

CPP 37: Organic-Inorganic Systems II: Energy Level Alignment (organized by O)

Time: Wednesday 10:30–13:00

Location: S054

Invited Talk

CPP 37.1 Wed 10:30 S054

Energy level alignment mechanisms at hybrid inorganic/organic semiconductor interfaces — ●NORBERT KOCH

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Understanding the energy level alignment at hybrid inorganic/organic semiconductor interfaces is indispensable to devise methods that allow for level control. This is needed to achieve a desired functionality of that heterostructure, as for instance, a type-II alignment facilitates charge separation while a type-I alignment is suitable for energy transfer and radiative recombination. For the inorganic semiconductors ZnO and GaN, the use of interlayers, based on strong molecular acceptors and donors, can be employed to tune the energy level alignment with respect to an organic semiconductor deposited on top. Depending on the level alignment achieved in this way, the hybrid heterostructure functionality, e.g., energy or charge transfer, can be selected. Finally, the impact of the doping level of the semiconductors on interface energetics is discussed for a prototypical hybrid p-n-junction.

CPP 37.2 Wed 11:00 S054

Work Function Increase of GaN and the Influence of Surface Gap States — ●THORSTEN SCHULTZ¹, RAPHAEL SCHLESINGER¹, JENS NIEDERHAUSEN^{1,2}, and NORBERT KOCH^{1,2}

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The two molecular organic acceptors HATCN and F6-TCNNQ were vacuum-deposited on non-intentionally doped GaN (0001), which had a residual donor concentration of 1016 cm⁻³. By means of ultraviolet photoelectron spectroscopy, a huge work function increase (up to 1.5 eV for HATCN and 1.7 eV for F6-TCNNQ) was observed for monolayer coverage, which stems mostly from an interface dipole between substrate and molecules. The contribution of band bending within GaN (ca. 0.35 eV, as determined from X-ray photoelectron spectroscopy) was found to be significantly smaller than expected from theoretical calculations that predict the contribution of band bending to be dominating for low doping concentrations. A qualitative model is introduced, which assigns the low band bending contribution to the presence of substrate surface gap states. These states donate electrons to the acceptor molecules, so less charge is transferred from the GaN donors. This results in less band bending change than expected from calculations, which did not take surface states into account. Our investigations show that the energy level tuning scheme via acceptor interlayers, already successfully employed for ZnO, holds great promise for GaN as well.

CPP 37.3 Wed 11:15 S054

Structure and stoichiometry prediction of zinc oxide surfaces

— ●PHILIPP HERRMANN, NAVID ABEDI KHALEDI, and GEORG HEIMEL — Institut für Physik, Humboldt Universität zu Berlin, Germany

Despite their great potential as transparent electrodes in organic electronics and as integral, active components in hybrid (opto-)electronic devices, full control over the surfaces of transition-metal oxides has remained elusive. Atomistic details of their structure and stoichiometry have proven hard to assess, rendering application-relevant surface properties, such as the work function, highly dependent on environment and preparation conditions.

Here, on the example of zinc oxide, I will present a revised approach to the *ab-initio* prediction of atomistic surface structure and stoichiometry as a function of environmental conditions, specifically temperature and atmospheric composition. The predicted structures will be discussed in terms of their experimental signatures in photoelectron spectroscopy, notably surface core-level shifts and work function.

This work thus paves the way for the targeted *in-silico* design of functional inorganic/organic hybrid interfaces.

CPP 37.4 Wed 11:30 S054

Density-Matrix Derived van der Waals Interactions: Many-Body Dispersion goes Mesoscale — ●MARTIN STÖHR^{1,2}, GEORG MICHELITSCH¹, JOHN TULLY², KARSTEN REUTER¹, and REINHARD MAURER²

— ¹Technische Universität München — ²Yale University

The applicability of highly accurate quantum chemical simulation

methods is limited to systems of small to moderate size. Density-Functional Theory (DFT), but also more approximate, semi-empirical methods such as Density-Functional based Tight-Binding (DFTB) have shown great success in addressing systems at longer time and length scales. However, a severe drawback of DFTB and many prevalent DFT functionals is the neglect of dispersion interactions, which is particularly consequential for the simulation of e.g. hybrid inorganic-organic systems. Here, we propose a novel approach to obtain effective C6 coefficients in the context of the Tkatchenko-Scheffler dispersion correction scheme [1]. The modified scheme derives atomic dispersion parameters directly from the density-matrix and is thus readily applicable to both full DFT and semi-empirical methods like DFTB, where the electron density is not explicitly constructed. At a fraction of the computational workload of a density-based approach, the scheme yields equally accurate dispersion energies up to the many-body dispersion level for intermolecular interactions in gas-phase and molecular crystals. We exemplify the robustness of the scheme by addressing organic-inorganic interfaces with DFTB using a minimal basis set. [1] A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009).

CPP 37.5 Wed 11:45 S054

Single molecules of Sexiphenyl on In2O3(111) — ●MARGARETA WAGNER¹, MICHAEL HOLLERER², MARTIN STERRER², MICHAEL RAMSEY², LYNN A. BOATNER³, MICHAEL SCHMID¹, and ULRIKE DIEBOLD¹

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Indium oxide is one of the most important transparent conductive oxides (TCOs), and commonly used as a contact material. Sexiphenyl (6P) is a rod-like molecule and twice as long as the substrate surface lattice parameter of the (111) surface of In2O3 single crystals.

Here, the adsorption of 6P is investigated with STM. We show that 6P has a specific adsorption site, but no well-ordered monolayer is formed. In empty states STM, the single 6P appears as a zig-zag line at bias voltages below +2V. At +2V the molecule starts to appear straight, which is associated with tunneling into the LUMO state. At +2.7V the apparent shape changes again into two bright features, corresponding to the LUMO+1.

CPP 37.6 Wed 12:00 S054

Optical transition energies of isolated molecular monomers and weakly interacting 2D aggregates — ROMAN FORKER¹, THOMAS DIENEL², ANDREAS KRAUSE³, ●MARCO GRUENEWALD¹, MATTHIAS MEISSNER¹, TINO KIRCHHUEBEL¹, OLIVER GRÖNING², and TORSTEN FRITZ¹

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We analyze the S₀→S₁ fundamental transition energies observed for 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) as a function of coverage on various surfaces with substantially dissimilar dielectric properties. Surprisingly, only two different spectral positions are found: (i) PTCDA_{HE} basically mimics the behavior of isolated monomers on the surface, while (ii) PTCDA_{LE}, red-shifted by approx. 70 meV, is attributed to a densely packed monolayer (ML) in a two-dimensional herringbone arrangement. This red-shift is in remarkable accordance with previous investigations for PTCDA on NaCl(100) and thus likely arises from the same physical effects, namely the formation of 2D excitonic bands and the polarizability of neighboring molecules within the ML. Possible contributions from substrate-induced molecular distortions and chemical interactions are discussed. Contrary to earlier studies, we conclude that the polarizability of the substrate is not the dominant factor responsible for the reported spectral positions.

CPP 37.7 Wed 12:15 S054

Photoemission study of thin films of the singlet fission compound 1,3-Diphenylisobenzofuran — ●DAVID NOBIS, JANEK RIEGER, DANIEL NIESNER, PEDRO B. COTO, MICHAEL THOSS, and THOMAS FAUSTER

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Singlet fission (SF) is the conversion of an optically excited, high-energy singlet exciton, into two optically dark, long-lived electronic excited triplet states via a spin-allowed process. This process might be used in next generation solar cells to harvest high-energy light. 1,3-Diphenylisobenzofuran (DPIBF) is a prototypical SF molecule, as has been shown by calculations and optical spectroscopy [1,2].

We investigated thin films of DPIBF on SiO₂ with UV photoelectron spectroscopy (UPS) and two-photon photoemission (2PPE). The UPS results show the HOMO located 6 eV below the vacuum level, in good agreement with DFT calculations.

The 2PPE spectra show the first singlet state S₁ at 2.8 eV above the HOMO. The triplet state is 1.4 eV lower in energy. Its high, long-lived population is explained by SF in agreement with literature [2].

[1] Schwerin A. F. *et al.*, J. Phys. Chem. A **114** (2010) 1457

[2] Johnson J. C. *et al.*, Phys. Rev. B **132** (2009) 16302

CPP 37.8 Wed 12:30 S054

Two-photon photoemission from tetraphenylporphyrins on Ag(100) — ●ANDREJ CLASSEN, REBECCA PÖSCHEL, GIANLUCA DI FILIPPO, and THOMAS FAUSTER — Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7, 91058 Erlangen, Germany

Ultrathin films of two different tetraphenylporphyrins (2HTPP and MgTPP) were grown in-situ under UHV-conditions on a well-defined Ag(100) single crystal. The molecules were deposited by evaporation from a home-built Knudsen-cell evaporator. The substrate was kept at room temperature and layer thicknesses range from one monolayer of molecules (1 ML) up to multilayer films (19 ML). We present an investigation of the electronic structure using ultraviolet photoelectron spectroscopy and monochromatic two-photon photoemission (2PPE). The occupied molecular orbitals of 2HTPP and MgTPP were measured using a photon energy of 21.22 eV (HeI-radiation). 2PPE probes the unoccupied molecular orbitals. The combination of both yields a HOMO-LUMO gap of 4.2 eV (MgTPP) and 4.3 eV (2HTPP) in accordance with literature [1]. Taking the measured work function

into account, the ionization potential is 5.9 eV (MgTPP) and 6.1 eV (2HTPP) [2]. The electron affinity is 1.7 eV (MgTPP) and 1.8 eV (2HTPP). The 2PPE intensity as a function of photon energy in the range from 3.08 eV to 3.38 eV follows the absorption spectrum (Soret band) of tetraphenylporphyrin.

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

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

CPP 37.9 Wed 12:45 S054

Work function tuning and electrostatic effects: embedded dipoles in aromatic self-assembled monolayers —

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Self-assembled monolayers (SAMs) are frequently used as intermediate films to modify charge-carrier injection from metal-electrodes into an organic semiconductor. This is usually achieved by use of the terminal dipolar groups comprising the SAM-ambient interface, affecting, however, the growth chemistry of the semiconductor. Here we suggest an alternative approach, viz. embedding dipolar element into the molecular backbone, decoupling the dipole control and the chemistry at the SAM-ambient interface. In this context, using a representative model system, we studied electronic and structural properties of aromatic SAMs that contain an embedded, dipolar group, viz. pyrimidine. Using a number of complementary characterization techniques combined with quantum-mechanical modeling, we show that such mid-chain substituted monolayers are highly interesting from both fundamental and application viewpoints, as the dipolar groups induce a potential discontinuity inside the monolayer, electrostatically shifting the energy levels in the regions above and below the dipoles relative to one another.