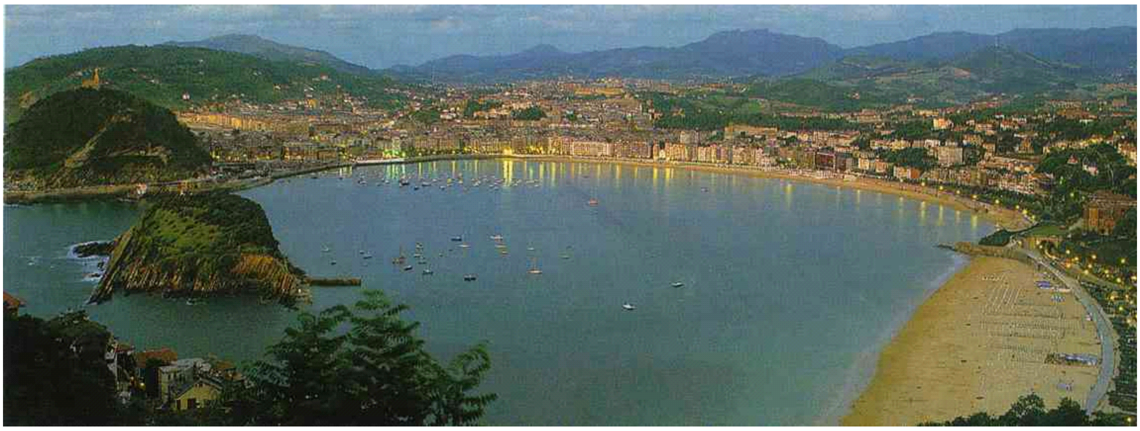
Interfaces2014

“International Summer School on Semiconductor Interfaces: Methods and Model Systems ”



Palacio de Miramar, Donostia-San Sebastián, Spain, July 28-31, 2014

Organizers:

Dr. Daniel Sánchez-Portal
DIPC, Centro de Física de Materiales CSIC, Dpto. Física de Materiales
UPV/EHU, Spain, Germany

Prof. Dr. Kerstin Volz
Philipps-Universität Marburg, Faculty of Physics and Materials Science Center,
Marburg, Germany

Scope

Interfaces between solids play a decisive role in modern material sciences and their technological applications. Among the most prominent examples are semiconductor devices, which have been miniaturized to such an extent that their optical and electronic properties are determined decisively by internal interfaces. Other relevant examples are interfaces in solar cells, the separation between carriers of opposite signs taking place there, and the organic/inorganic interfaces of functionalized particles and surfaces in biosensors.

This summer school is motivated by to this growing interest in the study of buried interfaces and aims to present the latest experimental and theoretical developments in the field. The school is aimed at a postgraduate level. We will have three lecturers/subtopics every day covering different aspects of the subject. The lecturers are internationally leading experts in their respective field. Every lecturer will give two lectures. A tutorial-like introduction to the state-of-the art in her/his field (60 min) followed by a talk covering her/his own latest work (30 min).

Institutional support and funding:

The course is organized within the Summer Courses of the University of the Basque Country and will be held at the Palacio de Miramar in Donostia-San Sebastián. The institutions that support the event are:

- Collaborative Research Center SFB 1083 "Structure and Dynamics of Internal Interfaces",
- Philipps-Universität Marburg, Germany
- Research Training Group "Functionalization of Semiconductors", Philipps-Universität Marburg, Germany
- University of the Basque Country UPV/EHU, Spain
- Centro de Física de Materiales UPV/EHU-CSIC, Donostia-San Sebastián, Spain
- Donostia International Physics Center (DIPC), Donostia-San Sebastián, Spain

Venue

The workshop will take place in the charming city of San Sebastian (or Donostia in the Basque language). San Sebastian is built in the seashore, within a nice and small bay, and has several beaches where you can walk and swim. This charming medium-size city is set in a picturesque countryside, on the edge of the Biscay Gulf and surrounded by mountains. You can find information about the city and the Basque Country, respectively, at:

http://www.sansebastianturismo.com (Spanish, English, French)

http://tourism.euskadi.net/en/ (Spanish, English, French)

The lectures are held in the unique environment of the Palacio de Miramar an historic place built as a vacation resort for Maria Christina of Austria who ruled Spain in the end of the 19th century. It is located in one of the most attractive spots in town (right in the middle of San Sebastián's bay).

Palacio de Miramar address:

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Technical Organization Committee:

Ms. María del Carmen Alonso, DIPC
Dr. Nico Armbrust, SFB 1083, Philipps-Universität Marburg
Dr. Francisco López Gejo, CFM CSIC-UPV/EHU
Dr. Helen A. Pfuhl, SFB 1083, Philipps-Universität Marburg

Program

Monday, July 28th, 2014	
9:00 - 9:30	Welcome & Introduction DIPC
9:30 - 10:30	Kronik (I)
10:30 - 11:00	Coffee Break
11:00 - 12:00	Zhu (I)
12:00 - 13:00	Duerr (I)
13:00 - 13:15	Coffee Break
13:15 - 13:45	Kronik (II)
13:45 - 16:00	Lunch break
16:00 - 19:00	Posters session
19:00 - 21:00	Welcome reception
Tuesday, July 29th, 2014	
9:00 - 9:30	Introduction SFB & GRK
9:30 - 10:00	Zhu (II)
10:00 - 11:00	Arnau (I)
11:00 - 11:30	Coffee Break
11:30 - 12:00	Duerr (II)
12:00 - 12:30	Arnau (II)
12:30 - 19:00	Excursion

Wednesday, July 30th, 2014	
9:00 - 10:00	Heinz (I)
10:00 - 11:00	Kuech (I)
11:00 - 11:30	Coffee Break
11:30 - 12:30	Stemmer (I)
12:30 - 12:45	Coffee Break
12:45 - 13:15	Kuech (II)
13:15 - 13:45	Stemmer (II)
13:45 - 16:00	Lunch break
16:00 - 19:00	Posters session
20:00	Dinner
Thursday, July 31st, 2014	
9:45 - 10:15	Heinz (II)
10:15 - 11:15	Wurth (I)
11:15 - 11:45	Coffee Break
11:45 - 12:45	Witte (I)
12:45 - 13:15	Wurth (II)
13:15 - 13:30	Coffee Break
13:30 - 14:00	Witte (II)
14:00	Closure of summer school and lunch
Friday, August 1st, 2014	
9:00 - 14:00	GRK Seminar (Satellite activity held at DIPC)

Poster session I (July 28th, 16.00 – 19.00):

E. Baal, R. Döring, S. Chatterjee and J. Sundermeyer
"Perylenediimides as switchable fluorescence probes for time-resolved photoelectron spectroscopy"

T. Breuer, A. Karthäuser, M. Klues and G. Witte
"Investigations of Interfaces between Fullerenes and (Functionalized) Acenes"

W. Bronsch, M. Wansleben, K. Zielke, C. Gahl and M. Weinelt
"*Ultrafast exciton dynamics in thin sexithiophene films"*

M. Chen, W. Hieringer, J. Shang, Y. Wang, K. Wu, Q. Fan, C. Wang, Y. Han, J. Kuttner, G. Hilt and J.M. Gottfried
"Honeycombenes: Novel conjugated macrocycles formed at reactive metal/organic interfaces "

I. Chung-Man and A. Troisi
"Interfacial charge transfer in dye-sensitized solar cells"

R. C. Döring, N. Rosemann and S. Chatterjee,
"Charge-transfer interaction at the PEN/C60 interface"

R. Felix, K.I. Gries, B.Haas, T. Breuer, G. Witte and K. Volz
"*Study of Codeposited PEN: PFP Films Grown on SiO2 "*

M. Graus, V. Feyer, A. Schöll, F. Reinert,
"Molecular Orbital Mapping of Phthalocyanines"

J. Güdde, J. Reimann and U. Höfer
"*Spectroscopy and dynamics of unoccupied electronic states of the topological insulators Sb2Te3 and Sb2Te2S studied by time-and angle-resolved 2PPE"*

S. Hietzschold, M. Scherer, J. Schinke, R. Lovrincic and W. Kowalsky
"Determination of Trap and Band States in Organic Field-Effect Transistors by Scanning Kelvin Probe Microscopy"

M. Ilyn, A. Magaña, L. Fernández, J.E. Ortega, F. Schiller
"Magnetic anisotropy and redistribution of electrons at Co/Ni and Co/Pd interfaces"

M. Kothe, A. Mänz and G. Witte
"*Orientational Controlled Growth of Phthalocyanine Films on Metal and Transparent Substrates"*

K. Kuroda, M. Ye, E. F. Schwier, M. Nurmamat, K. Shirai, M. Nakatake, S. Ueda, K. Miyamoto, T. Okuda, H. Namatame, M. Taniguchi, Y. Ueda and A. Kimura
"Experimental verification of the surface termination in topological insulator TlBiSe2 "

S. Laref, Ralf Tonner
“*Density functional study of tetrahydrofuran on Si(001)”*

F.Marchesin, P. Koval, D. Foerster, D. Sánchez-Portal
“*Study of Optical Properties and Electron Energy Loss Spectroscopy for Graphene Nanoflakes from Time – Dependent Density Functional Theory Calculations“*

I. Meyenburg, J.Helzel, M. Kothe, A. Karthäuser, M. Liebold, T. Breuer, G. Witte and W. Heimbrodt
"Optical Spectroscopy on Organic-Inorganic Hybrid Structures"

M. Müller, R. J. Maurer, K. Diller, and K. Reuter
“*Charge and intermolecular interactions: Modeling the interplay of free-base porphine molecules adsorbed on coinage metal surfaces”*

C. Nicholson, C. Monney, U. Krieg, M. Puppin, Y. Deng, C. Tegenkamp, H. Pfnür, K. Horn, R. Ernstorpher and M. Wolf
"Dimensionality and Metallicity of quasi-1D Ag:Si(557) Investigated by Angle-Resolved Photoemission"

D. Nobis, Gerrit Wrede and Thomas Fauster
"*Charge transfer states on thin films of pentacene derivatives"*

J. Pecher and R. Tonner
"Adsorption thermodynamics and kinetics of cyclooctyne and derivatives on silicon via DFT"

M. Reinmuth and S. Dehnen
"Functionalization of Tin Chalcogenide Clusters for Surface Binding"

M. Scholz, A. Schöll, W. Wurth
“Morphology Evolution and Electronic Structure of Organic-Metal Interface”

P. Springer, S. W. Koch, M. Kira
“Effect of Anisotropic Mass on Exciton Wave Functions”

A. Stöhr, S. Forti, U. Waizmann, T. Reindl, J. Baringhaus, A. Zakharov, C. Tegenkamp and U. Starke
"Epitaxial graphene nanoribbons on SiC"

S. Thussing and P. Jakob
"Vibrational properties and dynamical charge transfer of the CuPc/Ag(111) system"

S. P.Torsney*, B. Naydenov and J. J. Boland*
"*Formation of a self-limiting insulating monolayer on Cu(111) by Electrospray deposition"*

C. Volkmann and S. Schneider

"Special Interface Properties via Atomic Layer Deposition"

F. Wagner, J. Schwaben, N. Münster and U. Koert
"Synthesis and properties of novel pentacenes and benzophenazines"

R. Woscholski, M. Stein, M. Drexler, A. Rahimi-Iman and M. Koch
"Optical properties and carrier dynamics of III/V semiconductors"

N.L. Zaitsev, I. A. Nechaev and D. Sánchez-Portal
"Adsorption geometry and electronic structure of NTCDA/Ag(111): DFT-vdW calculations with the use of localized basis sets"

J. Zimmermann, A. Namgalies, N. Armbrust, J. Güdde and U. Höfer
"*Electronic Structure and Exitation Dynamics of the CuPc/PTCDA/Ag(111) heterointerface*"

M. Zugermeier, M. Chen, H.-J. Drescher, H. Zhou, B. Klein, C. Krug and J.M. Gottfried
"Reactive cobalt/porphyrin interfaces probed with hard X-ray photoelectron spectroscopy (HAXPES)"

Poster Session II (July 30th, 16.00 – 19.00):

C. Berger, U. Huttner, M. Mootz, M. Kira, S. W. Koch, J.-S. Tempel, M. Aßmann, M. Bayer, A. M. Mintairov and J. L. Merz
"Microscopic Theory of Semiconductor Lasers"

A. Beyer, K. Werner, A. Stegmüller, R.Tonner, J. O. Oelerich, S. Baranowskii, W. Stolz and K.Volz
"*Formation of the GaP/Si interface investigated by atomic resolution high angle annular dark field imaging*"

K. Brixius, K. Ishioka, A. Beyer, W. Stolz, K. Volz, H. Petek and U. Höfer
"Coherent Phonon spectroscopy of GaP/Si(001)"

J.-C. Deinert, D. Wegkamp, M. Meyer, C. Richter, M. Wolf, and J. Stähler
"*Ultrafast dynamics of exciton formation at the ZnO(10-10) surface"*

M.Drexler, M. Stein, R. Woscholski, A. Rahimi-Iman and M. Koch
"Comparison of Carrier Dynamics in Direct and Indirect GaInAs/GaAs/GaNAs Quantum Wells"

M. Lipponer, N. Armbrust, **M. Dürr** and U. Höfer
"*Reaction dynamics of exemplary organic molecules on Si(001) -a molecular beam study* "

M. Engelund, T. Frederiksen, A. García-Lekue and D. Sánchez-Portal
"*Electronic structure of dangling bond wires on the Si(001) and Ge(001) at different doping levels"*

J. P. Eußner and S. Dehnen
"*Functional Binary and Ternary Organotin Chalcogenide Clusters"*

S. Gies, P. Hens, C. Kruska, W. Stolz, K. Volz and W. Heimbrodt:
"*Type-II Excitons in (GaIn)As/Ga(NAs)-quantum wells on GaAs"*

A. Guerrero
"Role of light induced dipole generation in the activation of Organic solar cells containing TiOx cathode interlayers"

H. Han, A. Beyer, K. I. Gries, W. Stolz and K. Volz
"*Characterization of the interface structure of (GaIn)As and Ga(NAs) grown on GaAs*"

P. Hens, A. Beyer, H. Han, A. Ott, R. Straubinger, K. Volz and W. Stolz
"Metal Organic Vapor Phase Epitaxy of Semiconductor Heterostructures and Interfaces"

U. Kaiser, M. Wilhelm, N. Sabir, M. Schneider, P. Del Pino, C. Carrillo-Carrion, W. J. Parak and W. Heimbrodt
"Energy transfer characteristics of Mn doped CdS/ZnS quantum dots"

L. P. Kraft, Schaffner, H. Allmrodt, A. Potzuweit and H. Jänsch
"*An NMR-Approach to semiconductor internal layers"*

J. Kuhnert, P. Ludewig, K. Volz and S. Chatterjee
"*Photo-modulated reflection and temperature-dependent photoluminescence studies of Ga(AsBi) bulk and quantum well structures"*

A. Lerch, K. Brixius, A. Beyer, K. Volz and U. Höfer
"Second-harmonic generation at the Buried GaP/Si(001)-Interface"

C. Möller, A. Ruiz Perez, A. Ott, P. Hens, B. Breddermann, C. Berger, A. Beyer, K. Volz, W. Stolz and S. W. Koch
"Interface-Dominated Semiconductor Laser Structures"

J. O. Oelerich, A. Stegmüller, K. Werner, A. Beyer, R. Tonner, W. Stolz, K. Volz and S. D. Baranovskii
"Computer Simulation of Growth Kinetics of Compund Semiconductors"

A. Ostapenko and G. Witte
"*Preparation and characterization of phosphonic acid based self-assembled monolayers on ZnO substrates"*

A. Ott, A. Beyer, A. Ruiz Perez, B. Kunert, W. Stolz and K. Volz
"Investigation of antimonide-based materials grown on exactly oriented (001) silicon substrate by MOVPE"

S. Parui, L. Pietrobon, F. Casanova, L. E. Hueso

“Gate-controlled energy-barrier at graphene/molecular junction”

B. Pelaz, P. del Pino, M. Gamal and W. J. Parak
"*Surface modification of nanoparticles"*

P. del Pino
"*Smart Particles for Bio-Apps"*

M. Reutzel, G. Mette, M. Dürr, U. Koert, and U. Höfer
“Adsorption of Tetrahydrofuran and Diethylether on Si(001)”

P. Rosenow and R. Tonner
"*DFT-Study on the Adsorption of MOVPE-Precursors on III/V Semiconductors on Silicon and on Properties of III/V-Semiconductor Quantum Well Materials"*

N. Sabir, P. del Pino and W. J. Parak
"*Mn doped CdS, CdS/ZnS Nanoparticles Synthesis and characterization"*

A. Stegmüller and R. Tonner
"*Quantum Chemical Investigations of GaP/Si(001) Interface Formations and Elementary Growth Processes”*

E. Sterzer, A. Beyer, K. Werner, R. Straubinger, W. Stolz. C. v. Hänisch, J. Sundermeyer and K. Volz
"*Nitrogen incorporation in GaAs using alternative precursors containing As-N and Ga-N bonds*"

R. Straubinger, A. Beyer, K. I. Gries, C. Schneider and K. Volz
"High quality FIB lamella preparation for wide area, atomic resolution TEM investigations"

T. Stroucken and S.W. Koch
"Evidence for huge exciton binding in transition-metal dichalcogenides"

T. Wegele, A. Beyer, M. Zimprich, K. Jandieri and K. Volz
"*Investigations Focused on the Local Composition Determination of Dilute Nitride Quaternary Material Systems Grown on Si-substrates"*

N. Yumnam, Asman Tamang, Dietmar Knipp and Veit Wagner
"*Structured growth of ZnO nanorods for light trapping enhancement in organic solar cells*"

ABSTRACTS OF THE LECTURES

(Alphabetic order)

Prof. A. Arnau

Centro de Física de Materiales UPV/EHU-CSIC, San Sebastián, Spain

(I) "Electronic properties of molecular overlayers on surfaces".

In this lecture I will describe basic concepts and strategies to characterize molecular overlayer on surfaces using well stablished theoretical methods with their corresponding tools, as well as the way to contrast results with different spectroscopic techniques. Starting from the description of the pristine surface, I will continue with the case of simple atomic overlayers and then continue with molecular overlayers of different kind; from weakly couple hydrogen bonded networks to strongly couple overlayers. Special attention will be paid to surface states and its hybridization with molecular orbitals that give rise to interface states.

(II) "Electronic and magnetic properties of metar-organic coordination networks".

In this talk, I will present a few examples of metal-organic coordination networks formed by 3d transition metal atoms and strong electron acceptor molecules in which spin magnetic moments localized at the metal atoms can be ferro- or antiferromagnetically coupled, depending on subtle details of the electronic structure close to the Fermi level like, e.g., the presence of a spin polarized hybrid band with electrons delocalized along the whole system constituents, i.e., the metal atom and the organic ligand. Possible applications of interest, like the growth of thin ferromagnetic overlayers on topological insulators will be discussed as well.

Prof. M. Dürr

Justus-Liebig-Universität, Giessen, Germany

(I) “Reactions of organic molecules on semiconductor surfaces – part 1: mechanisms”.

Reactions on semiconductor surfaces, both of organic and inorganic molecules, are governed by the strong localization of electronic density in surface dangling bonds. Depending on the functional group of the organic adsorbates, different local electronic properties on the semiconductor surfaces control the respective surface chemistry. As a consequence, adsorption on semiconductor surfaces can be highly site specific. In this lecture, different classes of molecules and their specific reaction properties on semiconductor surfaces will be discussed and general trends will be developed. A special focus will be laid on the resulting energy potentials: many reactions proceed via an intermediate and the barrier between intermediate and final state governs the final adsorption configuration. The correlation between reaction mechanism, potential energy surface, and resulting kinetics is thus a key to understanding organic surface chemistry on semiconductor surfaces.

(II) “Reactions of organic molecules on semiconductor surfaces – part 2: towards controlled functionalization”

The general concepts developed in part 1 will be applied in more detail to model systems on the Si(001) surface. Especially the possibility to control surface chemistry via local distortion of the surface’s electronic structure will be demonstrated. E.g., for the adsorption of ethylene it could be shown that preadsorption of atomic hydrogen and the concomitant change in local electronic density leads to an additional adsorption pathway with high reactivity. Using molecular beam techniques, we have direct experimental access to the dynamics of the respective reaction channels; thus complementary information to imaging or spectroscopic methods, which focus on adsorption configurations, is obtained. With this information, further control of the reactions is envisioned.

Prof. T. Heinz

Columbia University, New York, USA

(I) "Electronic and optical properties of atomically thin 2D materials"

Layered van-der-Waals crystals have given rise to a fascinating set of stable 2D materials that can be prepared by exfoliation and growth techniques with thicknesses down to a single atomic layer. We will describe some of the distinctive electronic and optical properties of such materials, emphasizing particularly the newly emerging class of transition metal dichalcogenides such as MoS_2. The properties of these semiconducting materials will be compared and contrasted with the case of the 2D semimetal graphene, with its quasi-relativistic dispersion relation. The possibility of accessing the valley degree of freedom in the transition metal dichalcogenides will be discussed and recent experimental results presented.

(II) "Many-body effects in the optical response of atomically thin 2D materials"

The importance of many-body Coulomb interactions increases in materials of reduced dimensionality simply on the basis of phase space considerations. For the case of atomically thin 2D materials, however, Coulomb interactions are further enhanced because of the reduced dielectric screening that these ultrathin layers provide. We will discuss how this leads to non-local screening (distant dependent) screening and the consequence for optically excited states. We will describe the influence of strong many-body effects in graphene, which leads to the formation of saddle-point excitons in this metallic system. For the case of semiconducting transition metal dichalcogenide monolayers, pronounced many-body effects lead to excitonic transitions, with exciton binding energies of hundreds of meV and a distinctive non-hydrogenic set of excited excitonic states. The three- and four-particle correlated excited states, corresponding to charged excitons (trions) and biexcitons, are also readily observed.

Prof. L. Kronik

Weizmann Institute of Science, Rehovot, Israel

(I) “Understanding organic/inorganic interfaces from first principles”.

In this talk, I will review some of the fundamental physical mechanisms affecting the electronic structure at organic/inorganic interfaces. I will discuss how first principles calculations can be successful in elucidating such phenomena, but also discuss caveats in their application and avenues for further research.

(II) “Collective effects at organic/inorganic interfaces”.

Organic/inorganic interfaces often display strong collective phenomena, i.e., behavior not exhibited by their constituent elements. In this talk, I will describe several such phenomena, of both classical and quantum nature, and show how first principles calculations have helped in elucidating their underlying mechanisms.

Prof. Th. F. Kuech

University of Wisconsin- Madison, Madison, WI, USA

(I) “Epitaxial Formation of Multilayer Structures: The interplay of thermodynamics, kineticsand growth behavior”.

Modern technology relies on the formation of precision structures through the use of epitaxial growth techniques wherein multilayers of differing composition yet similar lattice structures are formed. The formation of these structures has been the subject of intense research and commercial development over the last 60 years. An understanding of these processes has been through the investigation of the thermodynamics of growth, those kinetic processes active on and within the material and the interplay of strain, defect and morphology. This talk will look the evolution of this understanding and its application to current crystal growth techniques. The interplay of the growth surface, primary chemical and physical processes and the inherent properties and thermodynamics of the system will be explored.

(II) “The Formation of Metastable Alloys”.

Most of the commercially viable technologies have relied on the formation and use of thermodynamically stable semiconductor materials and alloys. The advent of our abilities to computationally design and predict new materials has allowed us to explore compositionally complex alloys which have not been yet synthesized and are generally unstable under typical epitaxial growth conditions. We have now been able to form many materials deep within the compositional space for such inherently unstable materials. The technological extension to alloy systems that are immiscible in bulk form requires modification to conventional growth systems preventing the nucleation and simultaneous growth of multiple compositional phases. This phase separation is only facile on the growth surface and hence control over surface structure and chemical kinetics determines in large part our ability to form these interesting materials. The formation of these multi-component alloys is discussed in terms of their known thermodynamic behavior which can be altered by the presence of strain in the material, surface chemistry and the growth temperature. Additionally, the stoichiometry and reaction kinetics of the alloy constituents, particularly when using chemical vapor deposition processes, can impose kinetic constraints allowing for the formation of alloys within the miscibility gap.

Prof. S. Stemmer

University of California, Santa Barbara, CA, USA

(I) “Quantitative Scanning Transmission Electron Microscopy”.

High-angle annular dark field (HAADF) imaging in scanning transmission electron microscopy (STEM) provides chemically sensitive atomic resolution structure images that are more directly interpretable than conventional high-resolution transmission electron microscopy images. The first part of this presentation will focus on the quantitative interpretation of HAADF image contrast. We discuss that the interpretation of images in terms of the number and types of atoms present in the columns requires comparisons with image simulations. We show thatin both HAADF-STEM and bright-field STEM, experiments and theory agree quantitatively, to within a few percent. We will discuss the application of quantitative STEM to determine the number of atoms in the columns and the three-dimensional location of dopant atoms. We will also discuss a STEM-based diffraction method- position averaged convergent beam electron diffraction (PACBED) - that allows for accurate and precise determination of the local sample thickness and sample tilt and that is compatible with the thin specimens used in high-resolution STEM imaging. Moreover, we will discuss the application of PACBED to determining sample polarity and very small structural distortions with unit cell spatial resolution.

The work was carried out in collaboration with Jinwoo Hwang, Jack Zhang, James LeBeau, Les Allen, Scott Findlay and Adrian D’Alfonso.

(II) “Complex Oxide Interfaces”.

Two-dimensional electron gases (2DEGs) at interfaces between two insulating oxides have attracted significant attention because they can exhibit unique properties, such as strong electron correlations, superconductivity and magnetism. In this presentation, we will discuss emergent properties at interfaces and quantum wells formed between Mott insulating rare earth titanates (SmTiO3 and GdTiO3), and the band insulator SrTiO3. Such interfaces exhibit a high-density 2DEG, of approximately ½ electron per surface unit cell, providing ~ 3×1014 cm-2 mobile charge per interface. We will start with an overview of the basic properties of these materials, their physics, and recent advances in controlling growth and interface properties. We show that the subband structure can be probed using quantum oscillations and resonant tunneling studies. We investigate electron correlation effects due to short-range Coulomb interactions and metal-insulator transitions in narrow quantum wells bound by two such interfaces. We will also discuss the correlation between structure and metal-insulator transitions in thin oxide quantum wells.

This work was performed in collaboration with Clayton Jackson, Santosh Raghavan, Pouya Moetakef, Jack Zhang, Jinwoo Hwang, Evgeny Mikheev, Adam Kajdos, Leon Balents, and Jim Allen.

Prof. G. Witte

Philipps-Universität Marburg, Marburg, Germany

(I) “Principles of organic thin film growth”.

Organic semiconductor films are receiving large interest because of their versatile applications ranging from surface functionalization to optoelectronic thin film devices such as OLEDs, OEFTs or OPVs. Though some of these devices have already entered the market a detailed understanding of intrinsic optoelectronic properties of the organic semiconductor materials as well as their processing is still not as complete as for inorganic semiconductors. Related to the structure of the molecular entities and their packing in crystalline phases these properties exhibit a pronounced anisotropy in solids. Therefore, a precise control of the molecular packing and orientation in thin films and at interfaces is of vital interest in order to explore and utilize the structure-property interrelation. In this lecture I will discuss some guidelines how the crystalline structure and molecular orientation in thin organic films growth on various inorganic substrates can be controlled. Generally it is found that the resulting molecular orientation and film morphology depend critically on the roughness and chemical termination of the substrate, whereas growth rate and substrate temperature mainly affect the grain size. Though on metal substrates dense packed wetting layers are formed a pronounced island formation occurs upon further deposition or post deposition dewetting and results in non-contiguous films. Such dewetting phenomena can be effectively suppressed by first coating the substrate by self-assembled monolayers (SAMs). Smooth organic films are also obtained on inert inorganic substrates where the weak molecule-substrate interaction provides some flexibility to effectively reduce interface strain caused by a lattice mismatch of substrate and film. Despite this weak molecule-substrate interaction even heteroepitaxial growth and formation of extended crystallites or interface stabilized new polymorphs are obtained in some cases. Finally, I will also discuss some ordering and mixing phenomena occurring upon preparation of molecular heterostructures.

(II) “Opto-electronic studies of oriented organic semiconductor thin films”.

Highly ordered organic films with defined molecular orientation enable directional resolved measurements of their optoelectronic properties in the crystalline phase. In this lecture I will discuss some examples where scanning tunneling spectroscopy has been used to gain insight into the charge transport properties in crystalline molecular layers. In particular the importance of a lateral π-π coupling between neighboring molecules is highlighted. In case of transparent substrates (like oxides or alkali halides) optical measurements can be performed on locally crystalline films which provide details on the nature of the excitonic excitations in organic crystals. If the crystallites are sufficiently sized this enables even polarization resolved absorption measurements along specific crystalline and molecular axes. The potential of this approach is demonstrated for the case of highly ordered crystalline perfluoropentacene (PFP) films that are epitaxially grown on KCl(100) and NaF(100) substrates. The different molecular orientations adopted by PFP on both substrates (standing vs. lying) and their epitaxial ordering enable precise polarization-resolved measurements along individual crystallographic directions. This allows an unambiguous experimental determination of the polarizations of the IR modes. Together with theoretical models it enables a microscopic explanation for the experimentally observed Davydov splitting of some modes and the IR-inactivity of others due to the mutual coupling of the dynamical dipole moments of the two molecules within the unit cell. The same system has also been studied by time resolved pump-probe laser spectroscopy and exhibits a pronounced polarization dependent response which can be attributed to the anisotropic packing within the PFP lattice yielding additional evidence for a quasi-one dimensional electronic band structure. Moreover, the directional and time resolved data of the decay dynamics of excitons is explained by singlet exciton fission which depends critically on the crystalline directions and is greatly enhanced for a slip-stacked molecular arrangement.

Prof. W. Wurth

Universität Hamburg, Germany

(I) "X-ray spectroscopy - a great toolbox for the study of interfaces".

X-ray spectroscopic techniques allow to study chemical composition, electronic structure and magnetic properties at interfaces. In the talk the general properties of the most prominent x-ray spectroscopic tools (x-ray photoelectron spectroscopy, x-ray emission spectroscopy and x-ray absorption spectroscopy) will be discussed and examples for applications in the investigation of interfaces will be given.

(II) "Time-resolved x-ray spectroscopy at free-electron laser sources".

New light sources based on linear accelerators such as the free-electron laser FLASH at DESY in Hamburg in the XUV-spectral regime or the Linac Coherent Light Source LCLS in Stanford as the first x-ray free-electron laser provide ultrashort coherent pulses with unprecedented brilliance. With these new sources it is possible to extend the well-established x-ray spectroscopic techniques for the investigation of the static electronic structure of matter like e.g. photoelectron and x-ray emission spectroscopy to probing the evolution of the electronic structure after controlled excitation in the time domain. The talk will review recent time-resolved x-ray spectroscopy experiments illustrating the opportunities for the study of ultrafast dynamics in solids and at interfaces.

Prof. X.-Y. Zhu

Columbia University, New York, USA

(I) “ Excitons at Organic Semiconductor Interfaces”.

Excitons are quasi-particles, each consisting of a bound electron-hole pair. They result from optical excitation of materials, particularly those of low dielectric constants such as organic semiconductors. In bulk semiconductors, there are two main flavors: a Frenkel exciton consists of both the electron and the hole confined to unit cell and a Mott-Wannier exciton delocalized over many lattice sites. At material interfaces, the unique two-dimensional symmetry introduces a new flavor, charge transfer exciton with the electron and hole residing on two sides of the interfaces. Excitons at interfaces are particular importance to organic semiconductor based electronics and optoelectronics. In organic photovoltaics, photocurrent generation often requires the dissociation of Frenkel excitons into free electrons and holes at donor/acceptor interfaces. The low dielectric constant of organic semiconductors leads to strong Coulomb interactions between an electron and a hole, resulting in an energetic trap at the interface [Phys. Rev. Lett.2008, 101, 196403]. Using model organic semiconductor interfaces and femtosecond nonlinear laser spectroscopies, we provide real time views on how the initial Freneklexciton dissociation leads to hot charge transfer excitons across the interface [Nature Mater.2013, 12, 66-73]. We show how hot charge transfer exciton cooling and collapse of charge separation sets the fundamental time limit for competitive charge separation. We also discuss competitions between charge and energy transfer channels and the feasibility of generating multiple excitons from a single photon.

(II) “ Exciton Fission and Solar Energy Conversion Beyond the Limit”.

The maximum solar-to-electric power conversion efficiency of a conventional solar cell is determined by the Shockley-Queisser limit of ~31%. One viable approach to exceed this limit is to create two or more electron-hole pairs from the absorption of one photon in a process called singlet fission or multiple exciton generation. Recent measurements in our group by time-resolved two-photon photoemission (TR-2PPE) spectroscopy in crystalline pentacene and tetracene provided the first spectroscopic signatures in singlet fission of a critical intermediate known as the multiexciton state. More importantly, population of the multiexciton state is found to rise concurrently with that of the singlet state on the ultrafast time scale upon photo excitation. This observation provides an experimental foundation for a quantum coherent mechanism in which the electronic coupling creates a quantum superposition of the singlet and the multiexciton state immediately following optical excitation [Science2011, 334, 1541-1545; Nature Chem.2012, 4, 840-845; Acct. Chem. Res.2013, 46, 1321-1329]. We demonstrate the feasibility of harvesting the multiexciton state for multiple charge carriers or the triplets [J. Am. Chem. Soc.2012, 134, 18295–18302; Nature Commun.2013, 4, 2679.]. We outline a set of design principles for molecular materials with high singlet fission yield and for the implementation of singlet fission in solar cells with power conversion efficiency beyond the Shockley-Queisser limit.

ABSTRACTS OF THE POSTERS

Perylenediimides as switchable fluorescence probes for time-resolved photoelectron spectroscopy

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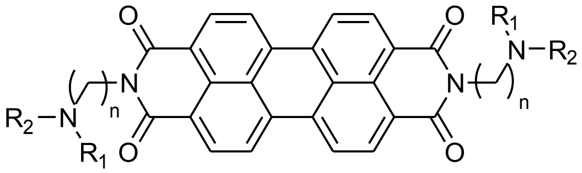
Perylene-3,4,9,10-tetracarboxylic acid diimides (PDIs) are excellent electron accepting materials due to their high thermal and photochemical stability, high electron mobility und high molar absorption coefficients.[1,2] Due to fluorescence quantum yields near unity, PDIs are used as fluorescence dyes in various electronical and optical applications.[3-5]



$R_1 = R_2 = H$
$R_1 = H, R_2 =$ *tert*-Butyl

$n = 0, 1, 2$

Figure 1: Chemical structure of N-amino-substituted perylene diimides (PDIs).

We synthesized a series of N-amino-substituted PDIs and naphthalene homologues, which exhibit a nearly absolute fluorescence quenching due to a photoinduced electron transfer (PET) from the electron donating functionality of the amino moiety. The fluorescence was recovered upon protonation. PDIs with different alkyl linkers we synthesised and characterised using time-resolved photoelectron spectroscopy to determine the influence of the amino moiety on the photoelectronic properties.

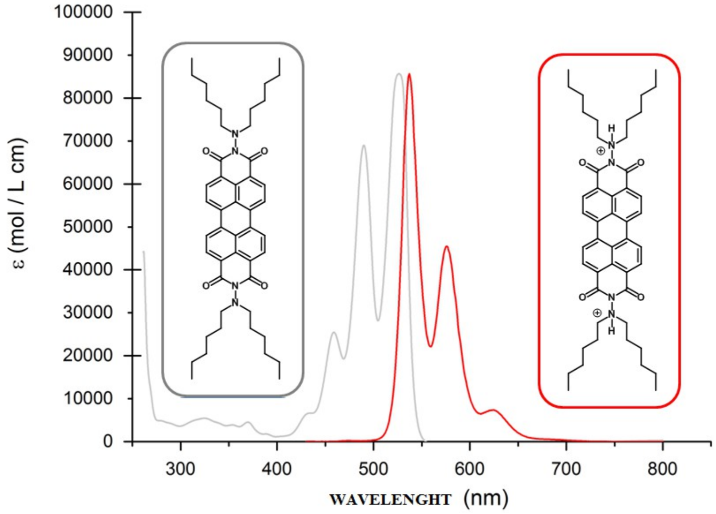


Figure 2: UV/vis absorption of neutral PDI (grey) and fluorescence spectrum of protonated PDI (red).

Acknowledgement: We thank DFG for funding within the SFB 1083 research cluster Marburg.

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Microscopic Theory of Semiconductor Lasers

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Abstract

We have performed studies on two different semiconductor-laser systems, quantum dots (QDs) in semiconductor microcavities and semiconductor heterostructures with a type-II band alignment.
For the QD system, we will present experimetally measured input/output (I/O) characteristics of optically pumped semiconductor microcavities and show that the I/O curve exhibits unexpected oscillatory nonlinearities around the expected linear slope in the excitation power regime below lasing [1]. A systematic microscopic analysis reproduces these oscillations identifying them as a genuine quantum-memory effect, i.e. a photon-density correlation accumulated during resonant excitation.
Secondly, a microscopic design of heterostructures with type-II band alignment for the (GaIn)As/Ga(AsSb) material system will be presented (Figure below). Furthermore, gain calculations as well as luminescence properties derived with a fully microscopic theory are discussed for the designed system.

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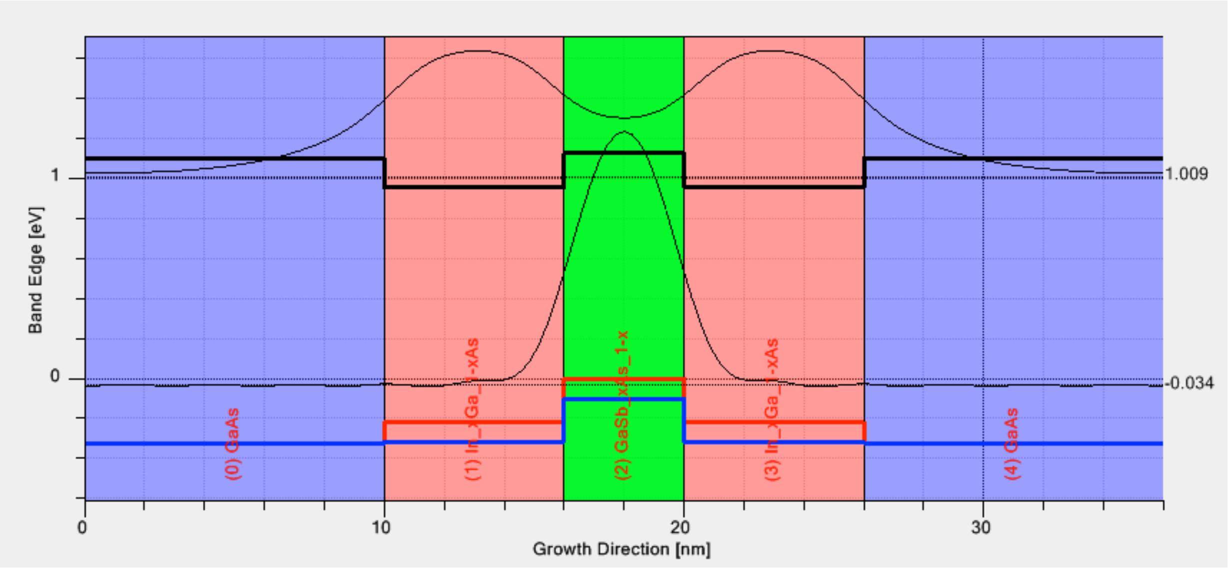
Figures



Formation of the GaP/Si interface investigated by atomic resolution high angle annular dark field imaging

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The integration of III/V layers on Si substrate offers a possibility to circumvent the bottlenecks of Si for example in terms of carrier mobility. High quality III/V layers on Si can allow the fabrication of optoelectronic devices with unprecedented performance. Nevertheless the growth of III/V material on Si holds several challenges, for example due to the transition from a non polar to polar material. GaP grown on Si can serve as a model system as GaP is almost lattice matched to Si. Because of the different valences of the group III, V and IV constituents, the structure of the interface of these materials is not trivial. To understand its actual structure and its formation, the hetero interface has to be investigated on an atomic scale.

GaP layers of different thicknesses were deposited on Si using metal organic vapour phase epitaxy (MOVPE). Electron transparent samples were prepared and investigated in an aberration corrected JEOL JEM 2200 FS (scanning) transmission electron microscope operating in high angle annular dark field (HAADF) mode. Complementary multislice simulations were carried out to model the scattering process and therefore allow quantitative evaluation of the measured HAADF intensities.

For the GaP layer with a nominal thickness of one monolayer which is depicted in Fig 1 (a), no complete GaP layer is observed but two amorphous layers exhibiting different intensities. In contrast to that thicker samples exhibit complete GaP layers with the intended thickness (Fig 1 (b)). We attribute these results to an incomplete thermal decomposition of the phosphorous precursor used during the MOVPE growth. We propose that the precursor decomposes catalytically in the presence of the Ga precursor instead. Our findings suggest that the current growth model assuming layer by layer growth has to be revised.

This contribution will show how HAADF in combination with adequate simulations can be used to investigate the processes during the formation of a hetero interface on an atomic scale.

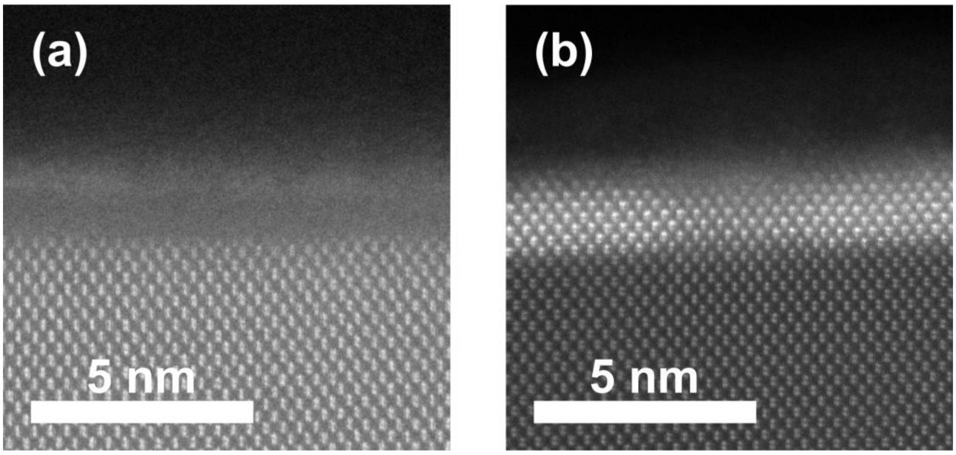

Fig 1: HAADF images of GaP layers grown on Si. The nominal layer thickness is one (a) and nine monolayers (b).

Investigations of Interfaces between Fullerenes and (Functionalized) Acenes

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Abstract

Their tunable electronic properties as well as their high photon cross-sections have resulted in increased research efforts in organic semiconductors (OSC) in the last decade. Due to their application relevance, especially thin films of OSCs are of interest. However, the complex nature of their physical characteristics and the correlation between structural and electronic properties have not yet been entirely elucidated and a number of fundamental questions remain. Our approach to promote the understanding of these aspects is to provide model systems, which combine application relevance with structural simplicity and therefore allow comprehensive analyses. To that purpose, we prepare highly ordered interfaces between Pentacene (PEN, $C_{22}H_{14}$) and Buckminster-Fullerene (C_{60}), which may e.g. serve as donor-acceptor pair in organic photovoltaic cells. Their different molecular geometry - rod-like molecules in the case of PEN, spheres in the case of C60 - results in two strikingly different mutual orientations at the interface: Either the C_{60} molecules are in contact with the aromatic backbone of PEN ("open interface", Fig. 1) or with the hydrogen-terminated sidefaces ("closed interface", Fig. 2). The different interfaces have been theoretically predicted to strongly influence the stability of the interface formation [1], as well as the electronic properties [2]. Here, we report on the experimental preparation and characterization of these interfaces by organic molecular beam deposition in ultrahigh vacuum. By choosing SiO_2 substrates, we have prepared crystalline PEN films in upright molecular orientation. Consequent deposition of C_{60} on top therefore yields molecules forming the closed interface. Using atomic force microscopy (AFM) we show, that this interface is not stable at room temperature conditions, but instead isolated, dewetted clusters at the PEN step edges are formed. However, external control over the diffusivity of C_{60} during the deposition process allows the preparation of a homogenously covered closed interface [3]. Furthermore, first results on the preparation of the open interface are presented. These can either be achieved by choosing appropriate substrates during PEN thin film growth or by preparation of crystalline C_{60} islands on NaCl(100) surfaces. Combining optical microscopy, atomic force microscopy and x-ray diffraction (XRD) we show that these films can be grown in exclusive molecular orientation with discrete epitaxial arrangement on the substrate (Fig. 3).

One helpful technique to analyze molecular orientation and mutual coupling at interfaces is x-ray absorption spectroscopy (NEXAFS). The dependence of resonance intensities on the relative orientation between molecules and light polarization allows a precise determination of the molecular orientation even in very thin and non-crystalline films, which cannot be analyzed by means of XRD. However, the exact nature of the resonances is in many cases unknown. Utilizing the quantum-chemical StoBe code, we present comprehensive results on the modelling of NEXAFS spectra and discuss their concurrence with experimental results [4].

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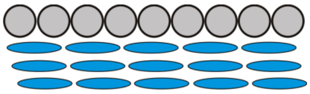
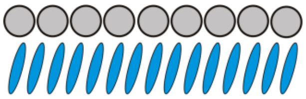
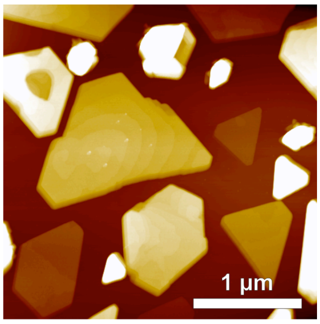
Figures


(1) Sketch of "open interface"


(2) Sketch of "closed interface"



(3) AFM micrograph of crystalline C60 film on NaCl(100)

Coherent phonon spectroscopy at GaP/Si(001)

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The investigation of the alignment of bulk bands at the interface between two solid materials is of crucial importance. The dynamics of charge transfer processes across the interface and the ultrafast dynamics of electronic and vibrational excitations directly at the interface can be modified by both the band alignment and certain states, which only appear due to new bonds at the interface.

Here we demonstrate the experimental evaluation of electron-phonon dynamics at the internal GaP/Si(001) interface by means of transient reflectivity measurements. For above-gap excitation at 3.1 eV, the anisotropic reflectivity response $\Delta R_{eo}/R$ of GaP/Si exhibits an amplitude beating arising from four long-lasting phonon modes: optical phonon of Si at 15.6 THz, LO phonon of GaP at 12 THz, and two other modes at 8 THz and 11 THz. The last frequency coincides with that of the TO phonon of GaP, though the Raman scattering by the TO phonon is forbidden in the present detection geometry. The amplitude of that mode depends sensitively on the growth conditions, such as GaP film thickness and intentional miscut of the Si substrate. The results suggest that the 11 THz mode is characteristic to the defect-free GaP/Si(001) interface and that it can be assigned to the presence and shape of anti-phase domains, where the Ga-polar crystal changes its phase to P-polar or vice versa.

Moreover a fast-decaying oscillation in addition to the three long-living phonon modes can be measured. Its frequency decreased with increasing photoexcitation density from the LO frequency towards the TO frequency of GaP. The pump-density dependence is comparable to that observed for the LO-*hole* plasma coupled mode of GaP, where the LO phonon of GaP couples with photoexcited hole plasma accumulated near the surface.

Ultrafast exciton dynamics in thin sexithiophene films

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Abstract

On our poster we discuss ultrafast exciton dynamics in thin sexithiophene (6T) films studied by time-resolved two-photon photoemission. For our experiments we use 6T functionalized gold and silicon surfaces. Our samples are prepared by the *in-situ* evaporation of 6T onto our substrates. This technique allows us to prepare well-defined organic/inorganic interfaces with molecular films varying from the sub-monolayer to the multilayer regime.

Time-resolved two-photon photoemission spectroscopy is an ideal method to investigate the electronic structure and charge carrier dynamics at the organic/inorganic interface from the femtosecond to the nanosecond regime. Within 6T thin films on gold surfaces the creation of Frenkel excitons due to the optical excitation of electrons from the HOMO into the LUMO of 6T molecules was observed. Those excitonic states are populated within 100fs, whereas their lifetime is coverage dependent. [1,2] These results will be compared with charge carrier dynamics in thin 6T films on silicon surfaces, which serve as model systems for hybrid solar cells.

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Honeycombenes: Novel conjugated macrocycles formed at reactive metal/organic interfaces

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Abstract

Molecular organic semiconductors and their interfaces with metal electrodes play an important role in modern electronic devices. Preparation of these interfaces is not always possible by deposition of the molecules onto metal surfaces, for example when the molecules are too large for vapor deposition or if a normal solution-based synthesis has not been achieved yet. Surface-assisted synthesis directly at organic-metal interface can provide an elegant workaround in such cases. An example where both factors come into play are [n]-honeycombenes, a novel class of planar conjugated hydrocarbon macrocycles of hexagonal geometry. [18]-Honeycombene or hyperbenzene ($C_{108}H_{72}$) consists of 18 phenyl rings and was first made by surface-assisted Ullmann reaction from 4,4''-dibromo-1,1':3',1''-terphenyl (DBTP) on Cu(111) (1). The molecules arrange in long-range ordered islands with hexagonal symmetry. Room-temperature stable organometallic intermediates with C-Cu-C bonds and cyclic or linear geometries were also observed in our combined STM/XPS study. [30]-Honeycombene, a hexagonal hydrocarbon macrocycle containing 30 phenyl rings ($C_{180}H_{120}$), was made on Ag(111) from 4,4''''-dibromo-1,1':4',1'':3'',1''':4''',1''''-quinquephenyl (DBQP). In both cases, the honeycombenes are accompanied by islands of zigzag-shaped oligophenylene chains. The DBQP precursor gives also access to strained planar macrocycles of heptagonal ($C_{210}H_{140}$), pentagonal ($C_{150}H_{100}$) and square ($C_{120}H_{80}$) symmetry. Using scanning tunneling spectroscopy (STS), the local electronic structure along the ring perimeter and the confinement of surface state electrons trapped inside the macrocycles were studied for the different species. The large inner diameters of >2 nm for [18]-honeycombene and >3.5 nm for [30]-honeycombene make both molecules promising candidates for surface nanotroughs that can act as templates for other molecules or nanoparticles.

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Interfacial charge transfer in dye-sensitized solar cells

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Abstract

Dye sensitized solar cells (DSSCs) are attractive economical alternatives to current expensive silicon solar cells. Whereas progress in n-DSSCs is promising [1], the development in p-DSSCs is considerably slow. Significant improvement in p-DSSCs' performance can perhaps pave the way to efficient pn-tandem DSSCs, in which experiments have shown that these tandem cells can be more efficient than high-performing n-DSSCs [2]. Charge dynamics at the semiconductor-dye interface in p-DSSCs appears to be an important factor for the low efficiency observed in p-DSSCs [3]. This study uses non-adiabatic charge transfer approaches [4-5] to model the charge transfer processes at the semiconductor-dye interface in p-DSSCs. In practice, the interface is prepared computationally based on electronic structure calculations (SIESTA [6]). It appears that hole recombination at the interface can be a critical reason for p-DSSCs' low efficiency.

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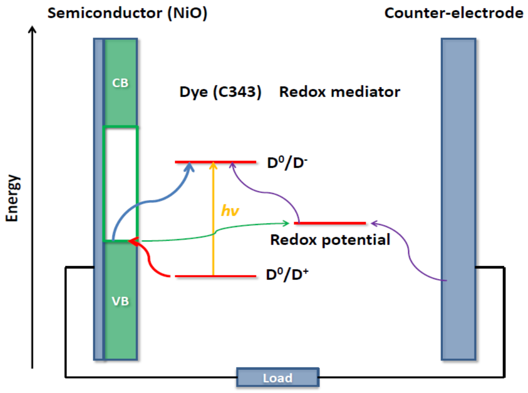
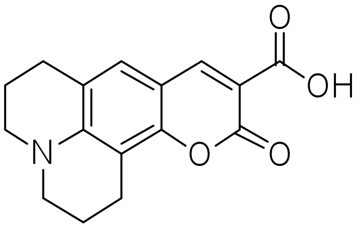
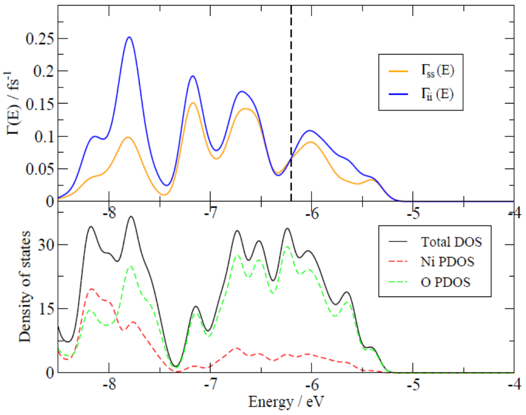
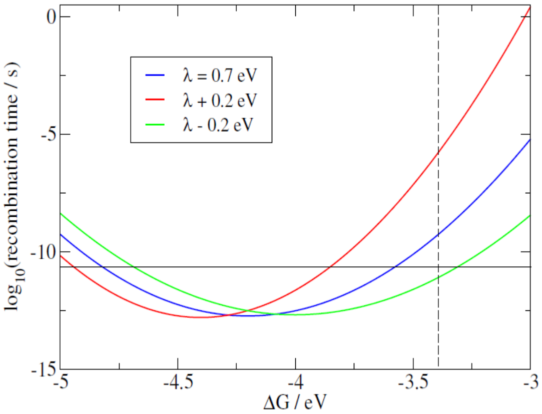
Figures





Coumarin 343 (C343)





Ultrafast dynamics of exciton formation at the ZnO(10-10) surface

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Zinc oxide (ZnO) is a promising electrode material for optoelectronic applications, especially in combination with functional organic molecules. Such hybrid inorganic/organic systems offer great potential as cheap and effective OLED or photovoltaics devices.

ZnO is transparent to visible light (band gap of 3.4 eV), natively n-type doped and abundant. Notably, a deep understanding of its highly complex surface properties and the associated surface charge carrier dynamics is not yet achieved. It is known, however, that hydrogen adsorption leads to the formation of a surface electron accumulation layer and thus metal-like behavior of the semiconductor-vacuum interface.

We study the ultrafast quasiparticle dynamics in and below the ZnO conduction band using femtosecond time-resolved two-photon photoelectron (2PPE) spectroscopy [1]. Above band gap excitation enables the investigation of the hot electron relaxation by electron-phonon scattering down to the Fermi level E_F on a femtosecond timescale. At 200 fs after excitation, surface exciton (SX) formation creates additional states below E_F. The SX exhibits a remarkable stability, showing lifetimes of several hundreds of picoseconds, most probably due to the very large binding energy with respect to the bulk conduction band. Tuning the excitation density towards the Mott limit, the SX formation probability is reduced due to transient screening of the Coulomb interaction in the high carrier density regime. Remarkably, even strong modification of the surface charge density by hydrogen termination does not change the population dynamics of the SX, showing that the exciton is localized in the subsurface region. Thus, its longevity and insensitivity with respect to surface termination make the SX highly relevant for application involving excitonic interfacial energy transfer such as Förster resonance energy transfer (FRET).

This comprehensive understanding of the ZnO-vacuum interface is utilized as a starting point for 2PPE experiments on ZnO-molecule interfaces. We show how adsorption of pyridine (C_5H_5N) leads to a drastic work function reduction by 2.9 eV and thus the ability for electrode work function tuning [2]. Furthermore, first results of interfaces with optically active molecules will be presented.

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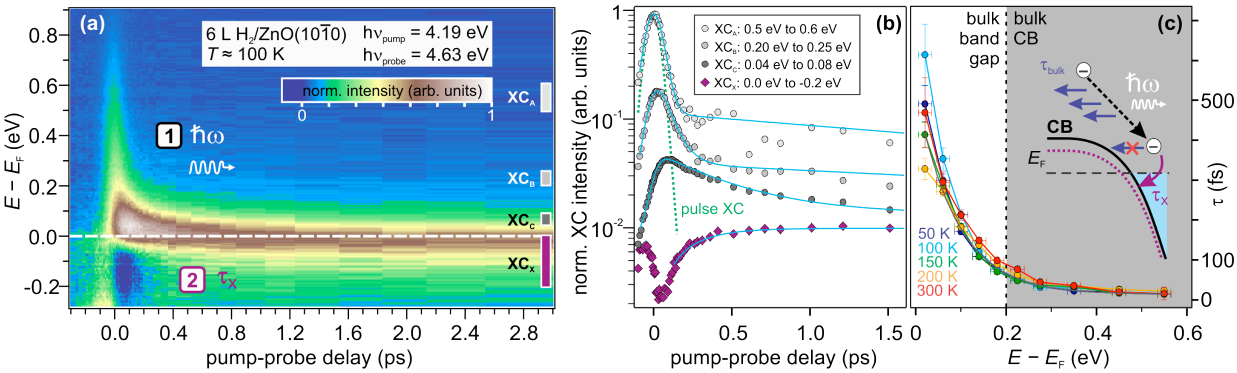

(a) Ultrafast electron dynamics at the ZnO surface below the Mott limit as probed by 2PPE spectroscopy. False colors represent photoelectrons created/depleted by pump pulse. Hot carriers in the CB relax on fs timescales by optical phonon emission. After a few 100 fs, additional electrons are verified below E_F, indicating that the surface exciton has formed. (b) Pump and probe XC traces at indicated energies above (hot electrons) and below E_F (exciton) and the corresponding double exponential fits to the data (solid lines). (c) Temperature dependence of the hot electron relaxation time and scheme of the different relaxation channels.

Charge-transfer interaction at the PEN/C60 interface

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The combination of Pentacene (PEN) and C60 is a promising model system for next generation solar cells based on organic semiconductors. Here, the C60 acts as an electron acceptor while PEN, on the other hand, attracts the holes. One of the remaining challenges in this system is the underlying charge-transfer mechanism. In general the efficiency of this charge separation will depend on the structural and electronic states at the interface. To study these dynamics, we performed time-resolved photoluminescence measurements on a thin PEN layer of standing molecules covered by C60. The data indicate the formation of correlated states across the interface. Namely, a long-lived PL signal is observed which energetically corresponds to the PEN LUMO – C60 HOMO transition. Further measurements show a signal at lower energies, possibly stemming from the PEN HOMO – C60 LUMO transition.

This work is supported within the framework of the CRC 1083 "Structure and Dynamics of Internal Interfaces"

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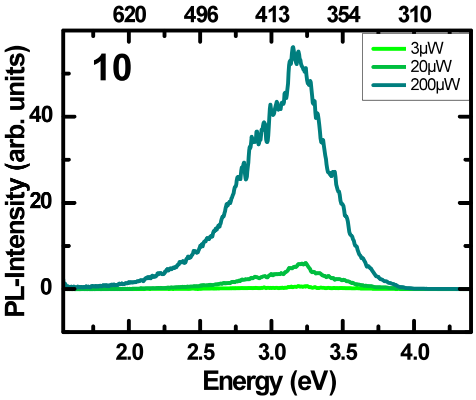

Figure 1: Excitation density dependency of photoluminescence spectra of PEN/C60 at 10K sample temperature.

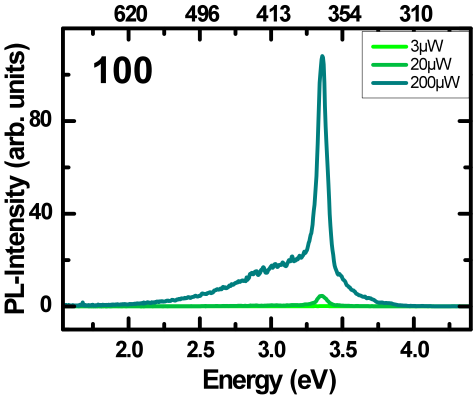

Figure 2: The same measurement performed at 100K sample temperature. A distinct signature arises at 3.3eV.

Figure 3: UPS spectra and energy level diagram of PEN/C60. From [1].

Comparison of Carrier Dynamics in Direct and Indirect GaInAs/GaAs/GaNAs Quantum Wells

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We investigate on the carrier dynamics in a set of 5xGaInAs/GaAs/GaNAs double-quantum wells by means of time-resolved photoluminescence. Within the set of six samples, the GaAs barrier width is varied as well as the N-concentration. For N-concentrations of 5%, indirect transitions across the barriers are expected. Within these indirect samples, the barrier varies from 1 nm, 3.4 nm and 6 nm. All three indirect samples show significant photoluminescence at energies below the lowest transition visible in linear absorption. Large time constants of at least >9 ns are found for the sub-bandgap luminescence of the 1 nm and 3.4 nm barrier samples under low density quasi-resonant excitation conditions. Whereas the luminescence at the bandgap of the thin and medium barrier samples occurs only at higher excitation densities and is without any notable lifetime, the luminescence of the thickest 6 nm barrier sample vanishes within tens of ps (Fig. 1 (b)) for low excitation densities. The sub-bandgap signal for this barrier thickness decays on timescales from ps to ns (Fig. 1 (c)), indicating several superimposed decay mechanisms. Combining these time-resolved photoluminescence data with pump-probe measurements will ultimately allow for further insight into the carrier transfer processes through the barrier and the interface.

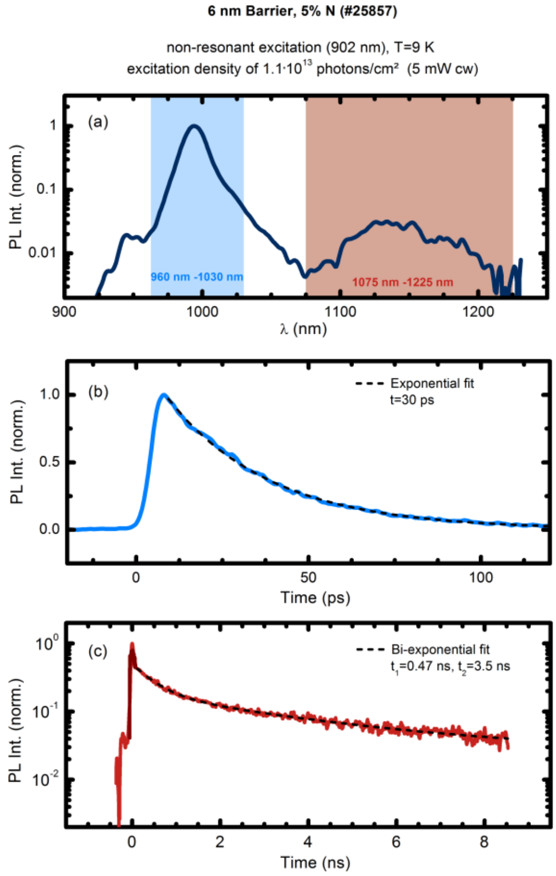

Figure 1: Dynamics of the photoluminescence of the 6 nm barrier sample. (a) Time-integrated spectrum. (b) Picosecond dynamics of the luminescence at the direct bandgap (blue). (c) Nanosecond dynamics of the sub-bandgap luminescence (red).

Reaction dynamics of exemplary organic molecules on Si(001) – a molecular beam study

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The functionalization of semiconductor surfaces by means of organic molecules is of great interest due to possible applications in the field of nanoelectronics. However, only little information is available on the reaction dynamics of organic molecules on semiconductor surfaces.

In this contribution, we show results from molecular beam studies of ethylene [1], tetrahydrofuran (THF), and cyclooctyne on Si(001). For ethylene and THF, we find that with increasing kinetic energy of the impinging molecules, the initial sticking coefficient decreases, as it is typical for a non-activated reaction channel. However, the decrease is much less pronounced in the case of THF when compared to C_2H_4, pointing towards a more efficient energy dissipation in the case of THF/Si(001). With increasing surface temperature, a decrease of the initial sticking coefficient is observed for both systems, which is interpreted in terms of an adsorption pathway via an intermediate or “precursor” state and quantitative information about the energetics is obtained.

For cyclooctyne, a highly strained cyclic molecule, a completely different behavior is observed. Our measurements of the initial sticking coefficient s_0 clearly show that s_0 does not depend on the surface temperature. This is a strong indication that cyclooctyne adsorbs via a direct, barrierless adsorption pathway, in agreement with previous STM experiments [2]. This barrierless adsorption pathway of cyclooctyne via its C-C triple bond, together with its well-ordered adsorption structure at high coverage [2], makes it a good candidate for chemoselective adsorption and controlled growth of an inorganic/organic interface on Si(001).

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Electronic structure of dangling bond wires on the Si(001) and Ge(001) at different doping levels.

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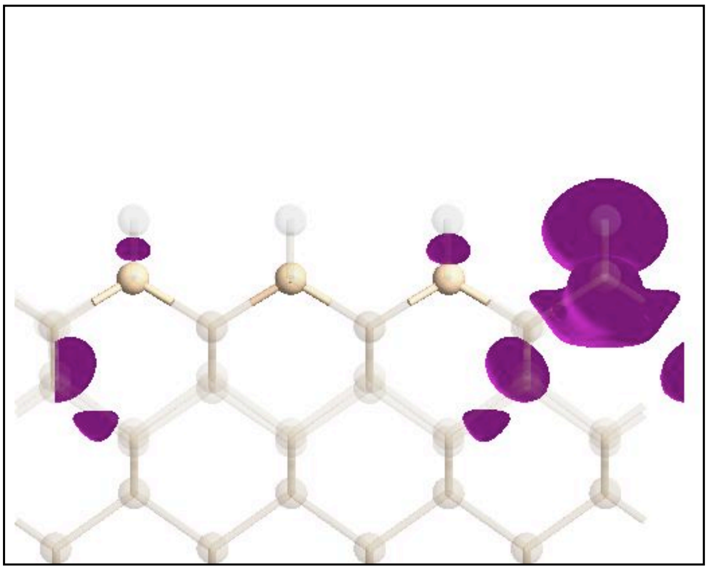
Abstract

We have theoretically investigated dangling bond (DB) structures on Si(001):H and Ge(001):H with the aim of finding a ballistically conducting wire without a band-gap. Different levels of doping have been explored to see if the Fermi level can be manipulated without fundamentally changing the electronic structure of the wires, thus allowing to move the Fermi level away from the gap. Our conclusion is that such an approach is possible for Ge, while for the Si wire, the electrons have a strong tendency to localize in one site, creating new structural distortions and opening new band gaps. Removing H from a full dimer row on the surface seems to be the best option to create a conducting wire on both substrates. However, inherent impurities and fluctuations will severely affect the conducting properties of such wires that are expected to depart from the behavior of ideal ballistic conductors.

Figure



Wire with one line of DB defect sites and isosurface of the density of a “dangling-bond” electron orbital. Rather than forming extended orbitals, the electrons self-trap in localized orbitals due to geometric distortions.

Functional Binary and Ternary Organotin Chalcogenide Clusters

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Functionalized organotin chalcogenide clusters increasingly attracted attention during the past years because of their intriguing chemical and physical properties.[1–3] Recent work of our group describes the synthesis, characterization, formation and derivatization of organotin chalcogenides with reactive organic groups.[4,5]

Herein, we report the synthesis of binary compounds with the general formula $[(R^1Sn)_xE_yCl_z]$ (R^1 = $CMe_2CH_2C(Me)O$, E = S, Se, Te), comprising functional organic substituents. The reaction of these binary compounds with transition metal complexes leads to the formation of ternary clusters. For example, the reaction of $[(R^1Sn)_3S_4Cl]$ with $[Cu(PPh_3)_3Cl]$ and $(SiMe_3)_2S$ yields a novel mixed-valent organotin sulfide cluster – $[\{(R^1Sn)_2S_2\}_2\{Cu(PPh_3)\}_2\{SnCl\}_2(\mu^3\text{-}S)_2]$ (**1**). The corresponding reaction with $[Au(PPh_3)Cl]$ affords $[\{(R^1Sn)_2S_2\}_2\{Au(PPh_3)\}_2(\mu\text{-}S)_2]$ (**2**). The optical properties are currently investigated in cooperation with the Chatterjee group.

The styrene-functionalized cluster $[(R^2Sn)_4S_6]$ (R^2 = *para*-vinylphenyl) (**3**) allows the functionalization of Si(001) surfaces. The structure and properties of this hybrid material are studied by the Volz group. Both collaborations are realized within the framework of GRK1782.

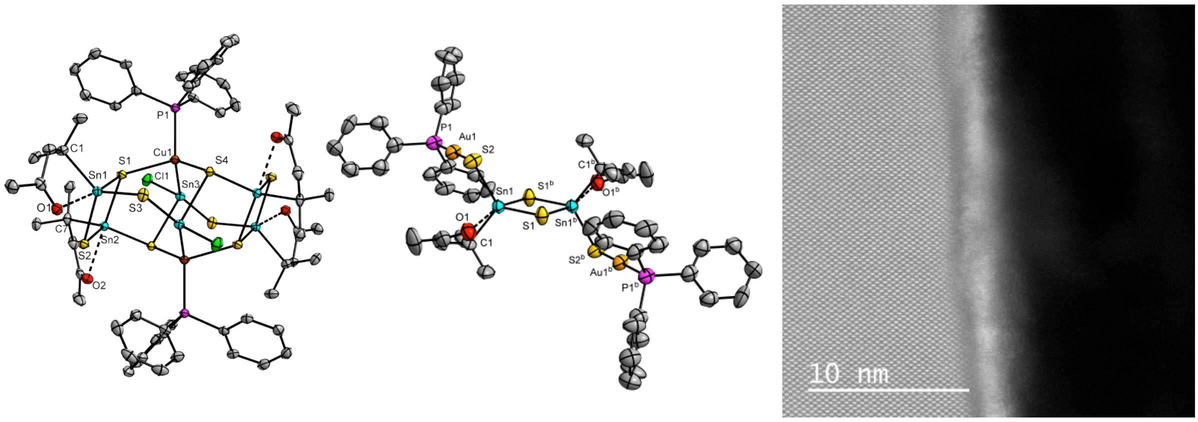

Figure 1. Molecular structure of the functionalized ternary organotin chalcogenide clusters $[\{(R^1Sn)_2S_2\}_2\{Cu(PPh_3)\}_2\{SnCl\}_2(\mu^3\text{-}S)_2]$ (**1**) (left) and $[\{(R^1Sn)_2S_2\}_2\{Au(PPh_3)\}_2(\mu\text{-}S)_2]$ (**2**) (center). TEM image upon deposition and decomposition of $[(R^2Sn)_4S_6]$ (**3**) on a Si(001) surface (right).

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Study of Codeposited PEN:PFP Films Grown on SiO_2

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Organic semiconductors have gained a great interest in the last years, due to their potential applications in electronic devices such as organic field-effect transistors (OFETs) and light-emitting diodes (OLEDs). Among these organic molecules, pentacene (PEN, C22H14), perfluoropentancene (PFP, C22F14), and above all, mixtures between both attract a special attention, because on the one hand they form donor/acceptor systems, and on the other hand they are expected to be structurally compatible due to their similar molecular geometry. Thus, they have been widely studied as a semiconductor p-type, n-type or p-n-junction, respectively, on various substrates such as halides for PFP [1] and PEN [2], SiO2/Si for PFP [3] or polymer gate dielectrics for PEN [4], and with optimal imaging conditions which minimize the radiation damage that destroys the organic materials [3].

Molecular orientation and ordering of different organic semiconductors depends on substrate interaction and substrate roughness. The arrangement of PEN:PFP grown on KCl has been studied in our group and it has been found that well ordered PEN films are grown on the substrate while PEN:PFP fibers are located on top of it [5].

In the presented study, we use Conventional Transmission Electron Microscopy (CTEM), Bright Field (BF) and Dark Field (DF) images, as well as Electron Diffraction (ED) to show the structure and the arrangement of PEN:PFP grown on SiO2. In this case we have an intermixed structure where a “tangle” of fibers can be observed and a global ordering of the PEN molecules do not appear. On these terms, the ED Patterns show mainly a polycrystalline arrangement. Experimental lattice distances (dhkl) from these ED Patterns were measured and compared with the lattice distances of pure PEN and a mixture of codeposited PEN:PFP (d_hkl^(PEN:PFP) values obtained from [6]). The overlaps show a good agreement with the PEN:PFP intermixed phase and “more or less” an agreement with pure PEN. Thus, until now it is not finally proofed, if this arrangement consists of an intermixed structure of PEN:PFP since the contribution of PEN molecules cannot be dismissed. Finally, Energy-dispersive X-ray spectroscopy (EDX) measurements were performed in Scanning TEM (STEM), showing an homogeneous distribution of carbon and fluorine atoms. This finding give evidence of an intermixed structure of PEN:PFP.

As can be seen, TEM characterization is an useful tool to understand local and extended crystal orientation by means of a combination of imaging and diffraction techniques.

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[7] The authors gratefully acknowledge funding from the **SFB 1083.**

Type-II Excitons in (Ga,In)As/Ga(N,As)-quantum wells on GaAs

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Abstract

Quantum Well (QW) structures are used in many semiconductor devices. These systems inevitably contain interfaces, that influence the charge carriers. Since the recombination of the excitons takes place across the interface their properties are influenced by the interface, making type-II excitons an excellent probe to study internal interfaces. Here, we present an analysis of the recombination of spacially indirect (type-II) excitons in (Ga,In)As/Ga(N,As)-MQWs on GaAs.

The MQW structures under investigation were grown epitaxially using metal-organic vapor-phase epitaxy. On the GaAs substrates a 10 nm thick $(Ga_{0.76},In_{0.24})As$ was grown. This layer is followed by a GaAs barrier of varying thickness between 1 and 7 nm and a QW consisting of Ga(N,As). The nitrogen content in this QW was chosen to be 0.5% to have type-I samples and 5% to have type-II samples. The final capping consists of 45 nm GaAs. No post-growth annealing was applied. Figure 1 shows the luminescence spectra of the type-II samples for different GaAs interlayer thicknesses. For the sample with a 6 nm thick interlayer the type-I transition of the (Ga,In)As is clearly visible at 1.250 eV. Additionally a broad IR-band around 0.8 eV is visible. This is most likely because of the EL2 level of the GaAs substrate. For decreasing interlayer thicknesses the type-I transition disappears and a new peak arises at approx. 0.950 eV. This is because of the type-II transition between the electron in the Ga(N,As) QW and the heavy hole (hh) in the (Ga,In)As. The type-II luminescence does not occur for the thickest interlayer because the special separation of electron and hole is too big. The type-I samples containing 0.5% of nitrogen only show the type-I (Ga,In)As transition, which is lowest in energy (not depicted). The inset shows the result of a quantum well calculation using the transfer matrix method. In this calculation we take strain into account. Conjuction of experiment and calculation reveal the heterooffest between the conduction bands of Ga(N,As) and GaAs to be 600 meV. For the heavy hole band within the errorbars no offset was found. Furthermore, we find the electron and the heavy hole wavefunction to be strongly confined to their respective QW supporting the explanation for the absence of the type-II transition in the PL spectra for a 6 nm thick interlayer. Additionally, we performed PL experiments using varying excitation intensities. These measurements reveal a second indirect transition for high excitation intensities. This transition is most likely because of the e1-hh2 transitions, which is possible because the selection rules are weakend for indirect transitions. Finally, we aim to present time resolved mearurements of the type-I and type-II transitions to reveal the recombination dynamics of the type-II transitions an their interplay with interface properties such as interlayer thickness and quality.

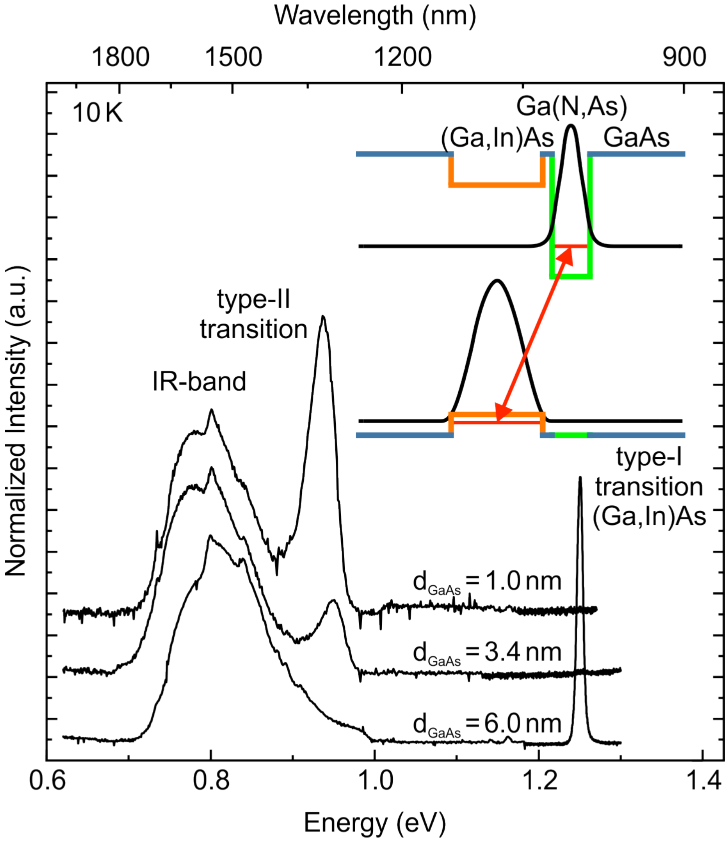

Figure 1: Low temperature PL spectra of the (Ga,In)As/Ga(N,As) type-II samples for different interlayer thicknesses. The inset shows the bandoffsets of the MQW structure and the energy levels and probability density of electron and hole contributing to the type-II transition.

Molecular Orbital Mapping of Phthalocyanines

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Abstract

Tomography of molecular orbitals using angle-resolved photoemission spectroscopy (ARPES) is a method to gain experimental access to electronic wave-functions of aromatic molecules adsorbed on surfaces, like thin layers of Phthalocyanines on a silver crystal. Hereby, the measured electron momentum distributions (see Fig. 1) represent the square of the absolute value of the Fourier Transform of the initial wave-function.[1,2] Together with low energy electron diffraction (LEED) experiments (see Fig. 2), the adsorption geometry of theses molecules can be determined, as illustrated in Fig. 3. Additionally, momentum mapping of the LUMO delivers information about charge transfer from the substrate into the molecules.[3]

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Figures

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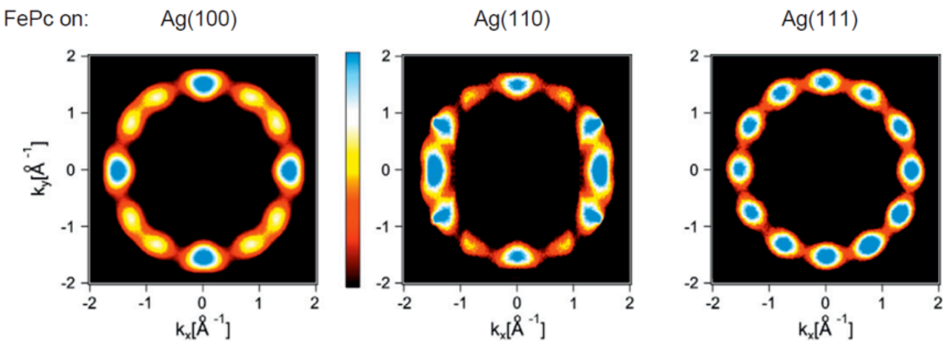

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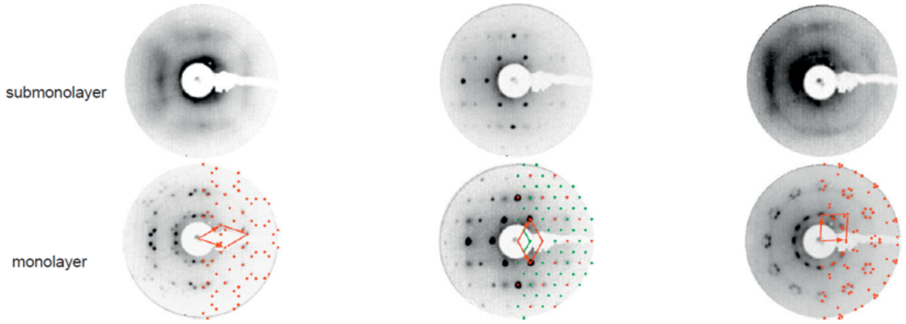

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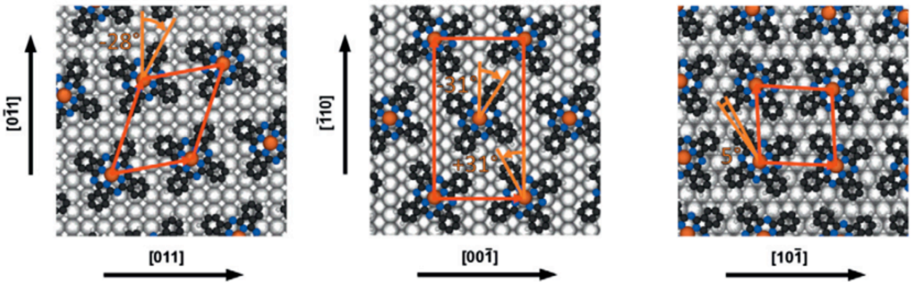

Spectroscopy and dynamics of unoccupied electronic states of the topological insulators Sb_2Te_3 and Sb_2Te_2S studied by time- and angle-resolved 2PPE

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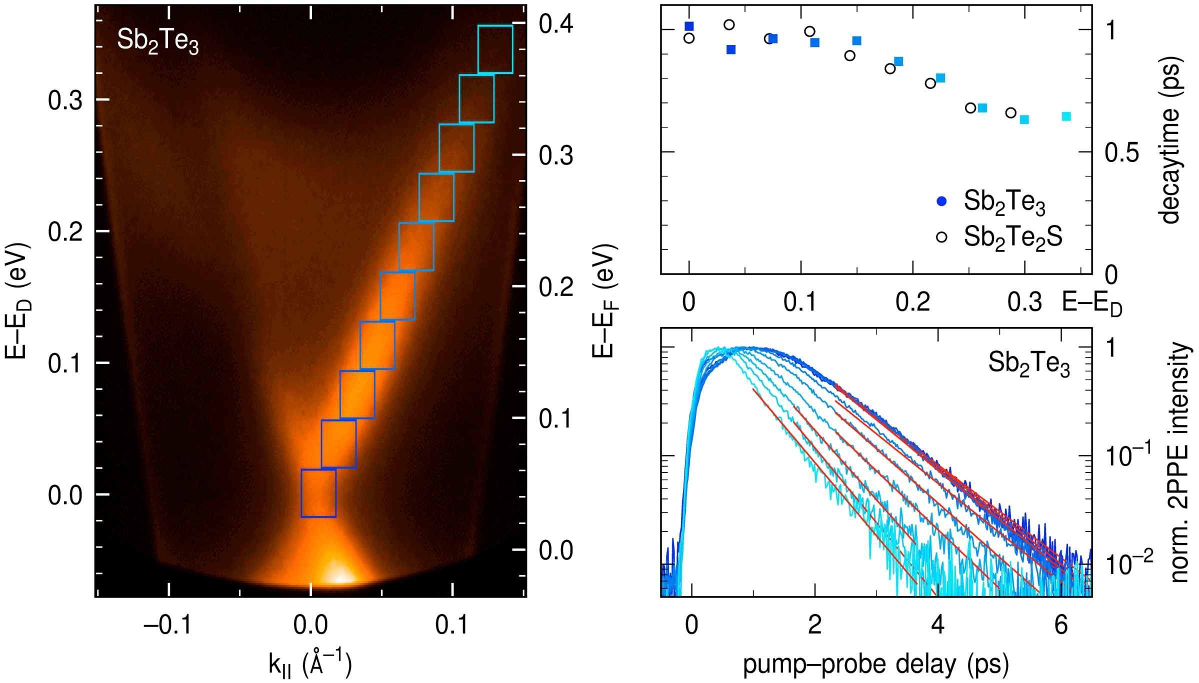
We present a comparative study of the electronic structure and ultrafast electron dynamics of the unoccupied states of Sb_2Te_3 and Sb_2Te_2S by means of time- and angle-resolved two-photon photoemission (2PPE). Sb_2Te_3 belongs to the same class of three-dimensional topological insulators as Bi_2Se_3 and Bi_2Te_3 which are characterized by a single Dirac cone around $\overline{\Gamma}$ and a relatively large indirect band gap. In contrast to Bi_2Se_3 and Bi_2Te_3, however, Sb_2Te_3 is found to be intrinsically slightly p-doped which makes it difficult for conventional ARPES investigations. In 2PPE short pump pulses populate unoccupied states before the electrons are photoemitted by subsequent probe pulses. Sb_2Te_3 thus makes an ideal system to study the electron dynamics within the topological surface state by this technique. Theoretical predictions suggest that the substitution of the central Te layer in the quintuple layers of Sb_2Te_3 by S leads to a substantial increase of the band gap. The comparison of Sb_2Te_3 and Sb_2Te_2S should thus allow exploring the role of electron transfer between the bulk bands and the topological surface states.

Our results show that both materials exhibit in fact a typical Dirac-cone structure with the energy of the Dirac-point E_D lying above the Fermi energy E_F. By identification of bulk and surface bands at higher energies we clearly verify the larger band gap of Sb_2Te_2S as compared to Sb_2Te_3. Optical excitation with 2.5-eV pump pulses results in a substantial population of the Dirac cone up to 350 meV above E_D for both materials. The time dependence of this population shows that it is to some extent created by a direct optical excitation, but predominantly by an indirect transfer from the bulk conduction band. Interestingly, both materials show a nearly identical decay dynamics on a picosecond time scale at room temperature, despite the different size of their band gaps. Preliminary experiments at low temperatures indicate that the decay gets faster with decreasing temperature.



Role of light induced dipole generation in the activation of Organic solar cells containing TiOx cathode interlayers

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Abstract

Organic photovoltaics have witnessed an impressive boost in efficiency during the last couple of years now reaching values of 9-10 %. A further efficiency improvement may only arise by a perfect understanding of all the operation mechanisms taking place in a working device. Of particular importance is the role of the selective interfacial layers which must allow the extraction of one of the carriers (electrons or holes) whilst blocking the other one. The underlying energetics of the organic semiconductor/electrode interface is an issue of primary concern for improving organic solar cell technologies. TiO_x interlayers are known in the literature to require a light soaking activation step to provide efficient devices. Here we use this effect to tune the selectivity of the cathode contact to electrons by the controlled action of UV light. Indeed, by controlling the exposure to UV-light the device can be monitored in different electrical states from a fully deactivated form (S-shape kink observed) to a fully activated configuration (high fill factor ~60 %). UV-light activation of complete cells alters the work function of the oxide that decreases about 650mV as observed by Kelvin probe measurements. The energy equilibration of the cathode contact at different activation levels are analyzed by measuring the flat-band voltage using capacitive techniques. A shift of up to 1.2 V under 1 sun illumination (w/o UV) is observed in flat-band voltage in the case of deactivated TiO_x interlayers. An increase in the magnitude of the dipole present at the oxide layer is proposed as the main responsible for the voltage shift. Although the sign of the dipole should favour the extraction of electrons the concomitant modification of the band bending in the organic semiconductor hinders an efficient extraction of carriers at positive voltages and originating the *S*-shaped characteristics.

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Characterization of the interface structure of (GaIn)As and Ga(NAs) grown on GaAs

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Abstract

Ternary (GaIn)As as well as Ga(NAs) materials are widely applied in the fields of glass fiber communication, solar cells, electronic and optoelectronic industries [1]. The physical properties of quantum wells can be significantly influenced by both the chemical composition and the interface morphology, whereas the latter can be controlled by the growth temperature and by the introduction of growth interruptions. As a result, it is of great importance to characterize the crystallographic interface structures for technological applications. In the present work, we are mainly focused on the characterization of the interface structure of quantum wells using atomic force microscopy (AFM) and transmission electron microscopy (TEM).

The (GaIn)As and Ga(NAs) quantum wells were grown with metal organic vapor phase epitaxy (MOVPE) on GaAs (001) substrate at temperatures of 525°C and 625 °C with different growth interruption times (0s, 20s, 40s, 120s). After growth of each quantum well, both smooth and island-like structures were observed with AFM as shown in Fig.1. To analyze the crystallographic structure and composition of the islands, high resolution TEM was utilized to investigate the interface between the ternary materials and the GaAs from both, [010] and [110], directions. TEM results, giving quantitative information from the cross-section of the samples, will be correlated with AFM data, which shows the surface of quantum wells. The results suggest that there is a characteristic island structure depending on growth conditions. The islands exhibit a height of about two atomic layers and a width of smaller than 10 nm. Hence, HRTEM in combination with AFM provides a good method to obtain information of the interface structures of quantum wells.

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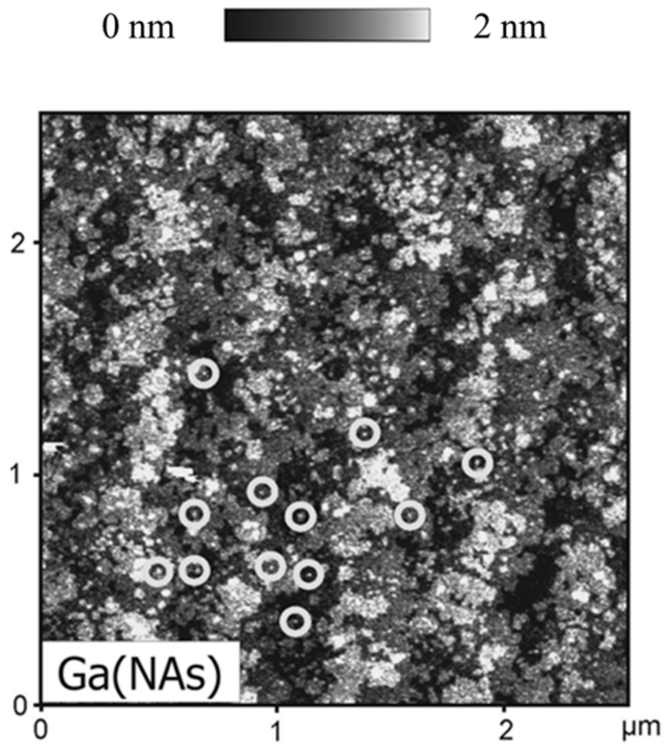
Acknowledgements

We gratefully acknowledge financial support of the DFG in the frame work of SFB1083.

Fig. 1 AFM micrograph of an interior Ga(NAs) interface; the island-like structures are marked by the white circles.



Metal Organic Vapor Phase Epitaxy of Semiconductor Heterostructures and Interfaces

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Metal Organic Vapor Phase Epitaxy (MOVPE) is a powerful tool for the realization of thin epitaxial semiconductor layers in research and industry. It allows for a wide variation of material compositions in a wide layer thickness range. Within the Collaborative Research Center (SFB 1083) it gives us the possibility to produce specifically tailored samples with characteristic interface configurations for subsequent structural, optical and electrical measurements. For example, the interface bonding configuration can be controlled by the process design and its influence on optical and electrical parameters can been studied.

Multiple quantum well structures based on the (GaIn)As/Ga(NAs) material system will provide a suitable test system for the spectroscopical analysis of type-II band alignment at the interfaces. The other type-II material system (GaIn)As/Ga(AsSb), studied in this project, is of particular interest for so called W-type semiconductor laser structures, as they will be studied in detail in cooperation with the partner project B7.

The interfaces between (GaIn)As and (GaIn)P can either be grown lattice matched or with a defined mechanical strain. In this model material system we can study the chemical intermixing and in particular exchange processes in the group-V component at the interface using high resolution transmission electron microscope (HR-TEM) investigations in the partner project A5. With the addition of specific interlayers at the interface it is also possible to tune the electronic structure as well as influence the before mentioned exchange processes.

First results from the MOVPE growth studies in these different model material systems as well as internal characterizations by means of high-resolution X-ray diffraction (HR-XRD), atomic force microscopy (AFM) as well as photoluminescence (PL) spectroscopy studies in combination with the feedback from various partner projects will be presented and discussed.

Magnetic anisotropy and redistribution of electrons at Co/Ni and Co/Pd interfaces

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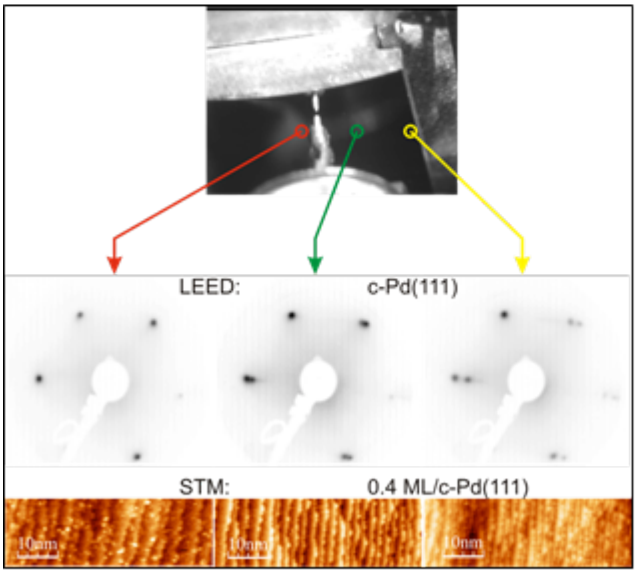
Abstract



Curved single crystals provide the unique opportunity to grow the thin-film samples on the vicinal surfaces with continuous variation of the miscut angle. Surface reconstruction leads to the formation of the terraces stretched along the axis of the rotational symmetry of the curved crystals. Width of the terraces decreases and the number of atomic steps per unit length increases when the miscut angle grows [1]. The surface electronic structure of the curved crystals changes from 1D quantum well to 2D state [1].

Ultrathin films of Co grow epitaxially on both Ni(111) and Pd(111) substrates and demonstrate Perpendicular Magnetic Anisotropy (PMA) [2]. Due to the 9% lattice mismatch Co grows incoherently on Pd(111) with negligible strain. Whereas the lattice mismatch between Co and Ni(111) is only about 2% and Co grows coherently on Ni(111) bearing substantial strain [2]. Strong variation of the anisotropy and the redistribution of the electrons with change of the Co thickness were observed at the Co/Ni(111) interfaces [3,4].

We present the results of the investigations of the magnetic anisotropy of ultrathin Co films grown on the curved Pd(111) and Ni(111) single crystals. The azimutal orientation of the miscut is along [11-2]. The miscut angles vary continuously from -15 to +15 deg. Co films with a thickness from submonolayer to few atomic layers were grown in UHV conditions. The surface reconstructions and the morphology of the films were probed by LEED and STM. Magnetic anisotropy was deduced from the data of XMCD measurements performed at the synchrotron radiation facility. Variation of the anisotropy with thickness and miscut angle was correlated with respective change of the growth mode and surface electronic states.

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Figures

Photo of the curved Pd single crystal (top panel). Variation of the period of the surface reconstruction with miscut angle revealed by the change of the splitting of the LEED pattern (medium panel). Change of the terraces on the surface of the substrate and morphology of Co islands with moving from the central (left image) to the lateral (right image) part of the crystal observed by means of STM (bottom panel).

Energy transfer characteristics of Mn doped CdS/ZnS quantum dots

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Abstract

Semiconductor quantum dots are a very promising material system for many application areas like biological sensing, quantum computing and even display technology. This wide field of applications can mainly be ascribed to the remarkable change of the optical characteristics of the material when reducing its dimensions.[1] Core shell CdS/ZnS quantum dots (QDs) are very prominent example of such a system. These QDs not only show a very high quantum efficiency regarding the optical excitation, but in addition the luminescence properties can be controlled in a well-defined manner by changing the size of the QDs.

The CdS/ZnS QDs we investigate are additionally doped with manganese in the ZnS shell,[2] which is itself a very potent luminescence center. Photoluminescence spectra show the successful doping of the ZnS shell by the identification of the typical Mn luminescence band around 580 nm. Time resolved measurements additionally conclude this by lifetime determination of this spin forbidden transition of 4ms. The Mn luminescence decay is depicted in Fig.1 by the red dots with a mono-exponential fitting curve shown by a red line.

With doping of the CdS/ZnS QDs we obtain a system with two very distinct luminescence bands around 450 nm from the CdS core and around 580 nm from the Mn in the ZnS shell.

The energy transfer between these two luminescence centers is not only determined by the spectral position of each band but additional by the interface between CdS and ZnS within the QD.[3] A study of the transfer characteristics consequently implies the study of this interface. A detailed analysis of the temporal behavior of both bands shows an interdependent decay characteristic.

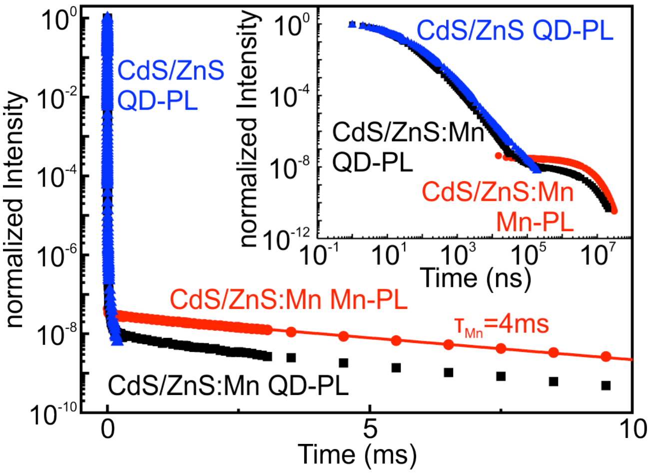

Fig.1: Luminescence decay of Mn doped and undoped CdS/ZnS QDs respectively. The inset shows the same transients in a log-log plot.

In Fig.1 is depicted the decay characteristics of the respective luminescence bands for Mn doped and undoped QDs. The undoped CdS/ZnS dot (blue triangle) shows a power-law like decay up to several microseconds. The Mn doped QDs not only show the slow decay of the Mn band (red dots), but exhibit a slow decay of the CdS core luminescence (black squares) as well, indicating an energy transfer from Mn states to QD states. The inset in Fig.1 also shows a slightly faster decay of the QD luminescence for shorter times in the case of a Mn doped ZnS shell, identifying an energy transfer from QD states to Mn states.

The interpretation of the resulting transients leads to the conclusion that the low energetic Mn state cannot only act as acceptor for the high energetic CdS transition, but also as donor. This surprising result leads to a tremendous enhance of the CdS lifetime from hundreds of ns in the absence of Mn to several ms with present Mn. As a consequence we can use Mn doped Cd/ZnS QDs to increase the application area of semiconductor quantum dots even further by establishing a new time region for semiconductor quantum dots.

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Orientational Controlled Growth of Phthalocyanine Films on Metallic and Transparent Substrates

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Phthalocyanines (Pc) and their derivates provide an interesting class of organic semiconductors for thin film applications which have been studied intensively in the past years [1]. The aim of the present work is twofold: on one hand we focus on the preparation of orientationally well defined Pc thin films to enable detailed optical studies. On the other hand the preparation of well defined Pc monolayer films and their use as contact primer layers on metallic substrates is studied with the aim to tailor the work function and energy level alignment between the Fermi level of the substrate and a subsequently deposited organic semiconductor film.

A systematic variation of transparent substrates is performed to control the molecular orientation adopted in phthalocyanine films. The resulting crystalline structure and morphology has been characterized by means of AFM and XRD. A prototypical behavior is shown in Fig. 2 for CuPc which adopts a lying orientation on KCl(100) substrates [2] and an upright orientation on glass substrates. The transparent substrates enable further optical characterization such as UV-Vis spectroscopy and optical polarization microscopy. In future work the optical properties will be analyzed to study the interaction with metal oxide substrates such as titanium dioxide which will be complemented by means of XPS and NEXAFS.
In this contribution, we have derived a thermal protocol to prepare nominal phthalocyanine monolayer films on metallic substrates by first depositing a thin multilayer films and subsequently desorbing the multilayer access, which has been exemplified for CuPc on Ag(111) substrates. The resulting monolayer yields a recumbent adsorption geometry as derived from the quantitative analysis of the NEXAFS dichroism. Interestingly the NEXAFS signature reveals no broadening as compared to the multilayer film which indicates an overall weak chemical interaction. The medium term goal of our study is to use such phthalocyanine monolayers as a contact primer layer for subsequently grown organic semiconductor films. As a first result along this direction Fig. 1 shows NEXAFS and AFM measurements of a pentacene submonolayer adsorbed on a CuPc monolayer on Ag(111). Both the dichroism of the NEXAFS spectrum and the line profile in the micrograph indicate the presence of upright standing pentacene molecules, in contrast to flat lying pentacene on clean a Ag(111) substrate [2].

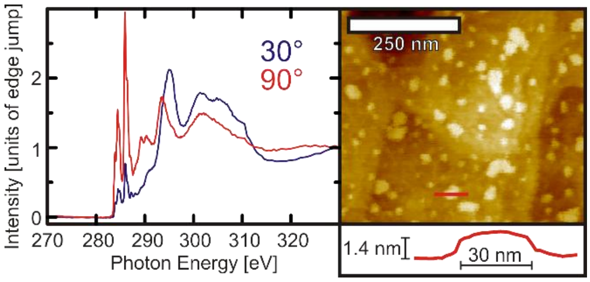

Figure 1: NEXAFS (left) and AFM (right) measurement of pentacene submonolayer on CuPc Monolayer on Ag(111) showing upright standing pentacene.

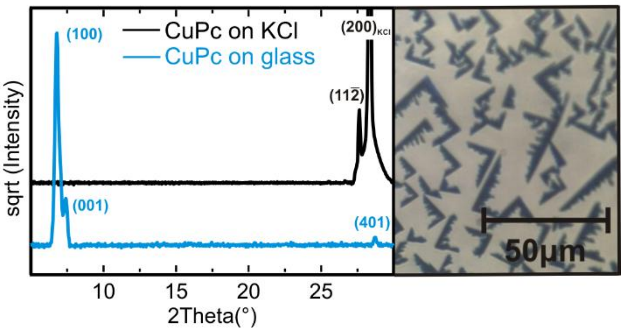

Figure 2: XRD (left) of CuPc multilayer on KCl showing lying and on glass showing standing orientation. Opitcal micrograph (right) showing crystallites of CuPc on KCl

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An NMR Approach to semiconductor internal layers

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Abstract

The ultimate goal of the current project is the investigation of internal layers by NMR techniques. Conventional NMR is by far not sensitive enough to address few layers of semiconductor material grown on a flat substrate. To enhance the sensitivity by 3 to 5 orders of magnitude dynamic nuclear polarization (DNP) will be employed. The highly polarized partner being 129Xe a possible probe nucleus being 31P.

The development of NMR probes simultaneously resonant to 129Xe and 31P in an UHV environment is a prerequisite for the usage of the DNP processes envisioned.

Here we describe the technical development of an NMR probe coil for double resonance experiments. The idea is to connect the coil to an electric network which contains two oscillatory circuits for two different resonance frequencies. Hereby the existing single resonance coil used with the present UHV setup can be left unchanged. The main task is the power and signal matching to 50 Ohm at two different frequencies simultaneously. Results of modelling and preliminary experiments are discussed. The aim is to obtain high q-factors for both frequencies while maintain tunability.

The DNP process is most efficient at close contact. Therefore a 13C graphene substrate may be a first material investigated. For a internal 31P layer inside a heterostructure the substrate must contain the layer within a few atomic distances from the surface.

Photo-modulated reflection and temperature-dependent photoluminescence studies of Ga(AsBi) bulk and quantum well structures

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Functionalization of GaAs based structures by adding bismuth is a promising approach for semiconductor lasers operating at telecom wavelength. In difference to other supplements, the admixing of bismuth to the GaAs alloy shifts the valence bands, rather than the conduction band. This way, the desired wavelength of 1.55µm is reached by incorporation of about 10% bismuth. In addition to the reduction of the band gap, spin orbit coupling is increased and the gap between the valence bands is increased[1]. This reduces losses due to auger processes and the efficiency is increased, even at elevated temperatures.

To quantify the influence of bismuth concentration, we investigated multiple Ga(AsBi)/GaAs bulk samples with different Bi concentrations by room temperature photo-modulated reflection spectroscopy. In addition, the same set of samples is studied using temperature-dependent photoluminescence spectroscopy. This way carrier localization due to defects can be identified. To further characterize confinement effects, a set of multi quantum well structures[2] is investigated using the same technique.

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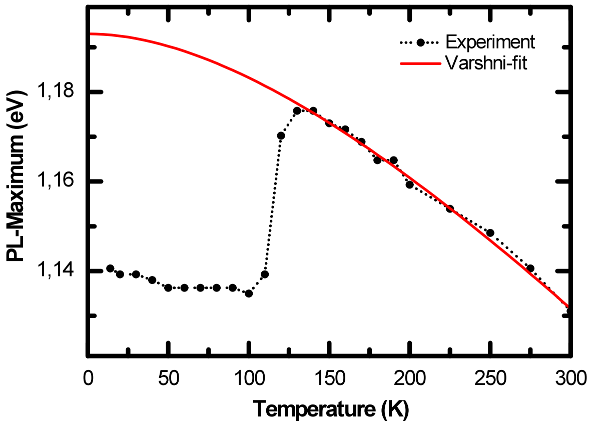

Figure 1: temperature dependency of photoluminescence peak of sample #17444 with a bismuth content of 3,8%. Laser pump-power 200mW.

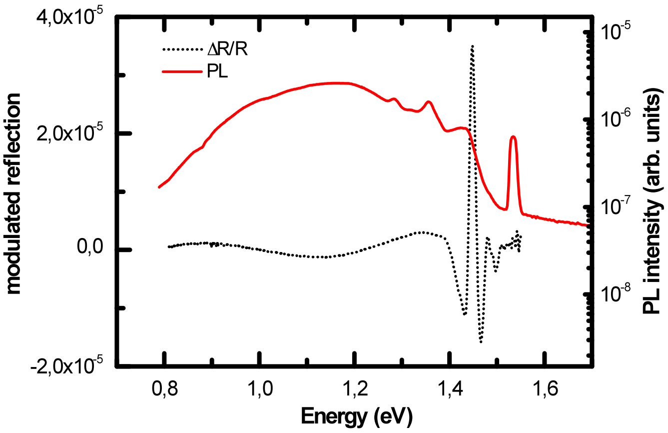

Figure 2: comparison of photoluminescence spectra and photo-modulated reflection-spectra of sample #17219 with a bismuth content of 0,9%

Experimental verification of the surface termination in the topological insulator $TlBiSe_2$

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Abstract:

We present the surface termination of the non-layered topological insulator $TlBiSe_2$ studied with the combination of surface and bulk sensitive probes. We have directly unmasked for the first time the characteristic surface morphology of the cleaved surface by scanning tunneling microscopy, which shows that island structures are formed by residual atoms on the cleaved plane. These islands are further explained by surface-sensitive photoelectron spectroscopy (PES) at BL-7 of Hiroshima Synchrotron Radiation Center and bulk-sensitive PES at BL-15 of SPring-8. We find that thallium core-level spectra are strongly deformed by a surface component in sharp contrast to the other elements. We finally propose a simple explanation for this behavior by assuming that the sample cleaving breaks the bonding between thallium and selenium atoms, leaving the thallium layer partially covering the selenium layer. These findings will assist the interpretation of future experimental and theoretical studies of this surface [1].

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Density functional study of tetrahydrofuran on Si(001)

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Abstract

Silicon surfaces are playing a decisive role for semiconductor devices, and adsorption of organic molecules on silicon can improve the physical and optical properties of the semiconductors [1]. Small organic molecules react with a surface dimer which is related to the reconstruction of the clean silicon (001) surface [2]. Recently, experimental results [3] could show that tetrahydrofuran (THF) molecules exhibit a peculiar reactivity with the Si surface-dimer. Based on this finding we used density functional theory to elucidate the main chemical reactions of THF on Si(001)c(4x2). All computational investigations were carried out within the Vienna *ab initio* simulation package [4] with the exchange-correlation functional PBE [5] and semi-empirical dispersion corrections [6]. We calculated adsorption energies and the kinetic barriers as well as the key geometries that characterize the chemical reactions of the dissociative states. A notable conclusion of this study is that the dissociation of the THF molecule exhibits a very low energy barrier across two dimer rows.

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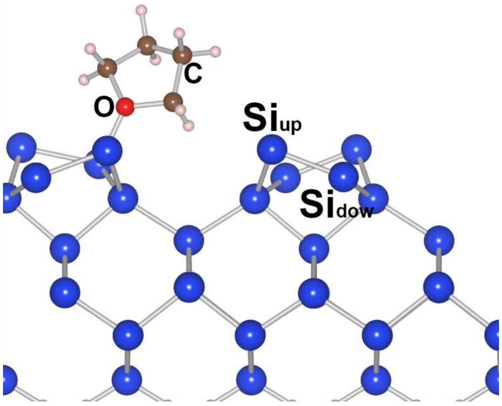

Figures 1: THF molecule on Si-dimer.

Second Harmonic Generation at the Buried GaP/Si(001)-Interface

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The experimental study of the electronic properties of buried semiconductor interfaces is a challenging task. Optical second harmonic generation (SHG) offers a preeminent potential to probe interfaces because of its intrinsic sensitivity on a breaking of symmetry. Gallium phosphide (GaP) has been proven as a promising candidate to combine III/V-semiconductors with silicon (Si) based technologies. Therefore the polar/nonpolar GaP/Si interface is an ideal model system of considerable interest for future applications.

In this study rotational anisotropy of second harmonic generation (RASHG) is used to investigate the GaP/Si interface. RASHG reveals a strong isotropic interface contribution, which is absent for the pure GaP and Si wafers while dominating the second harmonic signal originating from the GaP/Si(001) heterostructure. A correlation with scanning transmission electron microscopy (STEM) data allows for direct demonstration of the sensitivity of RASHG on twins, Ga-droplets, and anti-phase domains.

Time-resolved second harmonic generation (TRSHG) is employed to characterize the ultrafast carrier dynamics at the GaP/Si interface. The GaP/Si(001) hetero-structure exhibits a characteristic TRSHG which is attributed to a direct excitation involving a proposed interface state followed by the ultrafast build-up of an electric field via charge transfer across the GaP/Si(001) interface. The missing interference of the GaP bulk component with the electric field induced second harmonic generation (EFISH) component allows to separate the different TRSHG contributions. The dynamics are investigated at room temperature and at a sample temperature of 10 K. An influence of the lattice temperature on the dynamics via electron-phonon scattering is discussed.

Study of Optical Properties and Electron Energy Loss Spectroscopy for Graphene Nanoflakes from Time – Dependent Density Functional Theory Calculations

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Abstract

The unique properties of graphene[1], such as large conductivity, high mechanical strength, high thermal stability, tunable optical properties[2], have led to an intensive study since it was first isolated in 2004. It has become one of the most promising materials for applications such as optical signal processing and quantum information. Part of this interest stems from the possibility to control the properties of graphene by means of chemical and physical modifications. Apart from extended graphene structures, also graphene quantum dots, antidots, nanoribbons and moebius strips have attracted the interest of the scientific community.

In this work we focused our attention on the optical properties of hydrogen saturated and chemically modified graphene nanoflakes. We investigated in detail how the optical properties depend on the geometry and the size of the flakes. We performed our calculation with an efficient Time-Dependent Density Functional Theory code[3] based on the use of basis set of localized functions (atomic orbitals). In conjunction with the ab-initio SIESTA package[4] this allows to study flakes containing more than a thousand atoms.

We have chosen hydrogen-saturated hexagonal and rectangular planar flakes to characterize size and shape dependence of optical absorption.

Moreover, we found that chemically functionalized edges affect the absorption spectrum. We saturated the carbon flakes with oxygen, fluorine and hydroxyl groups. The obtained results open the way for tuning optical properties by changing the edge functionalization.

We also explored the spatial distribution of the density change induced by an external electric field with a given frequency.

In order to further characterize the optical excitations an alternative approach has been used. Casida's approach[5] allows us to get information about the nature of the single optical excitations and can help to characterize plasmonic peaks in the optical spectrum.

Finally, we developed a code for calculating electron energy loss spectroscopy (EELS) for finite systems. These calculations will allow us to analyze further the electronic excitations of nanostructures. In particular, we focused our attention on nanoflakes of graphene.

The results improve our understanding of graphene properties that could be useful for applications in the field of optical signal processing and quantum information.

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Optical Spectroscopy on Organic-Inorganic Hybrid Structures

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Abstract

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

We studied organic-inorganic hybrids consisting of organic layers, e.g. pentacene, phthalocyanine and ruthenium based dyes on inorganic substrates by optical spectroscopy in the temperature range between 10K and room temperature.

Tension could be revealed as an interface relevant effect by studying Pentacene on ZnO [1]. Pentacene layers with different thickness show different exciton energy shifts with temperature variation. This is due to different temperature dependent expansion coefficients of the organic and inorganic material and the resulting tension between them. As a result a strong interface dipole in dependence of the temperature occurs.

Exciton recombination across type **II** organic-inorganic interface can give access to the level alignment and interface properties of the organic-inorganic semiconductor structures. Starting with material combinations known from dye sensitized solar cells (DSSC) which imply a charge transfer from organic to inorganic structure some promising hybrid systems are investigated in order to find a recombination of charge carriers across the interface. Different organic molecules, e.g. TiO-Phthalocyanine [4] and ruthenium dyes like N719 [2][3] have been studied on single crystalline rutile TiO_2 and nanocrystalline anatase TiO_2 substrates.

In addition to type**II** investigations basic measurements are performed on organic-inorganic hybrid structures in order to learn about the influence of preparation method (OMBD and drop-coating) and substrate on resulting optical spectra (like TiO-Phthalocyanine on glass and KCl). Regarding the absorption spectra, in comparison to the organic molecules in solution, the spectra of formed crystalline layers are often broadened and even red-shifted due to weak intermolecular coupling and exciton formation, respectively.

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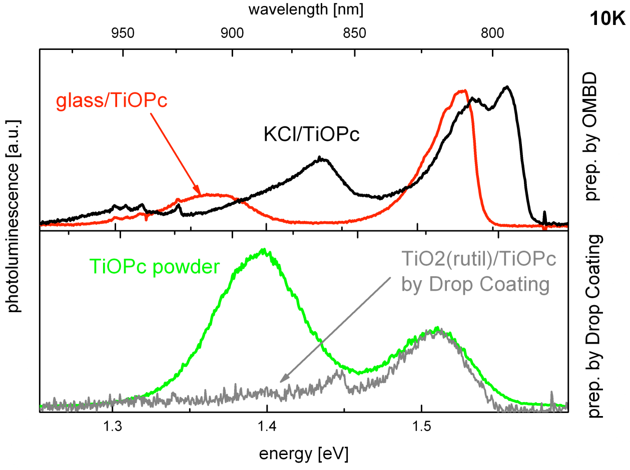
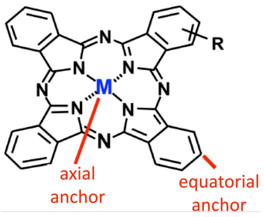
Figures





As a promising type**II** candidate of the wide variety of the group of phthalocyanines (right picture) **TiOPc** is investigated. TiOPc on different substrates (KCl and glass) shows strong difference in PL spectra which is probably due to occurrence of exciton photoluminiscence. Drop-coated TiOPc revealed a new low energy peak at 1.45eV. The peak was identified as PL of deeper states and is not due to type**II** recombination.

Interface-Dominated Semiconductor Laser Structures

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Abstract

III/V semiconductor lasers are widely used and still enormous effort is ventured with the pursuit of higher output powers and the exposure of gaps in the spectral coverage especially in the mid-infrared domain. To date, structures with type-I quantum wells (QWs) have dominated this field of investigation in both edge emitting and top emitting devices. Yet, the performance of type-I QW based devices is fundamentally limited by the Auger recombination in which excitation energy is converted into heat resulting in a reduced laser efficiency. The ultimate goal of this work is the development of type-II edge emitting lasers for the mid-infrared (>2 µm) range. In type-II QWs Auger recombination is suppressed which maintains the potential for efficient lasers at wavelengths above 1.3 µm.

The achievement of this ultimate goal requires the epitaxial growth of type-II QW structures which exhibit a sufficient quantum efficiency for laser operation. The design of a first laser prototype requires therefore an exact understanding of the carrier dynamics in the interfacial recombination processes. The measurements presented on this poster deliver the basis for a fruitful theoretical investigation of type-II QWs.

In detail, we investigate a type-II GaInAs/GaAsSb/GaInAs multi-quantum well with GaAsP strain compensating layers grown on GaAs substrate which is designed for an emission wavelength in the range of 1.3-1.55 µm. An Argon ion laser is employed for optical excitation at 514 nm. The sample is housed in a cryostat enabling temperature dependent observations in the range from 10 K to 400 K. A Germanium detector is used in combination with a monochromator to perform spectral resolved photoluminescence measurements. First results of the temperature as well as excitation density dependent PL-investigations will be presented and discussed. This analysis forms the basis for an iterative optimization of the intended type-II-quantum well structures in close cooperation between theoretical design, epitaxial realization and experimental optical characterization and analysis.

Charge and intermolecular interactions: Modeling the interplay of free-base porphine molecules adsorbed on coinage metal surfaces

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Porphyrins not only resemble essential molecular components in the live-giving circulatory systems of photosynthesis (chlorophyll) and aerobic respiration (heme) but also are promising ingredients for self-assembled devices harnessing their functionality in applications for photovoltaics, nano-catalysis, and data storage. For technical realizations it is highly desirable to achieve the self-assembly of fully controllable and ordered surface mounted molecular structures. A thorough understanding of the intermolecular interactions at the interface plays a key role in steering such supramolecular arrangements. We report on modeling free-base porphine, the parent compound of all porphyrins, adsorbed on clean Ag(111) and Cu(111) surfaces by means of semi-local dispersion corrected [1] density functional theory. We focus on a coverage dependent analysis of the charge transfer towards the molecule at the interface, as well as the adsorption energy with a specific focus on a partitioning into different contributing physical energy components. Hereby we investigate the influence of geometric deformations, van-der-Waals interactions, and electrostatics on the supramolecular arrangement. Our calculations support the findings of previously conducted experiments [2,3].

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Dimensionality and Metallicity of quasi-1D Ag:Si(557) Investigated by Angle-Resolved Photoemission

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Self-assembled quasi-one-dimensional (1D) atomic wires on semiconductor surfaces show a range of interesting physical phenomena, and are promising for nanoscale devices. While there are some prominent examples [1], the number of metallic systems available, often a requisite for use in such devices, is relatively small. Angle-Resolved Photoemission Spectroscopy (ARPES) is a powerful tool that can directly address the metallicity of these systems, and can additionally connect macroscopic conductivity to specific parts of the electronic band structure. We apply ARPES to Ag:Si(557): around 1ML coverage, plasmonic losses with a 1D dispersion have been observed at room temperature [2] in Electron Energy Loss Spectra (EELS), in contrast to insulating behaviour observed with EELS and ARPES at lower Ag coverage [3]. Such behaviour may be related but different to the 2D Ag:Si(111), which is semiconducting at 1ML coverage but metallic when excess atoms are added [4]. Preparation has been optimised by LEED and ARPES measurements, while high resolution ARPES measurements near the Fermi level, carried out at BESSY II in Berlin, allows us to search for metallic surface states and measure their dispersion, in order to assess their relation to the low-dimensional plasmonic excitations. Furthermore, we have developed a new high-repetition rate VUV light source for ultrafast time-resolved ARPES measurements, which will provide complementary dynamic information on such quasi-1D systems.

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Charge transfer states on thin films of pentacene derivatives

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Charge transfer states (CT) play a crucial role at semiconductor interfaces in organic photovoltaics. The CT at the semiconductor/vacuum interface is accessible by two-photon photoemission and could be regarded as a model system for the CT at a semiconductor/semiconductor interfaces [1]. Those CT states have been observed on pentacene films on Bi(111) and Si(111) [2].

In this work we are using bichromatic two-photon photoemission to investigate the charge-transfer states on thin films of pentacene and its derivatives (such as TIPS pentacene) on the Au(100) and the Si(100) surface.

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Computer Simulation of Growth Kinetics of Compund Semiconductors

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In the past few years growth of III/V semiconductor compounds on Si substrates has received a lot of attention in the scientific community because of its promising applications in functionalization of traditional semiconductors. While surface structures and properties of the grown materials are experimentally well accessible, little is known about the formation and structural characteristics of the interfaces between the Si substrate and the III/V semiconductor compound. To gain insight into the intermediate stages of epitaxial growth and the interface properties, we developed a Kinetic Monte Carlo (KMC) computer simulation package for the theoretical study of the kinetic characteristics of epitaxial growth.

Two particular problems were addressed with the simulation. It was recently observed that, despite the initially flat substrate, growth of GaP on the Si-{001} surface leads to significant intermixing of the two materials at their interface. In our atomistic computer simulation, supported by ab-initio modelling of the individual kinetic processes, we were able to identify the driving forces of the intermixing and reproduce the experimentally observed results with great accuracy. A comparison of the experimental and theoretical results is shown in Figure 1.

In addition, the package was used to simulate melt-back etching of Ga droplets on the Si-{001} surface. In another recent experimental study it was shown that deposition of Ga onto a Si substrate leads to formation of metallic Ga droplets, etching large, Si-{111} limited, pyramidally shaped structures into the bulk Si. We were able to reproduce this behaviour in our simulation and thereby study the intermediate stages of droplet formation and melt-back etching during the Ga deposition. A snapshot of the simulated sample after removal of Ga is shown in Figure 2, with the experimentally observed voids in the substrate clearly visible.

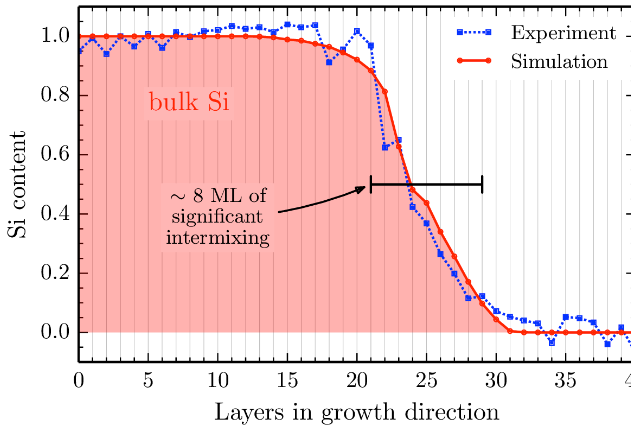

Figure 1: Intermixing at the Si-GaP interface. The initially flat substrate shows a significant intermixing of about 8 ML after the GaP growth.

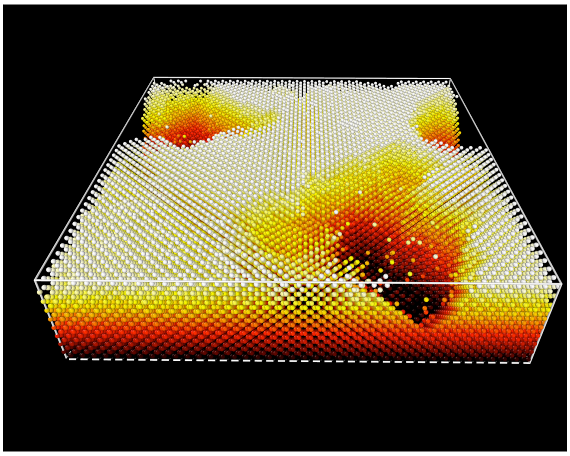

Figure 2: The Si substrate shows large, Si-{111} limited voids after Ga deposition and Ga droplet formation. This is a simulation snapshot.

Preparation and characterization of phosphonic acid based self-assembled monolayers on ZnO substrates

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Interfaces between semiconducting metal oxides and organic semiconductors have attracted considerable interest because of their applications in organic-inorganic hybrid systems such as transparent electrodes in light emitting devices or in dye-sensitized photovoltaic cells [1]. Electronic interfacial properties in such hybrid systems can be tuned by molecular films covalently bond to transparent conductive oxidic surfaces. Due to the ability to form robust films phosphonic acid based self assembled monolayers (SAMs) are promising linkages for dyes and enable to control the adsorption geometry of dye-molecules [2-5]. However, in contrast to widely used SAMs on gold surfaces, the molecular interaction and stability of such films on metal oxides have been less thoroughly studied. To derive a better understanding of the structure, binding strength and stability of such SAMs on metal oxides here we use phenylphosphonic acid (PPA) as a simple aromatic model system for complex chromophores. In order to educe microscopic structural properties molecular films were deposited on single crystalline zinc oxide samples when common studies on polycrystalline surfaces with undefined interfaces yield only average properties [6,7]. In this project we work with single crystalline ZnO substrates with different surface terminations: polar surfaces (O- and Zn- terminated) and non-polar surfaces (mixed-terminated). SAMs were investigated by combining x-ray photoelectron spectroscopy (XPS), near edge x-ray absorption fine structure spectroscopy (NEXAFS) and thermal desorption spectroscopy (TDS). Surface modification like the presence of H- or OH- groups affects the film formation [8,9]; therefore the role of hydroxylation of the various ZnO surfaces was also studied. Comparing films prepared by immersion and by organic molecular beam deposition method (OMBD) under UHV conditions effect of hydroxylation was investigated.

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Investigation of antimonide-based materials grown on exactly oriented (001) silicon substrate by MOVPE

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Antimonide-based materials, such as gallium phosphide antimonide (GaPSb), that are grown highly mismatched on silicon (001) substrates have interesting applications in high electron mobility III/V channel layers. As there are no III/V semiconductors with high electron mobility which can be grown lattice matched on Si, different buffer layers have to be studied and the defect formation within these layers has to be understood in detail to optimize the layer structures for later device application.

To avoid antiphase boundaries penetrating through the antimonide-based layer, a gallium phosphide (GaP) layer is grown between the silicon substrate and metamorphic buffer. The antiphase boundaries created by the growth of a polar material on the non-polar silicon substrate annihilate within the GaP [1]. The mismatch between GaP and Ga(PSb) is between zero to twelve percent, depending on the composition. The strain induced by the high mismatch due to the high antimonide content should be relaxed by misfit dislocations at the interface.

The interfaces between GaP and the metamorphic buffers have been investigated by conventional dark-field transmission electron microscopy (TEM) as well as high resolution TEM and HAADF (high-angle annual dark-field) scanning TEM (STEM) using a double Cs corrected JEOL 2200FS.

(S)TEM investigations have revealed that the misfit dislocations at the interfaces mainly are Lomer dislocations and 60° dislocations pairs. However, dark-field and high resolution TEM have shown that the bulk may contain other defects like stacking faults, twins and threading dislocations.

This contribution will provide an insight on the crystal structure of GaPSb and other metamorphic buffer layers which can be used to optimize their growth.

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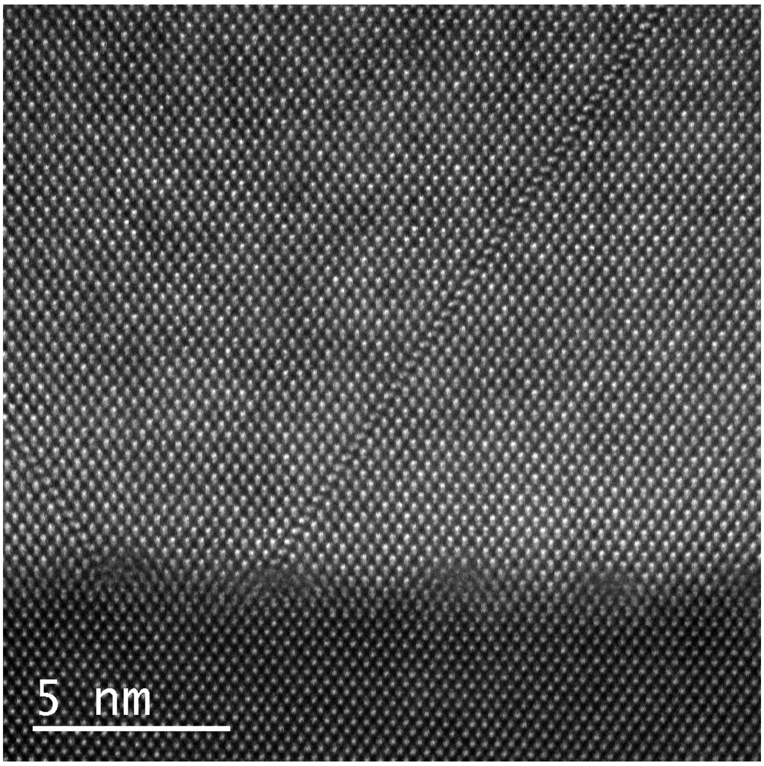

Gate-controlled energy-barrier at graphene/molecular junction

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The formation of an energy-barrier at a metal/molecular junction is a commonly observed phenomenon [1]. For these junctions, large energy-barrier provides rectification leading to a diodic behavior, whereas a relatively small energy-barrier provides nearly-ohmic behavior and efficient carrier injection into the molecular semiconductor. In general, a specific metal/molecular junction allows a fixed energy-barrier. In our work, we implement a graphene/C_{60}-molecular junction that shows both characteristics by using the concept of gate tunability [2] of the junction energy-barrier. We demonstrate a controllable switch of the energy-barrier such that the junction acts as a highly rectifying diode at negative gate voltages to a nearly-ohmic junction at positive gate voltages at room temperature. From our experimental data, we extract the energy-barrier modulation of up to 0.65 eV. A control over the graphene/C_{60} junction energy-barrier by the applied gate voltage leads to the operation of a graphene/C_{60}/metal vertical-field-effect-transistor (VFET) with a transconductance up to five orders of magnitude. Our ability to modulate such an energy-barrier provides a promising route towards molecular devices that combine a rectifying diode and a nearly-ohmic junction.

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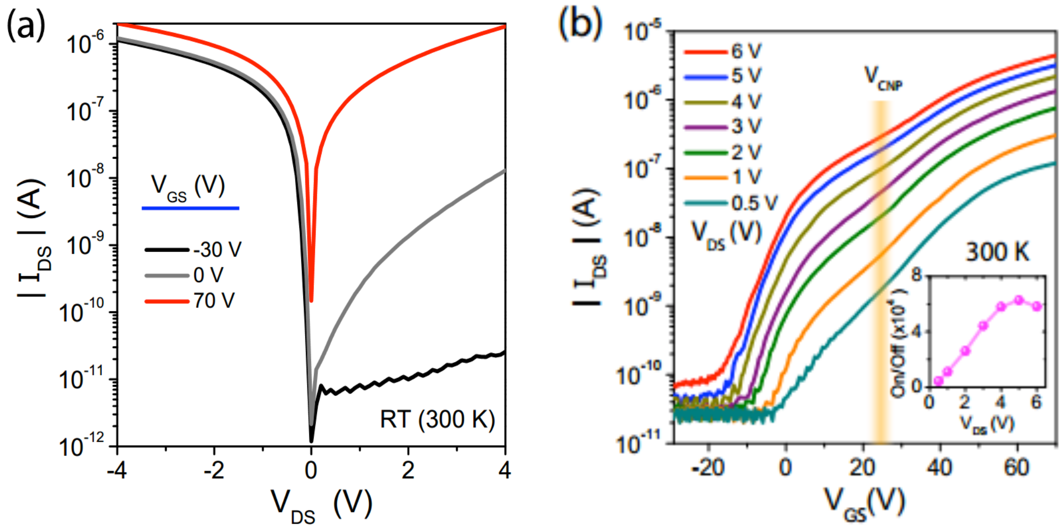

Figure 1. (a) A controllable switch of the energy-barrier of a graphene/C_{60} junction from a highly rectifying diode to a nearly-ohmic junction at room temperature. (b) Room temperature transfer characteristic for the graphene/C_{60}/Al vertical field effect transistor.

Adsorption thermodynamics and kinetics of cyclooctyne and derivatives on silicon via DFT

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Abstract

Due to the strong-binding character of their addition to the silicon (001) surface,[1,2] cyclooctyne and its derivatives promise to be ideal building blocks for the construction of organic/silicon interfaces (Fig. 1). In order to predict the properties of these interfaces, one has to understand the interaction between single molecules and the surface first. We use density functional theory in a periodic environment to model these systems and investigate thermodynamical aspects of different adsorption modes. Here, use of the latest quantum chemical methods with the addition of dispersion corrections ensures a physically correct description of the systems.

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Figures

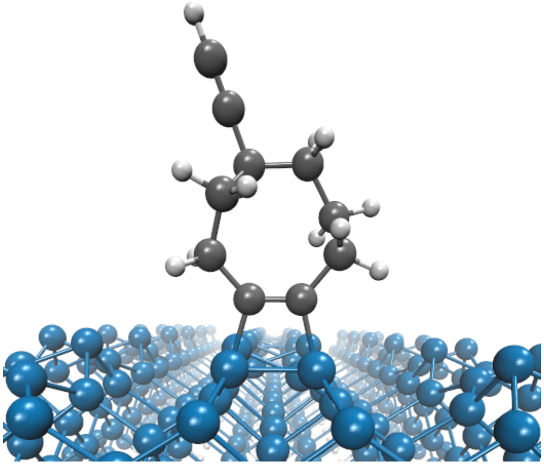

Fig. 1: 5-Ethinyl-cyclooctyne, a possible candidate for the construction of organic/silicon interfaces, bound to the Si(001) surface.

Acknowledgements

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Surface modification of nanoparticles

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Abstract

A variety of inorganic/organic materials has been developed to circumvent common limitations of traditional therapy approaches.[1] Recent progress in nanotechnology applied to medicine has spread the general optimism about the possibilities that nanomedicine may afford in many medical issues (therapy, early diagnosis, sensing, limits of detection, *etc*.). An ideal nanomedicine should be able to travel along the circulatory system, undetected by the immune system. Also, it should reach the targeted organ or tissue selectively, producing a detectable signal.[2]

The stability of these systems in physiological media as well as the design of their surface to achieve targeting and efficient cellular uptake are among the most importance and critical issues of bionanotechnology. One of the most employed methodologies to stabilize NPs in water solutions relies on the use of amphiphilic polymers.[3] This methodology allows for the generation of a universal nanoparticle surface for any type of nanoparticle.

Herein, opportunities and recent results concerning hybrid nanomaterials aimed as nanomedicines will be discussed

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Smart Particles for Bio Apps

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Recent years have witnessed the rapid development of inorganic nanomaterials for medical applications. At present, nanomedicines – nanoparticles (NPs) destined for therapy or diagnosis purposes – can be found in a number of medical applications including therapeutics (either self-therapeutics or drug carriers) and diagnosis agents (e.g. contrast agents for imaging or transducers in biosensors). Pushing the limits of nanotechnology towards enhanced nanomedicines will surely help to reduce side effects of traditional treatments and to achieve earlier diagnosis. As for all medical approaches, the ultimate aim of nanomedicine is improving the well being of patients. However, mixing nanomaterials with biological components such as fluids, living cells, and tissues does not always result as expected. The interplay between engineered nanomaterials and biological components is influenced by complex interactions which make predicting their biological fate and performance a non-trivial issue. Indeed, the structural integrity and the a priori function of nanomaterials can change dramatically due to unwanted nano-bio interactions. For medical applications in particular, any new nanomaterial has to be exhaustively studied when it comes in close contact with biological fluids and living cells or organisms. The motivation is clear: first, many unwanted effects can be turned on unexpectedly (e.g. leakage of toxic ions, ROS production, sequestration by the phagocytic system, etc.) and second, their purpose as therapeutic or diagnostic agent can be lost as they are transferred to the desired working environment. Herein some recent results concerning hybrid nanomaterials (inorganic core + organic coating formed by biomarkers) aimed as nanomedicines will be discussed. In particular, we will described the use of gold and iron oxide NPs derivatized with a number of molecules of biological relevance, i.e. cell-penetrating peptides (CPPs), proteins, monosaccharides, “anti-fouling” polymers, etc., for bioapplications such as gene therapy, photothermal therapy or optoacoustic imaging.

Functionalization of Tin Chalcogenide Clusters for Surface Binding

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Abstract:

Organic functionalized tin chalcogenide clusters have attracted increasing attention because of their interesting chemical and physical properties.[1–3] In the recent years our group developed a variety of binary clusters with reactive organic groups.[4] By coupling these organic groups to metal complexes inorganic/organic/inorganic multilayer clusters could be obtained.[5,6]

The motive of an inorganic cluster core and an organic ligand bonded to a metal atom can be transferred to surface chemistry by linking the tin chalcogenide cluster to surface active organic systems. Unsatured organic systems such as porphyrins, phthalocyanines, perylenes and cyclooctynes can interact with metal atoms on surfaces forming inorganic/organic interfaces.[7,8]

Our investigations will focus on interactions between the inorganic cluster core, the organic system and surface atoms and combine the concept of nano chemistry with surface chemistry.

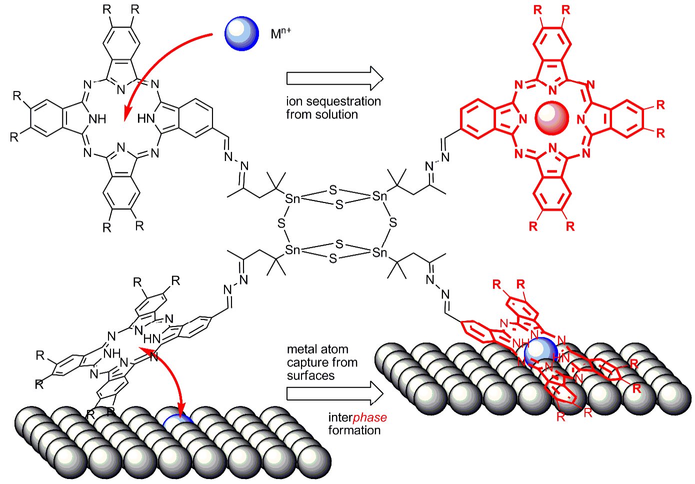

Figure 1.: Interface formation by metal atom capture from surfaces and ion sequestration from solution.

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Adsorption of Tetrahydrofuran and Diethylether on Si(001)

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A promising possibility to compete with the challenges of miniaturization in semiconductor device physics is the functionalization of inorganic semiconductor surfaces with organic molecules. It is thus important to understand the basic adsorption mechanisms of different classes of organic molecules. In this contribution, we investigate the adsorption properties of tetrahydrofuran and diethylether on the Si(001) surface as representatives for the functional group of ethers. We find a complex adsorption scheme which is similar for the two molecules.

At 50 K, a dative bond is formed via the donation of electron density of an oxygen lone pair into the D_{down} orbital of the c(4x2) reconstructed Si(001) surface. Heating the sample to 300 K leads to a surface mediated ether cleavage which results in covalently bonded adsorbates on two neighboring dimer rows. While the ring opening reaction of tetrahydrofuran leads to a bridging Si-O-$(CH_2)_4$-Si configuration, the linear diethylether is cleaved and leads to Si-O-C_2H_5 and Si-C_2H_5 adsorbates. The scission of diethylether further enables a tip induced intrarow hopping of the (-C_2H_5) fragment.

DFT-Study on the Adsorption of MOVPE-Precursors on III/V-Semiconductors on Silicon and on Properties of III/V-Semiconductor Quantum Well Materials

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Heterostructures of III/V-semiconductors epitaxially grown on silicon are promising candidates for laser devices integrated in semiconductor circuits. Control over the growth process and thus the properties of the resulting system can only be achieved, if the underlying mechanisms are understood. Modeling the adsorption of precursor molecules in the epitaxy process with first principles computational methods is a crucial ingredient in the process of understanding the elementary steps of the chemical reactions that occur at the surface. As a prerequisite for adsorption studies, the hydrogen coverage in thermodynamic equilibrium with the gas phase under epitaxy conditions has been studied with density functional theory-based *ab initio* thermodynamic and phonon computations. It could be shown that the surface is hydrogenated under the conditions in a MOVPE-reactor up to temperatures well above those present during growth processes. This laid the foundation for following adsorption studies based on *ab initio* molecular dynamics.

Another aspect is the computation of the electronic structure of the quantum well materials. These materials are multinary III/V-semiconductors. In order to assess the accuracy of available methods, the well-studied material GaAs has been used too find the most appropriate method for bandstructure computations. The meta-GGA functional MBJLDA proved to yield results comparable to hybrid functionals and GW-computations while still being feasible for larger systems that are required to model the multinary quantum well systems.

Mn doped CdS, CdS/ZnS Nanoparticles
Synthesis and characterization

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Over the last decade, Magnetic doped nanoparticles have gained increasingly more attention by researchers. These nanoparticles exhibit very unique and useful properties, enabling applications in fields such as biomedical diagnosis, solar cells, spintronics, light emitting diodes(LED) etc. Large Zeeman effects have been demonstrated in Mn-doped ZnS, ZnSe, and CdSe nanocrystals due to the presence of just few Mn^{2+} ions inside the nanocrystals.[1-9] Synthesis and characterization of Mn-doped CdS/ZnS core/shell nanocrystals[Fig.1,2], using a slightly modified method described previously by Yang et al., are discussed. [10]

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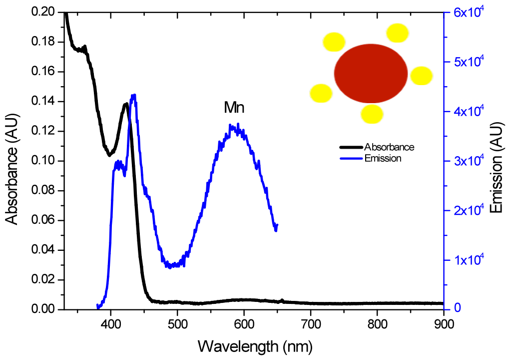
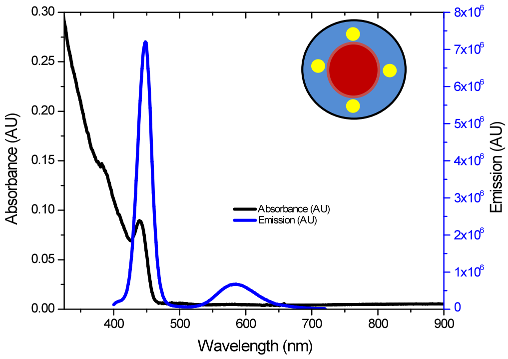
Figures



(1) Uv-vis absorbance/emission spectra of Mn-CdS NPs



(2) Uv-vis absorbance/emission spectra of CdS/Mn-ZnS NPs

Morphology Evolution and Electronic Structure of Organic-Metal Interface

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We present a time-dependent morphology study of organic thin films on a metal substrate [1]. On the example of NTCDA multilayer films, we identify several sub-processes involved in the structure formation. In a particular transient phase, which exists only for several minutes during the structure formation, we observe peculiar changes of the line shape and energy position of the C K-NEXAFS signal with respect to the bulk and gas phase spectra [2]. Of particular interest is the organic-metal interface; due to the structural rearrangement of the molecules and roughening of the film, we can identify the interface layer. This layer shows a peculiar excitation feature at the Fermi level, which can be related to a many-body excitation in the organic-metal system which can be explained within the single impurity Anderson model.

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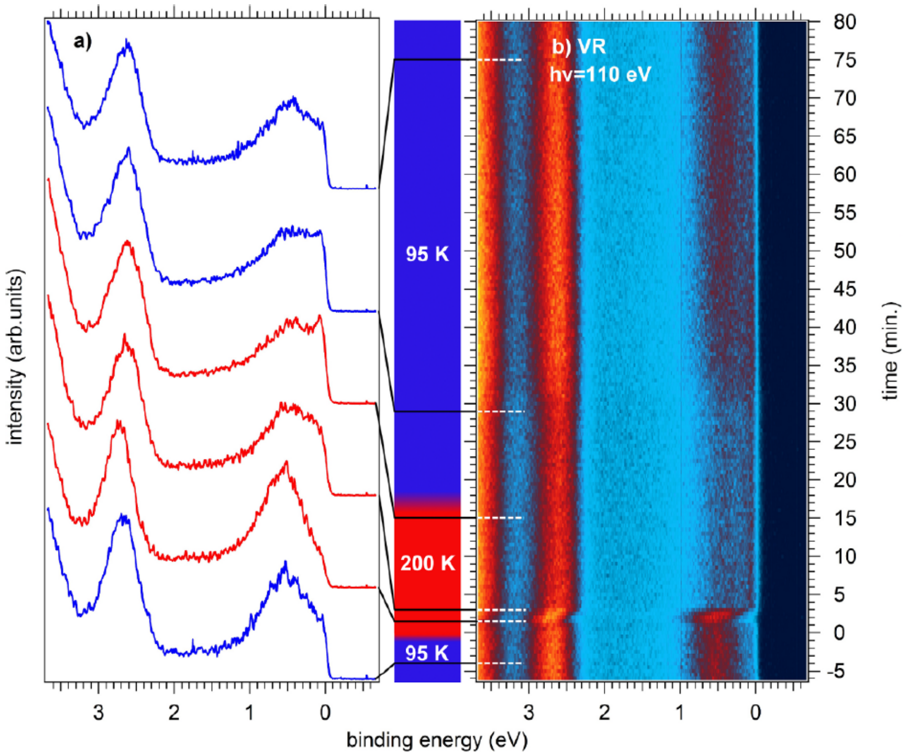

Figure 1: Time-dependent photoemission spectra of the valence region of an NTCDA multilayer film. a) Integrated PES intensity derived from the data shown in b) at the position indicated by dashed lines. Blue and red spectra refer to measurements at 95 K and 200 K, respectively. b) 2D colour-plot map of the PES spectra. The 8 ML thick film was prepared at 95 K.

Effect of Anisotropic Mass on Exciton Wave Functions

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We present a microscopic theory to calculate exciton wave functions for semiconductors with an indirect band gap. Such systems often have mass anisotropy [1], which modifies the symmetry of the exciton states [2]. A modified Wannier equation is derived coupling different angular momenta components of the wave function. As a result, the wave function becomes stretched or squeezed, depending on the mass difference in the indirect band gap (see Fig. 1).

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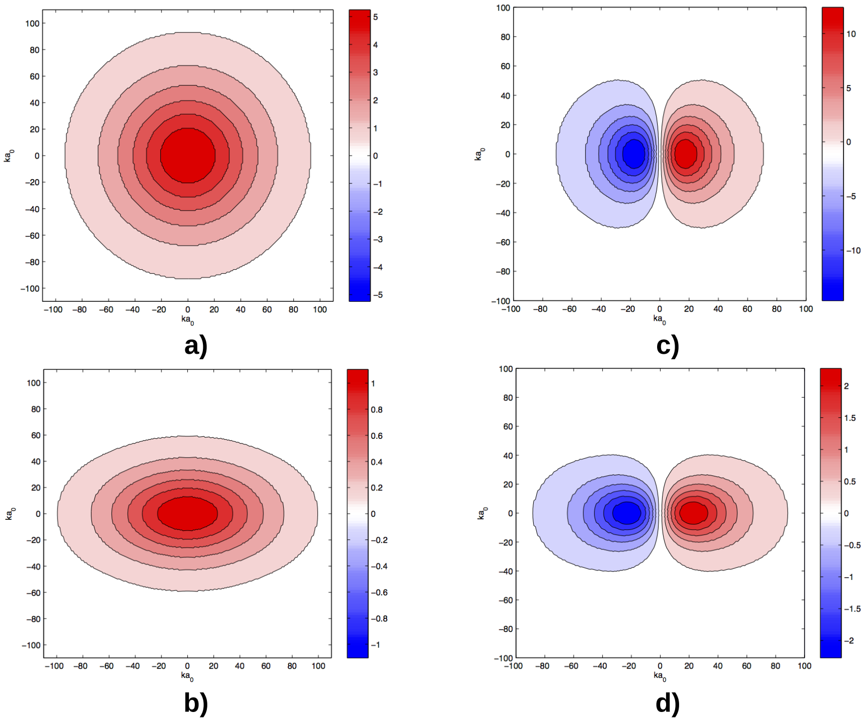

Figure 1: Indirect exciton wave functions. The 1s wave function is shown in a) and b) in the direct and indirect case, respectively. A comparison of the direct and indirect 2p wave functions is shown in c) and d).

Quantum Chemical Investigations of GaP/Si(001) Interface Formations and Elementary Growth Processes

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Abstract

The growth of mixed semiconductor materials from group 13 and 15 elements on a silicon substrate is investigated by periodic Density Functional Theory (DFT) calculations in a projector-augmented plane wave basis with atom core pseudo-potentials. Individual elementary processes occurring in Metal-Organic Vapour Phase Epitaxy of galliumphosphide (GaP) were selected ranging from precursor decompositions[1] to atomic surface hopping. The entity of those processes determines the turn-over frequency of the material and, moreover, the structure of the resulting crystal. As the electronic structure is among the critical properties of the developed materials and depends dominantly on the structural quality, the insights gained from the elementary details can guide researchers to improve growth conditions and material composition.

Experimental Transmission Electron Microscopy (TEM) imaging [2] and kinetic Monte Carlo simulations (kMC) [3] unveiled that intermixing of Si, Ga and P atoms occurs under certain conditions during the growth of GaP on a Si(001) wafer. The intermixed regions at the interface show trigonal shapes in the TEM micrographs. A three-dimensional pyramidal shape of those formations was assumed and confirmed by kMC where one adatom species was set less mobile with respect to surface hopping. DFT calculations of an adatom model showed that in fact the P adatom exhibits significantly elevated hopping barriers with respect to Si and Ga species. Energetic hopping barriers on Si(001) and GaP(001) substrates are presented as well as partial charges from a Natural Bond Orbital analysis of the transition states of the elementary steps.

The energetics/thermodynamics of these interface phenomena were analysed by calculations of intrinsic interface formation stabilities. Those were determined via both periodic bulk and slab model supercells and evaluated by highly accurate DFT (PBE-D3). It was found that indeed the formation of an interface in <001> direction is less stable then e.g. in <112> or <111> direction. Direct termination of Ga-Si (instead of P-Si) was found to be favourable in each direction. A quantum chemical analysis of those interfaces including a partial charge analysis is presented in order to discuss the origin of the (structurally) intrinsic stabilities of the GaP/Si interface. In general, those interfaces with a large number of direct Ga-Si or P-Si contacts are less stable than those with a small number of Ga-Si and/or P-Si bonds. However, direct correlation to the energetic differences could yet not be found and remains an object for quantum chemical investigations.

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Epitaxial graphene nanoribbons on SiC

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In recent years a lot of effort was put into the realization of graphene devices, in view of their unique electronic properties and the potential application in logical circuits. However, for the use in logical electronics a band gap would be required. This can be achieved by confining the electrons into quasi-one-dimensional graphene strips, called graphene nanoribbons [1,2]. When patterning graphene, the altering of the electronic properties by the mechanical attack on the ribbon edge as well as residual resist is always an issue [3]. For that matter we chose to structure the SiC-samples before growing graphene, using electron beam lithography and reactive ion etching, following the method developed by de Heer [4]. Subsequently, the graphene was grown at elevated temperatures, which also removed the residual resist. As a result one-dimensional stripes could be obtained and were decoupled from the substrate by intercalation of hydrogen [5]. Characterization by low energy electron microscopy and angle resolved photoemission spectroscopy proves the development of quasi-free standing monolayer graphene ribbons.

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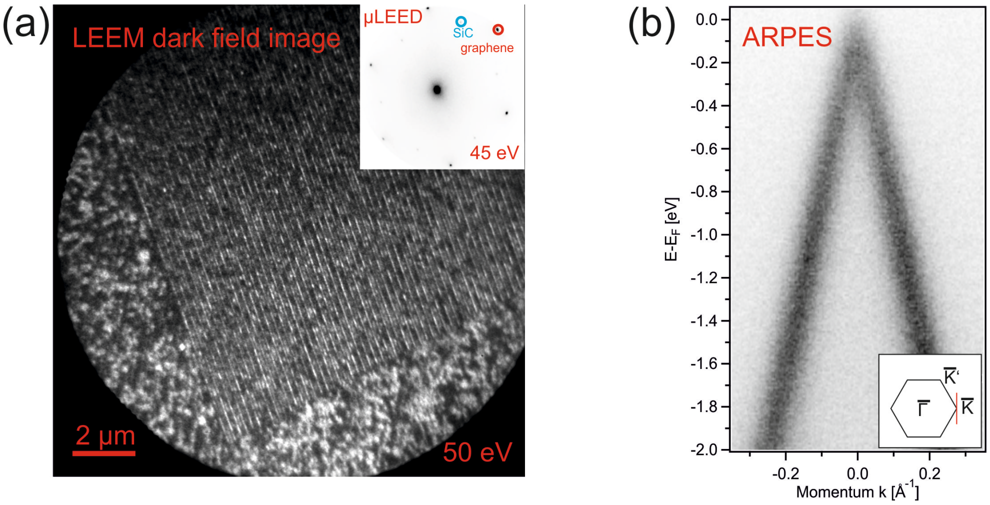

Fig.: (a) Low energy electron microscopy dark field image of the graphene(10)-spot. (b) Angle-resolved photoelectron spectroscopy spectrum at the K-point of graphene taken at an photonenergy of 75 eV.

Evidence for huge exciton binding in transition-metal dichalcogenides

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Since its first isolation by Novosolev and Geim 2004, graphene and graphene based systems have attracted lots of interest, both for fundamental reasons and technological applications. Meanwhile, a variety of graphene-analogues materials like h-BN, silicene or transition-metal dichalcogenides (TMDs) have been fabricated. Unlike graphene, the band structure of these novel materials exhibits a gap in the visible range. Particularly interesting among this class of materials are monolayers of TMDs, exhibiting unique linear and nonlinear optical properties. The linear optical spectra are dominated by strong resonances, with a peak absorption of more than 10%, and the breaking of inversion symmetry allows for an efficient second harmonic generation (SHG).

Though initially assigned to free particle transitions, meanwhile the excitonic nature of the strong optical response is widely accepted. Nevertheless, the precise role of the Coulomb interaction in these structures remains unclear and is still under intensive investigation. Recent linear and nonlinear optical experimental studies on WS_2 [1-3] report huge binding energies for the lowest bright exciton transition ranging from 0.32-0.71 eV and strong deviations from the usual hydrogenic Rydberg series.

However, due to the difficulty to observe the band gap directly, these values have been extracted either from the energetic separation between different resonances, or by comparison with ab initio predictions, and thus depend critically on the correct assignment of optically active states. The widely accepted assignment of the lowest observed resonance to the 1s-exciton ground state not only leads to a large uncertainty in the estimated exciton binding energy, but also leads to mutually contradicting conclusions drawn from different experimental techniques on nominally equivalent samples.

In our contribution, we critically analyze a variety of recent experiments on WS_2 [1-3] and WSe_2[4]. We show that the experimentally observed resonances correspond to the excited states of a 2D hydrogenic Rydberg series. This observation allows for a simple interpretation of all the different experimental results.

Our result demonstrates that the important role of the Coulomb interaction in TMDs has been drastically underestimated. Extrapolation of the observed Rydberg series predicts an almost perfect cancelation of the binding of the 1s exciton ground state and the Coulomb renormalization of the band gap. The merging of the lowest exciton level with the ground state level not only explains the absence of its signature in the observed optical spectra, but also may indicate an excitonic ground state.

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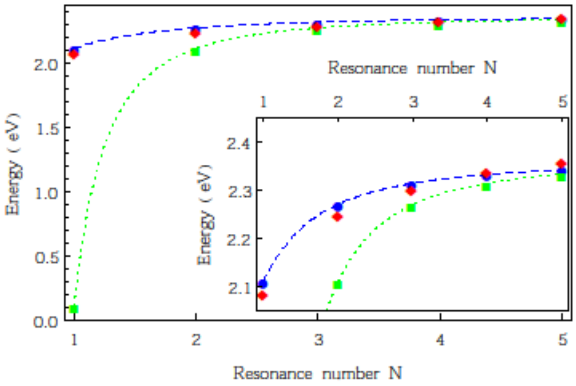

Spectral position of the energetically lowest bright excitonic transitions in WS2. The blue squares are the computed results starting with the n=2 exciton, the red dots show the experimental data taken from [1], and the green diamonds indicate the theoretical predictions if one incorrectly assignes the lowest resonance to the 1s-exciton. The x-axis label denotes the number N of the experimentally observed bright exciton resonances. The inset to the figure shows the results for the energetically higher states with a finer energy resolution

Vibrational properties and dynamic charge transfer of the CuPc/Ag(111)-system

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Abstract

The vibrational properties and thermal evolution of ultra-thin films of copper-phthalocyanine (CuPc) grown on Ag(111) have been investigated using Fourier-transform infrared absorption spectroscopy (FTIRAS), spot-profile-analysis low energy electron diffraction (SPA-LEED) and thermal desorption spectroscopy (TDS). Thereby, various phases in the submonolayer regime could be distinguished and characterized (Fig. 1). Bilayer and multilayer are largely decoupled from the Ag(111) substrate and display a distinctly different spectroscopic signature. Mono- and bilayers are orientated parallel to the Ag(111) (Fig. 1 and Ref. [1]) surface whereas a slightly inclined geometry prevails for the multilayers. The monolayer phases are subject to a pronounced interfacial dynamical charge transfer (IDCT) (Fig. 1 B). Interestingly, this process is attenuated upon growth of the bilayer which indicates a residual electronic coupling between these layers. TDS spectra reveal intact desorption for the bilayer and incomplete desorption for the CuPc monolayer; at about 600K a second pathway becomes dominant with fragments desorbing in variable amounts.

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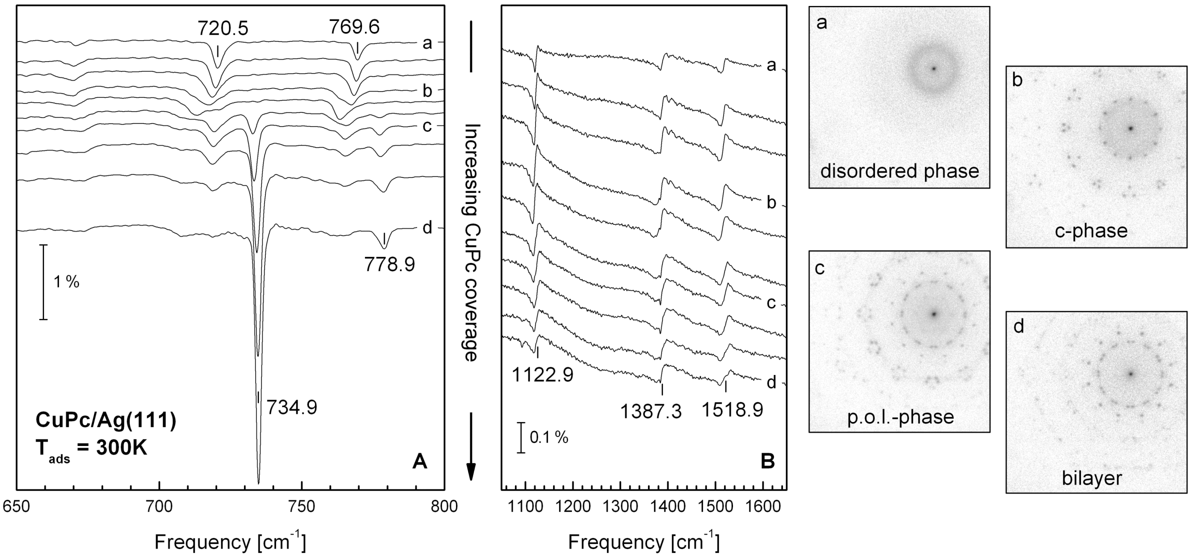
Figure 1



IR absorption spectra of increasing coverages of CuPc on Ag(111) deposited at a sample temperature of 300K. Panel (A) shows vibrational bands in the frequency range of 650 – 800 cm^{-1} associated with out-of-plane modes, panel (B) shows vibrational bands in the frequency range of 1050 – 1650 cm^{-1} representing in-plane modes. A series of SPA-LEED images corresponding to the vibrational spectra are depicted in panels (a)-(d). All measurements have been performed at 77K. The IR spectra are vertically offset for clarity of presentation.

Formation of a self-limiting insulating monolayer on Cu(111) by Electrospray deposition

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Abstract

The decomposition of chloroform on the Cu(111) surface has been studied previously [1]. At room temperature it adsorbs dissociatively followed by the desorption of ethyne product and the formation of a Cl/Cu(111) - $\sqrt{3} \times \sqrt{3}\ R30^\circ$ layer. This method of preparing the chorine adlayer has the advantage that it can be formed via electrospray deposition and that the chlorine coverage is self-limiting, whereas depositing molecular chlorine requires precise control to avoid the formation of more dense phases [2] up to Cl/Cu(111) - 1×1. The method is UHV compatible and we show that the Cl/Cu(111) - $\sqrt{3} \times \sqrt{3}\ R30^\circ$ layer is well suited to decouple electronic states of adsorbed molecules from those of the Cu(111) surface.

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Special interface properties via Atomic Layer Deposition

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Abstract

Atomic Layer Deposition[2] (ALD) is a new tool in Göttingen to build special interfaces and study their energy properties. Surface energy dissipation dependence on the thickness or bilayerd structures is a main interest of the SFB 1073. With ALD we are able to generate highly pure and conformal structures of less than 10 nm thickness. An other advantage of ALD is the huge diversity of different materials that can be deposited with chemical control of the process: materials range from simple oxides[3] (Al_2O_3) or nitrides[4] (TiN) to pure metal (W[5], Mo[5], Os[6], Ta[7], Si[8]) depositions.

Because miniaturization in the semiconductor industry has led to the requirement for atomic level control,[2] ALD is a powerful tool to generate these interfaces: capacitor electrodes as ultrathin high-κ dielectric films, interconnect diffusion barriers for Cu and many other applications[9].

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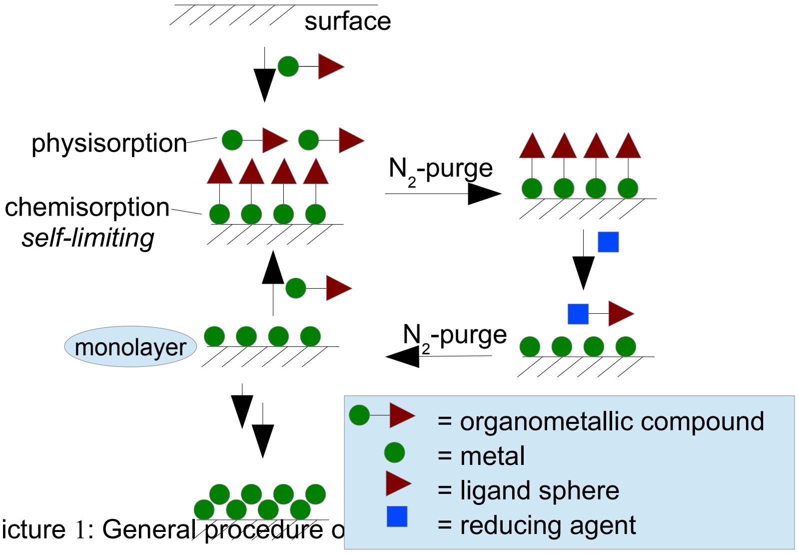
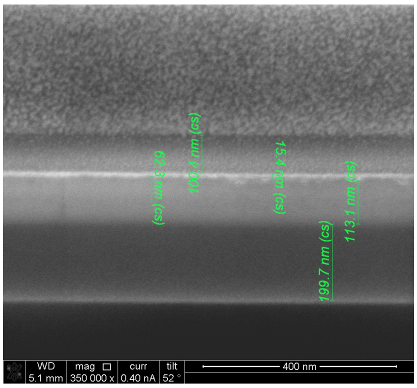


Picture 1: General procedure o



Picture 2: SEM-Image of deposited Al_2O_3 (~120 nm): Layers from top to bottom are $Pt/Pt/Al_2O_3/SiO_2/Si$.

SYNTHESIS AND PROPERITIES OF NOVEL PENTACENES AND BENZOPHENAZINES

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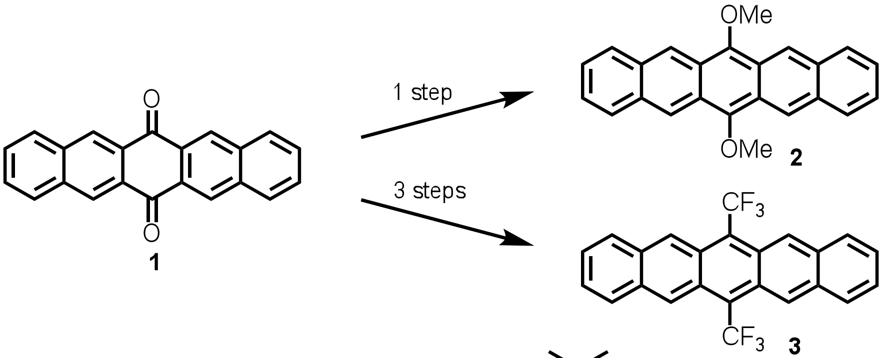
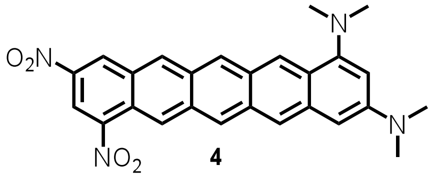
Large acenes and heteroacenes are a class of molecules with interesting electronic properties that have a significant application potential. For high performance in thin film devices 2D p-stacking interactions between the molecules are elemental. Creating complementary pairs of acenes or self-complementary acenes could be improve the nature of intermolecular overlap and therefore the electron mobility.

As pairs of complementary pentacenes we synthesized bis(dimethoxy)pentacene **2** and bis(trifluoro)pentacene **3** from pentacenchinone (**1**).[1] Due to the arduous task of cocrystallisation we envisioned the east-west self-complementary substituted pentacene **4** as suitable target.





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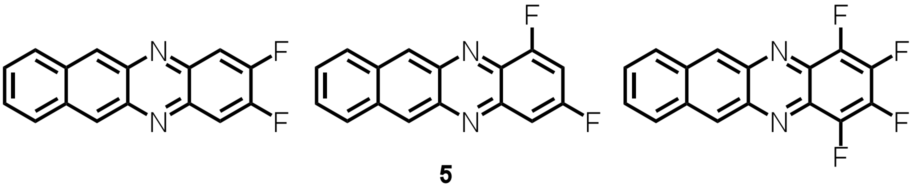
In addition we focus on synthesizing self-complementary heteroacenes with a strong dipole moment in the molecule. We will present recent progress towards the synthesis of fluorobenzophenanzins **5** and their packing motifs.



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Investigations Focused on the Local Composition Determination of Dilute Nitride Quaternary Material Systems Grown on Si-substrates

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The epitaxial growth of multi-component semiconductor layers such as $Ga(N_xAs_yP_{(1-x-y)})$ enables the improvement of laser and transistor devices because of the tunable band gap and lattice constant. However, many physical aspects of the formation such complex materials are still unknown and the determination of the chemical composition as well as understanding of the local effects pose a true challenge for an investigator.

In order to improve optical properties according to the earlier experiments [1] post-growth annealing is applied to the multi-quantum well (QW) heterostructures. The look inside the material and especially the advantage of the high resolution attainable in scanning transmission electron microscope (STEM) can answer the question, what influence the annealing treatment has on the specimen on the atomic scale. We investigated $Ga(N_xAs_yP_{(1-x-y)})$-quantum wells in the Si-based laser structures. The investigations were performed using a double C_s-corrected JEOL JEM 2200 FS. The annular dark-field STEM-images of the annealed specimens reveal local structural changes in the $Ga(N_xAs_yP_{(1-x-y)})$-QWs, that were not observed in the specimens without a thermal treatment. In order to understand and to explain the nature of these changes as well as the possible reason of their appearance a series of the high resolution STEM-images were acquired for different detector angular ranges. The intensities in the experimental images were evaluated using in-house written software. To prove the interpretation of the experimental results several simulations based on the absorptive potential [2] method were carried out and compared with the experimental contrast.

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Ultrafast exciton dynamics in thin sexithiophene films

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Abstract

On our poster we discuss ultrafast exciton dynamics in thin sexithiophene (6T) films studied by time-resolved two-photon photoemission. For our experiments we use 6T functionalized gold and silicon surfaces. Our samples are prepared by the *in-situ* evaporation of 6T onto our substrates. This technique allows us to prepare well-defined organic/inorganic interfaces with molecular films varying from the sub-monolayer to the multilayer regime.

Time-resolved two-photon photoemission spectroscopy is an ideal method to investigate the electronic structure and charge carrier dynamics at the organic/inorganic interface from the femtosecond to the nanosecond regime. Within 6T thin films on gold surfaces the creation of Frenkel excitons due to the optical excitation of electrons from the HOMO into the LUMO of 6T molecules was observed. Those excitonic states are populated within 100fs, whereas their lifetime is coverage dependent. [1,2] These results will be compared with charge carrier dynamics in thin 6T films on silicon surfaces, which serve as model systems for hybrid solar cells.

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Optical properties and carrier dynamics of III/V semiconductors

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Metastable nitrogenous and boracic III/V semiconductors are a promising material system for optoelectronic applications. The deeper understanding of the optical properties and the carrier dynamics of such quantum well materials on Si-substrates is of high interest. Here we present the research done on differently processed samples fabricated in the framework of the GRK by means of photoluminescence and absorption measurements. We analyze the suitability of these spectroscopic and time-resolved methods in consideration of the sample properties. For example short recombination times require a time resolution at least in the picosecond regime, while the broad and featureless absorption spectrum makes absorption measurements difficult. Furthermore we investigate the effects of different sample processing, such as different annealing parameters or the thinning of the substrate, on the optical properties.

Structured growth of ZnO nanorods for light trapping enhancement in organic solar cells

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Organic photovoltaic cells are promising candidates for large-area and low-cost production of solar cells. However, their performance is limited due to short diffusion length of excitons and low absorption in the active semiconductor layer. Our work focuses on the investigation of light trapping mechanism of hybrid organic solar cells based on electrochemically grown ZnO nanorod on ITO and an active layer of conjugated polymer P3HT and PCBM. The nanorods can diffusively scatter light into the active semiconductor layer. Combined with reflecting metal electrode, the optical path length of the scattered light is elongated and hence, there is enhanced absorption in the active layer. The ITO surface has been modified by self- assembled monolayer (SAM) of 11-mercaptoundecanoic acid to control the ZnO nucleation. During electrodeposition of ZnO on the SAM covered ITO, the ZnO nanorods nucleate through the pinholes in the SAM. Thus, the density of ZnO nanorods can be effectively tuned by the SAM quality. The size and the structure of the ZnO nanorods have been varied by changing the parameters of electrochemical deposition such as temperature, reference overvoltage, growth time and concentration of electrolyte. The electrical performance of solar cells with ZnO nanorods showed superior performance to the ones without any nanorod. The power conversion efficiency increased from 1.6% to 2.0 % after the incorporation of ZnO nanorods. Angle resolved scattering measurements have been employed to investigate the amount of light scattered by the nanorods. The sample with the best light scattering property showed the optimum device performance.

Adsorption geometry and electronic structure of NTCDA/Ag(111): DFT-vdW calculations with the use of localized basis sets

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Abstract

Monolayer of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (NTCDA) molecules on Ag(111) surface form different commensurate structures depending on preparation conditions [1]. The relaxed phase of NTCDA/Ag(111) contains two molecules in the surface unit cell which are arranged in parallel with respect to a row of silver atoms. The more densely packed compressed phase has four molecules in the cell which are differently oriented with respect to the substrate atoms. Although molecules in both phases have a similar adsorption distance, two photon photoemission spectroscopy (2PPE) reveals that the interface state (IS) energy of the compressed phase lies 100 meV above the IS energy of the relaxed phase.

In this work we investigate the geometrical and electronic structure of NTCDA/Ag(111) within the framework of DFT calculation with using of localized basis set. In order to account for dispersive forces and the substantial intermolecular interaction we used density functionals that incorporate long-range dispersive interactions (vdW-DF) [2].

Our final adsorption geometry of the relaxed phase is in excellent agreement with experiment when sufficiently extended orbitals are used for the whole substrate or only for surface silver atoms (which reduces considerably the computational cost).

We have shown that the position of the interface state strongly depends on the lattice constant of the substrate and that, apparently, the difference in the interface states of the two phases can not be explained only in terms of the different adsorption geometry.

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Electronic Structure and Excitation Dynamics of the CuPc/PTCDA/Ag(111) Heterointerface

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Abstract

Thin films of Copper(II)phthalocyanine (CuPc) and Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) deposited on a Ag(111) substrate are an ideal model system for an organic donor-acceptor interface in the vicinity of a metal. These organic molecules form commensurate flat-lying layers and the structure is well understood in terms of growth characteristics and binding mechanisms [2].

We use time- and angle-resolved two-photon photoemission spectroscopy to investigate the electronic structure and carrier transfer processes at this hetero interface. The application of a new optical parametric oscillator (OPO) provides us a flexible choice of the pump-pulse photon-energy, which enables a selective excitation of the intermolecular states. In combination with an independently tuneable photon energy of the probe-pulse, we are able to determine the binding energies, effective masses and decay dynamics of both occupied and unoccupied states in the full energy range from just below the Fermi edge up to the vacuum level.

Upon adsorption of CuPc onto PTCDA we find a strong resonant behaviour in the excitation of the Shockley-type interface state of PTCDA/Ag(111) [1] by choosing a pump wavelength of 685 nm. This can be associated to one of the adsorption maxima of the CuPc HOMO-LUMO transition.

The selective excitation of this transition will allow us to induce a maximum density of excited electrons within the CuPc layer which is an important prerequisite with regard to a systematic investigation of charge-transfer excitons.

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Reactive Cobalt/Porphyrin Interfaces Probed With Hard X-ray Photoelectron Spectroscopy (HAXPES)

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Abstract

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. 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 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. Cobalt on tetraphenylporphyrin (Co/2HTPP) was used as a model system, for which we have previously shown that Co atoms react with adsorbed 2HTPP at room temperature to cobalt(**II**) tetraphenylporphyrin (CoTPP) [1]. Since the N 1s XP signals of 2HTPP and CoTPP can easily be distinguished, this reaction provides a monitor for the diffusion depth of the Co atoms in the 2HTPP matrix. From the energy dependence of the XP signals, information about the extension of the reacted CoTPP layer between the pure metal (Co) and the pure organic phase (2HTPP) was determined. Additional insight was obtained by simulation of the XP spectra using the partial-intensity approach for the electron-solid interaction [2].

References

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Maps

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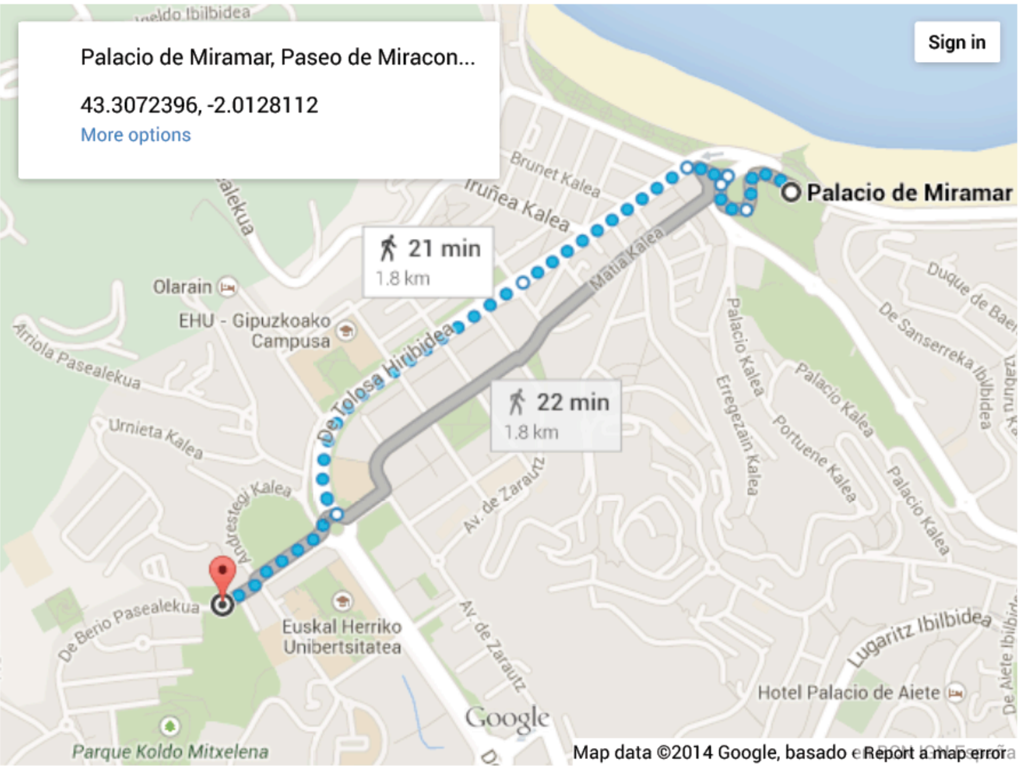
Accommodation

Accomodation during the International Summer School on Semiconductor Interfaces will be a shared double room in the Residencia Agud Querol. This students residence is ten to fifteen minutes away from the Palacio de Miramar by walk.



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Some of the participants will be lodged at the NH Aranzazu hotel, also walking distance to Palacio de Miramar

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