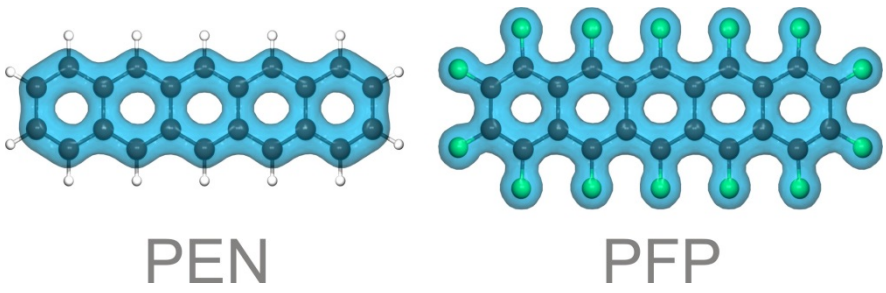


Fig. 1: Accumulated electron density of all π-orbitals within the electronic ground state of pentacene (PEN) and perfluoropentacene (PFP).

Correlation of carrier dynamics and molecular packing in pentacene-perfluropentacene hybrids

Andre Rinn, Tobias Breuer, Gregor Witte, and Sangam Chatterjee
Faculty of Physics and Materials Science Center, Philipps-Universität Marburg, Germany
e-mail: andre.rinn@physik.uni-marburg.de

Aromatic molecules are among the most promising materials in the field of organic optoelectronic due to the favorable properties of delocalized π-electron system present in those molecules. One of the most studied systems in this material class is the planar molecule of pentacene. A promising application for pentacene is the incorporation into a donor-acceptor heterojunction in combination with perfluropentacene. Both materials can be grown lattice-matched on one another. The out-of-plane π-electrons of both materials can lead to significant coupling of both systems, enabling the formation of charge-transfer excitons across the heterointerface. Hence, studying this model system forms the optimal platform to investigate exciation transfer and charge separation in organic solar cells.

Here, we present a comprehensive study of the optical properties of pentacene -perfluropentacene hybrid systems. The samples are grown as thin films in different morphologies. Time resolved luminescence and linear absorption spectroscopy are performed to obtain the carrier dynamics of the charge transfer states and response of the pure materials. The influence of different packing motives on the optical properties is investigated.

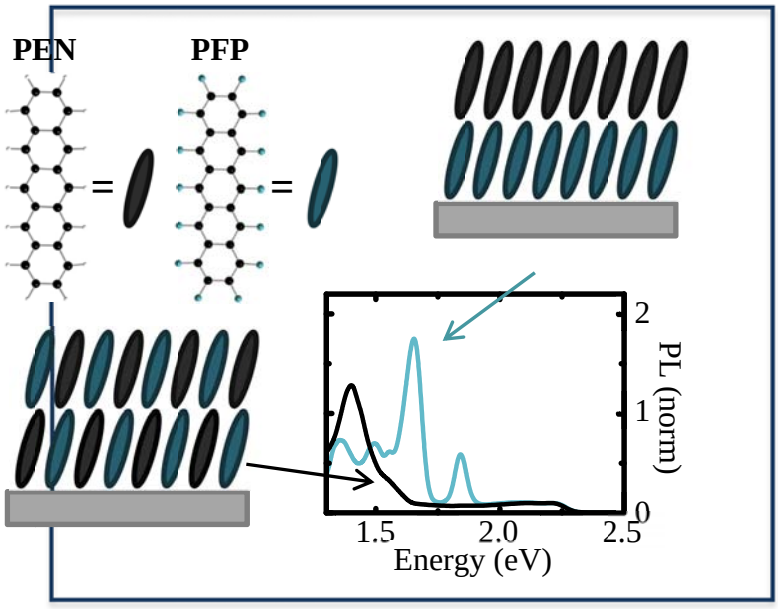


Fig. 1: Pentacene and Perfluropentacene hybrid systems and their respective luminescence

TEM analysis of codeposited pentacene:perfluoropentacene grown on SiO_2 substrate

Rocío Félix [1], Katharina I. Gries [1], Tobias Breuer [1], Gregor Witte [1] & Kerstin Volz [1]
[1] *Department of Physics, Philipps-Universität Marburg, Germany*
e-mail: rocio.felix@physik.uni-marburg.de

The interest in organic semiconductors (OSCs) has increased in the last years since they are a promising alternative to existing inorganic semiconductors. Among other OSCs, pentacene (PEN, $C_{22}H_{14}$) and perfluoropentancene (PFP, $C_{22}F_{14}$) blends attract a special attention since they can form donor/acceptor systems and are expected to be structurally compatible. However, for good optical and structural properties, a coupling between both at molecular levels is needed. Until now, PEN:PFP blends have only been studied by averaging characterization methods [1-4], whose spatial resolution is no high enough to get microstructural information. Then, local methods, i.e. transmission electron microscopy (TEM), are also demanded to give information about the local crystallinity and crystallographic phases. Here, we show a study of codeposited PEN:PFP on SiO_2 with different mixing ratios: [1:1] (Fig. 1a), [2:1] (Fig. 1b) and [1:2] (Fig. 1c). The characterization of the structure and morphology of them were performed by atomic force microscopy (AFM) and TEM techniques (SAED patterns, conventional dark field (DF) and bright field (BF) pictures, and STEM analyses). The SAED patterns taken from large length scales show polycrystalline character and diffraction rings of a "common phase" that systematically appears for all blend ratios. This phase can be assigned to a new "mixed crystal" previously observed [3]. Moreover, SAED measurements performed at small length scales (Fig. 1d), display the possible monocrystalline diffraction pattern of this new "mixed phase" for the first time. This SAED pattern is rather similar to pure PEN in the [001] expected orientation normal to SiO_2 substrates, suggesting that the crystalline structures of both (the "mixed phase" and pure PEN) should be very similar.

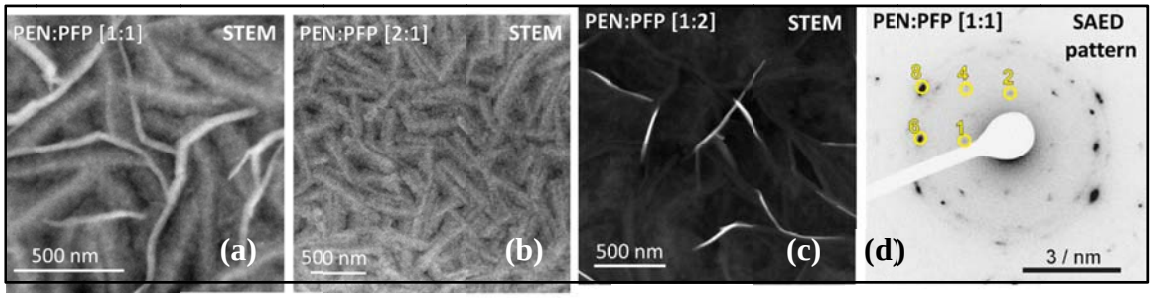


Fig. 1. STEM pictures of PEN:PFP blends with different mixing ratios: (a) [1:1] equimolecular, (b) [2:1] with excess of PEN and [1:2] with excess of PFP. (d) SAED pattern of the PEN:PFP [1:1] blend.

[1] Broch, K. et al. Phys. Rev. B 2011, 83, (24), 245307.
[2] Salzmann, I. et al. Langmuir 2008, 24, (14), 7294-7298.
[3] Hinderhofer, A. et al. J. Chem. Phys. 2011, 134, (10), 104702.
[4] Breuer, T. et al. J. Chem. Phys. 2013, 138, (11), 114901.

Charge carrier dynamics at the Pentacene - C_{60} interface

Robin C. Döring, Andrea Karthäuser, Tobias Breuer, Gregor Witte, and Sangam Chatterjee
Department of Physics, Philipps-Universität Marburg, Germany
e-mail: robin.doering@physik.uni-marburg.de

Efficiency of photovoltaic devices is generally limited by the Shockley-Queisser limit which may be overcome by Singlet fission. Here, one optically excited singlet-exciton state splits into a triplet pair state, hence doubling the number of generated charge carriers. These need to be extracted efficiently to ensure an effective application in photovoltaics: the bound electron-hole states, i.e., excitons, must dissociate and thus carriers must be separated. Pentacene (PEN)–fullerene heterojunctions are commonly regarded as model systems for this process and, indeed, quantum efficiencies exceeding unity are reported [1].

Here, we study the carrier dynamics at a model PEN-C60 interface to reveal the charge generation, transport and dissociation by time-resolved photoluminescence spectroscopy for various excitation energies. Clearly, the low-energy CT state is observed for exciting the C60 or the CT state directly. The latter is relatively weak to the inherently small absorption cross-section of a CT exciton state. Intriguingly, an additional long-lived high-energy emission is observed for UV excitation. It is associated with the high-energy CT state with homo in PEN and lumo in C60. A detailed analysis of the optical data allows to deduce the relative positions of the contributing energy levels and individual relaxation rates.

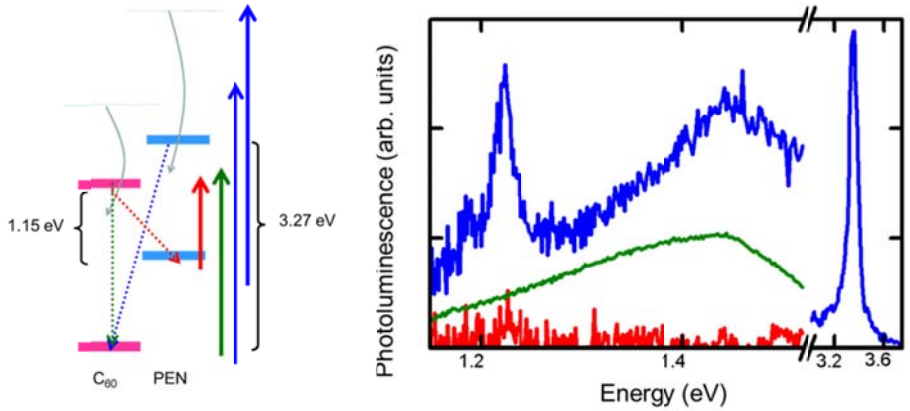


Fig. 4: Energy Level aligment (l.h.s.) at the PEN-C60 interface. Solid arrows indicate excitation at different excitation energies while the dotted one show corresponding recombination channels. Right hand side: Spectra at different excitation energies where the color of spectra correspond to the excitation energies of 4.5 eV (blue), 3.0 eV (green) and 1.5 eV (red), respectively.

[1] D. N. Congreve, J. Lee, N. J. Thompson, E. Hontz, S. R. Yost, P. D. Reusswig, M. E. Bahlke. S. Reineke, T. van Voorhis, M. A. Baldo, "External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission-Based Organic Photovoltaic Cell," Science **340**, 334–337 (2013).

Controlling C_{60} layer morphology and crystallinity in organic heterostructures: influence of pentacene bottom layers

Andrea Karthäuser, Tobias Breuer and Gregor Witte
Department of Physics, Philipps-Universität Marburg, Germany
e-mail: Andrea.Karthaeuser@physik.uni.-marburg.de

Organic electronic devices typically consist of different functionalized molecular layers. In organic phovoltaic cells, the key process of the carrier separation takes place at the interface between these layers, most prominently between the acceptor and donor layer. To systematically understand the interrelation of the interface structure and fundamental optoelectronic excitations, heterojunctions with well-defined interfaces have to be investigated. Therefore, we report on the preparation of such model-like organic interfaces for the acceptor/donor pair Buckminster Fullerene (C_{60}) and Pentacene (PEN, $C_{22}H_{14}$).

Buckminster-Fullerene and its derivatives are frequently used in prototypical organic electronic devices, e.g. due to its large thermal stability. The structural quality of most processed thin films is, however, rather poor. We show that precoating SiO_2 substrates with a PEN buffer layer enables the preparation of crystalline C_{60} films for appropriate process parameters. Combining precise preparation strategies with atomic force microscopy (AFM) and X-ray diffraction (XRD) analyses, we identify strong correlations between the grain sizes, the interface morphology and the crystallinity of the C_{60} layers with the PEN buffer layer thickness. In addition, we observe heteroepitaxial growth of C_{60} on top of the PEN layers, revealing that not only the vertical crystallinity, but also the azimuthal alignment of the C_{60} films is controlled by the pentacene buffer layer.

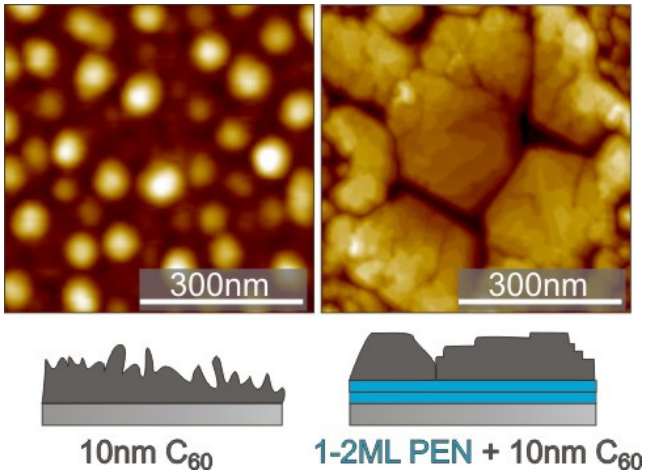


Fig: C_{60} forming small clusters on bare SiO_2 (left) and crystals on top of 2 ML Pentacene (right).

Electrospray ion-beam deposition (ESI-IBD) of organic molecules as an alternative to vapor deposition

Nicolas Bock, Benedikt P. Klein, and J. Michael Gottfried
Department of Chemistry, Philipps-Universität Marburg, Germany
e-mail: bockni@students.uni-marburg.de

During the past decade, great progress has been made in the preparation and characterization of well-defined organic-metal interfaces. However, vapor deposition of molecules as a frequently used preparation technique is only feasible if the organic material reaches sufficiently high vapor pressures before decomposition sets in. Large conjugated molecules or biomolecules often do not fulfil this requirement. A rarely used, but powerful alternative is Electrospray Ionization Ion Beam Deposition (ESI-IBD).[1–4] The electrospray ionisation (ESI) process is well-understood because of its widespread application in mass spectrometry.[5] ESI starts with a solution of the molecules, which are turned into a gas-phase ions during the ESI process at atmospheric pressure. The ions then pass through several differentially pumped ion-guide devices, including an ion funnel, quadrupols, and electrostatic lenses. The major processes occurring on the ions' path are beam collimation, removal of neutral solvent, mass selection of the desired ion, and beam focussing. Finally, the ions are deposited on a solid support under HV or UHV conditions using soft-landing.[6-8] A well implemented ESI-IBD technique ensures full chemical and spatial control over the deposition process. Our group builds an ESI-IBD device based on the groundbreaking design developed at the Max Planck-Institute for Solid State Research in Stuttgart.[4] This design is optimized for high ion fluxes and will enable us to deposit molecules which are too large and too instable for common UHV preparation techniques on surfaces. As a result of the high ion fluxes, the deposition can be completed on a practically usable timescale.

[1] Q. Hu, P. Wang, P. L. Gassman, J. Laskin, *Anal. Chem.* **2009**, *81*, 7302–7308.
[2] G. Rinke, S. Rauschenbach, S. Schrettl, T. N. Hoheisel, J. Blohm, R. Gutzler, F. Rosei, H. Frauenrath, K. Kern, *Int. J. Mass Spectrom.* **2015**, *377*, 228–234.
[3] G. Dubey, R. Urcuyo, S. Abb, G. Rinke, M. Burghard, S. Rauschenbach, K. Kern, *J. Am. Chem. Soc.* **2014**, *136*, 13482–13485.
[4] G. Rinke, S. Rauschenbach, L. Harnau, A. Albarghash, M. Pauly, K. Kern, *Nano Lett.* **2014**, *14*, 5609–5615.
[5] J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, C. M. Whitehouse, *Science* **1989**, *246*, 64–71.
[6] M. Pauly, M. Sroka, J. Reiss, G. Rinke, A. Albarghash, R. Vogelgesang, H. Hahne, B. Kuster, J. Sesterhenn, K. Kern, et al., *Analyst* **2014**, *139*, 1856–1867.
[7] K. D. D. Gunaratne, V. Prabhakaran, Y. M. Ibrahim, R. V. Norheim, G. E. Johnson, J. Laskin, *Analyst* **2015**, *140*, 2957–2963.
[8] G. E. Johnson, Q. Hu, J. Laskin, *Annu. Rev. Anal. Chem.* **2011**, *4*, 83–104.

List of Participants

Aeschlimann, Martin	ma@physik.uni-kl.de	Tu 11:30
Aldahhak, Hazem	aldahhak@mail.uni-paderborn.de	PII – 13, PII - 14
Anargirou, Eleni	Eleni.Anargirou@ScientaOmicron.com	
Armbrust, Nico	nico.armbrust@physik.uni-marburg.de	PII – 10
Baal, Eduard	baale@staff.uni-marburg.de	PII - 15
Barnscheidt, Hans Peter	Hans.Peter.Barnschscheidt@ScientaOmicron.com	
Bechstedt, Friedhelm	bechsted@ifto.physik.uni-jena.de	Fr 11:20
Berger, Christian	christian.berger@physik.uni-marburg.de	PI - 07
Berger, Robert	Robert.Berger@chemie. uni-marburg.de	
Beyer, Paul	pbeyer@physik.hu-berlin.de	PII - 01
Bock, Nicolas	bockni@students.uni-marburg.de	PII - 40
Bohamud, Tamam	tamam.bohamud@physik.uni-marburg.de	PI - 36
Botti, Silvana	silvana.botti@uni-jena.de	We 09:00
Breuer, Tobias	tobias.breuer@physik.uni-marburg.de	Th 10:20
Chatterjee, Sangam	sangam.chatterjee@physik.uni-giessen.de	Th 12:10
Chen, Jinghao	jinghao.chen@uni-due.de	PI - 18
Dehnen, Stefanie	dehnen@chemie. uni-marburg.de	
Di Filippo, Gianluca	gianluca.filippo@fau.de	PII - 26
Dobrich, Anja	anja.dobrich@tu-ilmenau.de	PI - 05
Döring, Robin C.	robin.doering@physik.uni-marburg.de	PII - 38
Dornsiepen, Eike	eike.dornsiepen@chemie.uni-marburg.de	PI - 24
Döscher, Henning	henning.doescher@physik.uni-marburg.de	PI - 04
Dürr, Michael	Michael.Duerr@ap.physik.uni-giessen.de	
Eyer, Moritz	moritz.eyer@physik.hu-berlin.de	PII - 06
Félix, Rocío	rocio.felix@physik.uni-marburg.de	PII - 37
Fernández, Laura	Laura.Fernandez-GR@physik.uni-marburg.de	PII - 20
Flade, Sebastian	Sebastian.Flade@physik.uni-marburg.de	
Fritz, Torsten	torsten.fritz@uni-jena.de	Tu 09:40
Fuchs, Christian	christian.fuchs@physik.uni-marburg.de	PI - 06
Gahl, Cornelius	c.gahl@fu-berlin.de	Th 14:40
Gerbert, David	Gerbert@uni-heidelberg.de	PII - 30
Gerhard, Marina	marina.gerhard@physik.uni-marburg.de	PII - 03
Geringer, Eugenie	eugenie.geringer@chemie.uni-marburg.de	PI - 24
Gies, Sebastian	Sebastian.gies@physik.uni-marburg.de	PI - 08
Gottfried, Michael	Michael.Gottfried@chemie. uni-marburg.de	
Gries, Katharina I.	katharina.gries@physik.uni-marburg.de	PI - 02
Güdde, Jens	Jens.Guedde@physik.uni-marburg.de	PI - 19
Guo, Jing	Jing.guo@Physik.tu-chemnitz.de	PII - 24

Han, Han	han.han@physik.uni-marburg.de	PI - 03
Hannappel, Thomas	thomas.hannappel@tu-ilmenau.de	Fr 09:40
Hansmann, Anna-Katharina	Hansmana@students.uni-marburg.de	PII - 33
Heimbrodt, Wolfram	Wolfram.Heimbrodt@physik. uni-marburg.de	
Heine, Johanna	johanna.heine@chemie.uni-marburg.de	PI - 26
Höfer, Ulrich	hoefer@physik.uni-marburg.de	PI - 31
Hofmann, Philipp	philipp.hofmann@chemie.uni-marburg.de	PII - 34
Hone, James	jh2228@columbia.edu	We 10:00
Huttner, Ulrich	ulrich.huttner@physik.uni-marburg.de	PI - 16
Ishioka, Kunie	ISHIOKA.Kunie@nims.go.jp	Fr 10:00
Jäckle, Sara	sara.jaeckle@helmholtz-berlin.de	PII - 04
Jakob, Peter	Peter.Jakob@physik.uni-marburg.de	
Jänsch, Heinz	Heinz.Jaensch@physik. uni-marburg.de	
Jauernik, Stephan	jauernik@physik.uni-kiel.de	PII - 21
Jeschke, Harald O.	jeschke@itp.uni-frankfurt.de	We 16:40
Jung, Sebastian	Sebastian.Jung@physik.rwth-aachen.de	PII - 32
Kakavandi, Reza	reza.kakavandi@physik.uni-marburg.de	PII - 08
Karthäuser, Andrea	Andrea.Karthaeuser@physik.uni.-marburg.de	PII - 39
Kira, Mackillo	mackillo.kira@physik.uni-marburg.de	Fr 09:00
Klein, Benedikt P.	kleinbe@students.uni-marburg.de	PII - 27
Klues, Michael	michael.klues@physik.uni-marburg.de	PII - 35
Koch, Martin	Martin.Koch@physik. uni-marburg.de	
Koch, Norbert	norbert.koch@physik.hu-berlin.de	Th 09:00
Koch, Stephan W.	Stephan.W.Koch@physik. uni-marburg.de	
Koert, Ulrich	koert@chemie.uni-marburg.de	Tu 17:00
Kolenda, Jürgen	Juergen.Kolenda@coherent.com	
Koppka, Christian	christian.koppka@tu-ilmenau.de	PI - 34
Kothe, Michael	michael.kothe@physik.uni-marburg.de	PII - 25
Kuhnert, Jan	jan.kuhnert@physik.uni-marburg.de	PI - 29
Lammers, Christian	christian.lammers@physik.uni-marburg.de	PI – 10
Landmann, Marc	landmann@mail.uni-paderborn.de	PI - 01
Lerch, Alexander	alexander.lerch@physik.uni-marburg.de	Th 15:20
Liebold, Martin	lieboldm@staff.uni-marburg.de	PII - 23
Louie, Steven G.	sglouie@berkeley.edu	We 11:50
Maercks, Franziska	maercks@physik.rwth-aachen.de	PI - 37
Mänz, Alexander	maenz@uni-marburg.de	PII - 19
Martin, Johannes	johannes-martin@chemie.uni-marburg.de	PI - 22
Mathias, Stefan	smathias@uni-goettingen.de	Th 16:00

Matsumoto, Yoshiyasu	matsumoto@kuchem.kyoto-u.ac.jp	Tu 16:00
Mette, Gerson	gerson.mette@physik.uni-marburg.de	PII - 28
Meyenburg, Ingo	ingo.meyenburg@physik.uni-marburg.de	PII - 05
Meyer, Michael	Michael.Meyer@specs.com	PI - 40
Möller, Christoph	christoph.moeller@physik.uni-marburg.de	PI - 11
Morbec, Juliana M.	juliana.morbec@uni-due.de	Th 15:40
Munakata, Toshiaki	munakata@chem.sci.osaka-u.ac.jp	Th 14:00
Namgalies, Andreas	Andreas.Namgalies@Physik.uni-marburg.de	PII - 16
Niesner, Daniel	daniel.niesner@fau.de	We 09:40
Nikodemiak, Paul	paul.nikodemiak@chemie.uni-marburg.de	PI - 39
Nobis, David	david.nobis@fau.de	PII - 09
Oelerich, Jan Oliver	jan.oliver.oelerich@physik.uni-marburg.de	PI - 32
Opitz, Andreas	Andreas.Opitz@hu-berlin.de	Th 10:00
Otto, Felix	felix.otto@uni-jena.de	PII - 11
Paszuk, Agnieszka	agnieszka.paszuk@tu-ilmenau.de	PI - 33
Pecher, Josua	josua.pecher@chemie.uni-marburg.de	PI - 38
Persson, Anna I. H.	anna.persson@fysik.lth.se	Fr 11:30
Petek, Hrvoje	petek@pitt.edu	We 17:00
Pöschel, Rebecca	Rebecca.Poeschel@fau.de	PI - 20
Rahimi-Iman, Arash	a.r-i@physik. uni-marburg.de	PI - 23
Reimann, Johannes	johannes.reimann@physik.uni-marburg.de	PI - 21
Reutzel, Marcel	marcel.reutzel@physik.uni-marburg.de	PI - 35
Riechert, Henning	riechert@pdi-berlin.de	We 11:10
Rinn, Andre	andre.rinn@physik.uni-marburg.de	PII - 36
Rinn, Niklas	rinn@students.uni-marburg.de	PI - 25
Rittich, Julia	jrittich@physik.rwth-aachen.de	PII - 31
Rohlfing, Michael	michael.rohlfing@uni-muenster.de	Tu 12:10
Schiller, Frederik	frederikmichael.schiller@ehu.es	PII - 22
Schlettwein, Derck	schlettwein@uni-giessen.de	Th 09:40
Schmid, Martin	schmidm5@staff.uni-marburg.de	Tu 16:40
Schneider, L. Maximilian	a.r-i@physik.uni-marburg.de	PI - 23
Schultz, Thorsten	tschultz@physik-.hu-berlin.de	PII - 07
Stähler, Julia	staehler@fhi-berlin.mpg.de	Th 11:10
Stanton, Christopher J.	stanton@phys.ufl.edu	Fr 10:20
Stein, Markus	markus.stein@physik.uni-marburg.de	PI - 17
Steiner, Hanno	Hanno.Steiner@physik.uni-marburg.de	
Stolz, Wolfgang	wolfgang.stolz@physik.uni-marburg.de	Fr 11:10
Sundermeyer, Jörg	jsu@staff. uni-marburg.de	

Supplie, Oliver	oliver.supplie@tu-ilmenau.de	PI - 30
Syed, Abdul Samad	abdulsamad.syed@uni-due.de	PI - 14
Tautz, F. Stefan	s.tautz@fz-juelich.de	Tu 17:20
Thussing, Sebastian	thussins@staff.uni-marburg.de	PII - 18
Tonner, Ralf	Ralf.Tonner@chemie. uni-marburg.de	
Turkina, Olga	turkina@physik.hu-berlin.de	Th 11:50
Udhardt, Christian	Christian.Udhardt@uni-jena.de	PII - 29
Vänskä, Osmo	vaenskae@staff.uni-marburg.de	PI – 12, PI - 13
Veletas, Julian	julian.veletas@physik.uni-marburg.de	PI - 09
Volz, Kerstin	kerstin.volz@physik.uni-marburg.de	Tu 10:20
Wagner, Bettina	thomasb@students.uni-marburg.de	PI - 26
Wagner, Frederic	Frederic.Wagner@chemie.uni-marburg.de	PII - 34
Wallauer, Robert	robert.wallauer@physik.uni-marburg.de	PI - 28
Wang, Qiankun	qiankun@physik.hu-berlin.de	PII - 02
Weseloh, Maria	maria.weseloh@physik.uni-marburg.de	PI - 07
Winterfeld, Lars	lars.winterfeld@tu-ilmenau.de	PI - 15
Witte, Gregor	Gregor.Witte@physik.uni-marburg.de	
Wurstbauer, Ursula	wurstbauer@wsi.tum.de	We 16:00
Zaitsev, Nikolay	nikolay.zaitsev@chemie.uni-marburg.de	PII - 17
Zimmermann, Jonas	jonas.zimmermann@physik.uni-marburg.de	PI - 27
Zugermeier, Malte	zugermeier@chemie.uni-marburg.de	PII - 12