

O 38: Organic-Inorganic Hybrid Systems and Organic Films V

Time: Tuesday 14:00–16:00

Location: WIL A317

Invited Talk

O 38.1 Tue 14:00 WIL A317

Tuning excitonic excitations in molecular layers — ●MARTIN WEINELT and CORNELIUS GAHL — Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Excitons constitute the fundamental optical excitations in organic materials. Here intermolecular interactions lead to delocalization and transport of excitons and thereby influence the response of the molecular film. We will discuss two examples where excitonic excitations play an important role.

In azobenzene-alkanethiolate self-assembled monolayers quenching of the optical excitation by the supporting gold substrate is avoided by decoupling the azobenzene chromophore via an alkane linker. However, intermolecular coupling in the SAM strongly shifts and broadens the absorption bands. One strategy to reestablish efficient photoisomerization is to introduce additional molecules as lateral spacers. As a consequence the excitonic coupling of the chromophores can be tuned between single molecules and aggregates, which strongly influences optical switching.

Sexithiophene/gold is a model system for an organic semiconductor/metal - interface. Here we investigated the exciton dynamics by time-resolved two-photon photoemission spectroscopy. We show that resonant excitation and vibrational dissipation of excess energy both lead to exciton population on an ultrafast time scale resulting in a long lived final state. Again the morphology of the organic layer (crystalline vs amorphous) strongly influences the excited state dynamics and energetics relevant for organic electronics.

O 38.2 Tue 14:30 WIL A317

Probing complex adsorbate systems using Angle-Resolved NIXSW — ●GERBEN VAN STRAATEN, MARKUS FRANKE, and CHRISTIAN KUMPF — Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich and Jülich Aachen Research Alliance (JARA) – Fundamentals of Future Information Technology (FIT), 52425 Jülich, Germany

The Normal Incidence X-ray Standing Waves (NIXSW) technique is a popular and very efficient technique for studying adsorbate structures, but unfortunately, it is only of limited use when adsorbate atoms display a range of adsorption heights. In this presentation we show that angle-resolved NIXSW measurements can take advantage of the limited mean-free path of photoelectrons and that more information about the adsorbate distribution can be obtained. This can be used to study vertical disorder in monolayer structures.

O 38.3 Tue 14:45 WIL A317

Multiscale Modeling of Ion-Sensitive Sensor Devices — ●JÖRG BUCHWALD, RAFAEL GUTIÉRREZ LALIGA, and GIANAURELIO CUNIBERTI — Institute for Materials Science and Max Bergmann Center of Biomaterials Dresden University of Technology, 01069 Dresden, Germany

An ion-sensitive field effect transistor (ISFET) can be considered as a FET in which the gate is in contact with an ionic solution and covered by a self-assembled monolayer of biomolecules that are able to bind to these specific ions. The number of bound ions is thereby assumed to be a function of ion concentration and determines the gate potential and current of the FET.

We present a continuum model that treats both parts separately. The source-drain current is determined via a drift-diffusion model of the semiconductor parts under given source-drain voltage and gate potential. Whereas the gate potential can be calculated from a Poisson-Nernst-Planck model of the ionic solution in which the biomolecules are acting as sources/sinks of the mobile ion concentrations.

Additionally one has to consider binding kinetics, conformational changes of the biomolecule and charge transfer from the biomolecule to the surface acting as an aggregated static charge. Both information can be obtained via atomistic/ab-initio methods.

O 38.4 Tue 15:00 WIL A317

Adsorbate-induced restructuring of crystalline and amorphous ZnO surfaces upon formation of phosphonic acid self-assembled monolayers — ●TOBIAS KLÖFFEL¹, HANNAH SCHLOTT¹, ALEXANDRA OSTAPENKO², GREGOR WITTE², and BERND MEYER¹ — ¹Interdisciplinary Center for Molecular Materials and Computer-

Chemistry-Center, FAU Erlangen-Nürnberg — ²Fachbereich Physik, Philipps-Universität Marburg

Among the inorganic oxides, ZnO is of special interest for hybrid organic-inorganic interfaces in molecular electronics due to its high charge carrier mobility. Phenyl phosphonic acids (PPAs) are commonly used linker groups and functional organic units for creating such interfaces. Recent experiments and DFT calculations showed, however, that self-assembled PPA monolayers are only metastable and etch the ZnO substrate [1,2].

DFT calculations were performed to explore systematically the possible PPA monolayer structures on crystalline and amorphous ZnO model surfaces. In addition to regular PPA adsorbate structures on unmodified substrates we find that the PPA molecules can induce strong structural changes in the ZnO surfaces. Configurations with additional Zn and O ions between PPA molecules show a similar thermodynamic stability, which might be the origin of the observed structural instability of the PPA monolayers.

[1] A. Ostapenko, et al., *ACS Appl. Mater. Interfaces* **8**, 13472 (2016).[2] A. Ostapenko, et al., *Langmuir* **32**, 5029 (2016).

O 38.5 Tue 15:15 WIL A317

Understanding the planarization of shuttle-cock shaped subphthalocyanine molecule on Cu(111) surface — ●SHASHANK S. HARIVYASI¹, OLIVER T. HOFMANN¹, NAHID ILYAS², OLIVER L.A. MONTI², and EGBERT ZOJER¹ — ¹Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria — ²University of Arizona, Tucson, Department of Chemistry & Biochemistry, 1306 E. University Blvd., Tucson, AZ 85721, USA

The structure of an organic semiconductor plays a determining role in its adsorption on a metal surface. Large planar molecules like planar phthalocyanines, pentacene and PTCDA typically lie completely flat on most metal surfaces. The situation becomes more complex in case of non-planar molecules. They generally show a tendency to planarize upon adsorption but the extent of this planarization varies from negligible to almost complete for various metal-molecule combinations.

Here, we try to understand the reasons for this planarization by studying an extreme example exhibiting almost complete planarization: adsorption of shuttle-cock shaped Chloroboron subphthalocyanine on Cu (111). Using DFT, we study the steps of the adsorption process by gradually increasing the van der Waals interaction between the adsorbate and the substrate and following the evolution of the molecule's electronic and geometrical structure. We identify the bonding of the molecule as a two-stage process involving Fermi-level pinning followed by a rehybridization of the molecule's frontier orbitals. Especially the observed evolution of charge rearrangements help us to explain why we see an almost complete planarization.

O 38.6 Tue 15:30 WIL A317

Electronic and optical excitations at the pyridine@ZnO hybrid interface — ●OLGA TURKINA, DMITRII NABOK, ANDRIS GULANS, CATERINA COCCHI, and CLAUDIA DRAXL — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Insight from *ab initio* theory is essential in order to gain an understanding of opto-electronic properties of organic-inorganic hybrid materials, such as the correct level alignment and the creation of hybrid excitons. We investigate a prototypical system composed of a pyridine molecule that is chemisorbed on a non-polar ZnO(10-10) surface. We employ all-electron density-functional theory in combination with many-body perturbation theory (G_0W_0 /BSE). The G_0W_0 approximation describing one-particle excitations is used to determine the electronic structure, while the Bethe-Salpeter equation describing two-particle excitations is solved to obtain the absorption spectrum. We reveal the nature of the optical excitations at the interface by analysing the character of the involved transitions and visualizing the exciton wave-function. Thus, we find evidence of excitons exhibiting different character across different spectral regions. The onset of the spectrum is dominated by bright and strongly bound hybrid and ZnO character excitons. In particular, the first strongly bound and most intense exciton at 1.8 eV is of hybrid nature. In the visible region, we find predominantly low intensity hybrid excitons, whereas in the UV region, we find dark excitons exhibiting charge-transfer character, with the corresponding electron and the hole delocalized on either ZnO or pyridine.

O 38.7 Tue 15:45 WIL A317

Interaction of an Ionic Liquid Adlayer with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Influence of Pre- and Post-deposited Lithium - A Model Study of the Electrode|Electrolyte Interface — •JIHYUN KIM¹, FLORIAN BUCHNER², and R. JÜRGEN BEHM^{1,2} — ¹Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

Well-defined spinel lithium-titanium-oxide, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (111), which is a promising anode material for a lithium-ion batteries, was generated by a solid state reaction ($\text{LiOH} + \text{TiO}_2$ (111)) and its crystallinity and stoichiometry were confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. To mimic the elec-

trode|electrolyte interface (EEI) (crucial for the battery performance), we vapor deposited a monolayer of the battery-relevant ionic liquid (solvent/electrolyte) 1-butyl-1-methyl-pyrrolidinium bis(tri-fluoromethyl-sulfonyl)amide ([BMP][TFSA]) on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (111) at 300 K. XPS reveals that [BMP][TFSA] is partially decomposed, forming products such as LiF , Li_xS , Li_xSO , SO_x and LiN_3 . Post-deposition of 1 ML of Li on a ([BMP][TFSA]) adlayer at 300 K increases the amount of decomposition products in the adlayer. After pre-deposition of 1 ML of Li on pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (111) at 300 K, XP spectra reveal that lithium diffuses (intercalates) into the bulk, most likely forming a Li-rich $\text{Li}_x\text{Ti}_5\text{O}_{12}$ ($4 < x < 7$) phase. Future work will concentrate on the interaction of [BMP][TFSA] with both the Li-poor ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) and the Li-rich ($\text{Li}_x\text{Ti}_5\text{O}_{12}$) phases in different temperature ranges.