

DS 19: Fundamentals of Perovskite Photovoltaics III (jointly with CPP/HL)

Time: Tuesday 9:30–12:30

Location: ZEU 222

Invited Talk

DS 19.1 Tue 9:30 ZEU 222

Investigation of hybrid organic/inorganic perovskite systems and interfaces by photoelectron spectroscopy — ●SELINA OLTTHOF — University of Cologne, Germany, Luxemburgerstrasse 116, 50939 Cologne

In recent years, the interest in hybrid organic - inorganic perovskites rose at a rapid pace due to their tremendous success in the field of photovoltaics. In addition to the thin film properties of the active layer, the performance of optoelectronic devices strongly depends on the appropriate energetic alignment between the active- and adjacent layers. In order to choose adequate transport materials for the increasingly complex hybrid perovskite compositions in a non-trial-and-error fashion, it is important to understand how the induced changes in band gap relate to shifts in the valence and/or conduction band.

In this talk, I will discuss recent findings regarding measurements of the electronic structure of various hybrid perovskites, covering lead as well as tin based systems and a variety of halogens using UV-, inverse, and x-ray photoelectron spectroscopy measurements (UPS/IPES/XPS). Furthermore, using these surface sensitive techniques the alignment at interfaces between different layers can be probed in-situ as well by performing a stepwise film preparation. Looking at various bottom contacts we find that chemical interactions, band bending, and interface dipole formation play an important role. Therefore, the nature of the substrate not only determines the energetic alignment but can lead to chemical reactions and influence film formation and crystallinity.

DS 19.2 Tue 10:00 ZEU 222

Influence of air and water on the electronic structure of CH₃NH₃PbI₃-xCl_x mixed halide perovskite film surfaces — ●MARYLINE RALAIARISOA, FENGSHUO ZU, and NORBERT KOCH — Humboldt-Universität zu Berlin, Institut für Physik & IRIS Adlershof, Brook-Taylor-Str. 6, 12489 Berlin, Deutschland

Water and oxygen under environmental conditions reveal to be both beneficial for device performance as well as detrimental to the stability of perovskite based solar cells and films. Within this controversy, an accurate and comprehensive description of the influence of these factors is still lacking, particularly on the electronic structure of perovskite films. We investigated the effect of water and air on the ionization energy (IE) and the electronic structure of perovskite films. To this end, we used photoelectron spectroscopy to monitor the electronic structure of perovskite films following a range of procedures, including thermal post-treatment, as well as air and oxygen exposure. After air exposure, we observe changes of work function (WF) and IE similar to those after pure oxygen exposure. Furthermore, our observations indicate that even without prior ambient air exposure residual water (from processing in a typical glove-box environment) can still be present on the surface of perovskite films, even under vacuum conditions. Such water adsorption seemingly increases the WF of the perovskite films. Our results underline how environmental conditions substantially affect the electronic structure of perovskite films, which will likely impact the energy level alignment in perovskite-based photovoltaic cells.

DS 19.3 Tue 10:15 ZEU 222

Modulated surface photovoltage spectroscopy of CH₃NH₃Pb(I,Br)₃ thin films — ●CELLINE AWINO, THOMAS DITTRICH, EVA UNGER, and BERND RECH — Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium-Photovoltaik, Kekuléstr. 5, 12489 Berlin, Deutschland

The investigation of electronic properties of CH₃NH₃Pb(I,Br)₃ and their dependence on aging and light soaking is important for better understanding of the stability of solar cells based on related materials. Modulated surface photovoltage spectroscopy allows for the ex-situ and in-situ characterization of the band gap, tail states and deep defect states in the band gap, direction of modulated charge separation and diffusion length. It has been found, for example, that the Tauc gap and the energy of exponential tail states sensitively depend on the substrate and on soaking in nitrogen atmosphere and that light soaking has strong influence on the direction and amplitude of modulated charge separation.

DS 19.4 Tue 10:30 ZEU 222

Revealing the impact of the potential distribution within high performing Lead Methylammonium Tri-Iodide solar cells with organic contact materials — ●CHRISTIAN MÜLLER^{1,2,3}, BERND EPDING^{2,3}, RAMOS BWALYA^{2,3}, MICHELE SESSOLO⁴, LIDÓN GIL-ESCRIG⁴, HENK BOLINK⁴, ROBERT LOVRINCIC^{1,3}, and WOLFGANG KOWALSKY^{1,2,3} — ¹IHF, TU Braunschweig, Germany — ²KIP, Universität Heidelberg, Germany — ³InnovationLab, Heidelberg, Germany — ⁴Instituto de Ciencia Molecular, Universidad de Valencia, Spain

Over the last few years the power conversion efficiency of organometal-halide perovskite (such as CH₃NH₃PbI₃, MAPI) based solar cells has skyrocketed at an unprecedented rate to values around 22%. However, the understanding of the physical process in the solar cells drags behind the progress of efficiency. For example, the influence of the potential distribution in such cells on their performance is so far not sufficiently studied.

We focus in this work on high performing fully vacuum processed MAPI solar cells with organic contact materials [1]. We will present SKPM measurements on p-i-n and n-i-p solar cell cross sections that map the potential distribution within the device with high spatial resolution. Performing measurements under different conditions enables us to determine the influence of potential barriers at the contact interfaces and of a poling on the cell efficiency.

[1] Energy Environ. Sci., 2016, 9, p. 3456-3463, C. Momblona et al.

DS 19.5 Tue 10:45 ZEU 222

Impact of Illumination on the Electronic and Chemical Structure of Mixed Halide Perovskites — ●FENGSHUO ZU¹, PATRICK AMSALEM¹, INGO SALZMANN¹, RONGBIN WANG^{1,2}, MARYLINE RALAIARISOA¹, STEFAN KOWARIK¹, STEFFEN DUHM², and NORBERT KOCH¹ — ¹Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — ²FUNSOM, Soochow-University, Suzhou, China

The seemingly n-type behavior of the perovskite films is largely intriguing since these films are calculated to be bipolar conductive. For exploring the fundamental physics of the n-type behavior, we investigate the effect of white-light illumination on the electronic structure of mixed halide perovskite thin films and of CH₃NH₃PbI₃ single crystals using X-ray and ultraviolet PES, as well as UV-Vis absorption spectroscopy. The samples are found to be strongly n-type and, upon illumination, the valence band features shift by up to 0.7 eV to lower BE. We show this effect to be correlated with initial surface band bending due to the presence of donor levels likely consisting of reduced lead (Pb⁰) acting as surface traps. Upon short-time illumination, this phenomenon is found to be partially reversible, for prolonged illumination, however, a high concentration of metallic Pb⁰ is generated inducing strong Fermi-level pinning. This effect is accompanied by the formation of PbI₂ defects within the film and a deficiency of iodine in the surface region. Experiments performed on CH₃NH₃PbI₃ single crystal reveal the presence of a relatively high concentration of reduced Pb⁰ at the sample surface after cleaving, likewise, strongly pinning the Fermi-level even under high intensity illumination.

15 min break

DS 19.6 Tue 11:15 ZEU 222

Giant Rashba Splitting in (CH₃NH₃)PbBr₃ Organic-Inorganic Perovskite — DANIEL NIESNER¹, MAX WILHELM¹, IEVGEN LEVCHUK², ANDRES OSVET², SHREETU SHRESTHA², MIROSLAW BATENTSCHUK², CHRISTOPH BRABEC^{2,3}, and ●THOMAS FAUSTER¹ — ¹Lehrstuhl für Festkörperphysik, FAU Erlangen-Nürnberg, Staudtstr. 7, D-91058 Erlangen, Germany — ²I-MEET, Department of Materials Science and Engineering, FAU Erlangen-Nürnberg, Martensstr. 7, D-91058 Erlangen, Germany — ³ZAE Bayern, Haberstr. 2a, D-91058 Erlangen, Germany

A Rashba-type spin-split band structure has been predicted for organic-inorganic perovskite semiconductors. The effect has been proposed as one of the origins of the exceptionally long carrier lifetimes in the materials, forming the basis of their successful application in optoelectronics. Using angle-resolved photoelectron spectroscopy, we investigate the band structure of (CH₃NH₃)PbBr₃ single crystals cleaved in ultrahigh vacuum. The orthorhombic low-temperature phase and

the cubic room-temperature phase are studied. We apply a modified leading-edge method to identify the dispersion of the valence band edge. It reveals two valence band maxima, separated in k -space by 0.043 \AA^{-1} . The dispersion is indicative of Rashba splitting. This interpretation is supported by the observation of circular dichroism in the orthorhombic phase. Extracted Rashba parameters of $\alpha_o = 7 \pm 1 \text{ eV \AA}$ and $\alpha_c = 11 \pm 4 \text{ eV \AA}$ in the orthorhombic and the cubic phase are amongst the largest reported to date.

DS 19.7 Tue 11:30 ZEU 222

Exploring the electronic band structure of (organo-)metal halide perovskite via photoluminescence anisotropy of individual nanocrystals — •DANIELA TÄUBER¹, MIRKO GOLDMANN^{1,2}, JUANZI SHI¹, ALEXANDER DOBROVOLSKY¹, and IVAN SCHEBLYKIN¹ — ¹Chemical Physics, Lund University, Lund, Sweden — ²TU Ilmenau, Germany

Understanding electronic processes in metal halide perovskites requires unraveling the origin of their electronic transitions. Light polarization studies can provide important information regarding transition dipole moment orientations. Investigating individual lead trihalide perovskite nanocrystals enabled us to detect the polarization of photoluminescence intensity and photoluminescence excitation, hidden in bulk samples by ensemble averaging. Polarization properties of $CH_3NH_3PbI_3$ crystals were correlated with their photoluminescence spectra and electron microscopy images [1]. We propose that distortion of PbI_6 octahedra leads to peculiarities of the electronic band structure close to the band-edge. Namely, the lowest band transition possesses a transition dipole moment along the apical Pb-I-Pb bond resulting in polarized photoluminescence. Excitation of photoluminescence above the bandgap is unpolarized because it involves molecular orbitals delocalized both in the apical and equatorial directions of the perovskite octahedron. Trap-assisted emission at 77 K, rather surprisingly, was polarized similar to the bandgap emission.

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[1] Täuber, D. et al., *Nano Letters* 16, 5087-5094, 2016.

DS 19.8 Tue 11:45 ZEU 222

Band Edge Engineering of Hybrid Halide Perovskites for Solar Cell Applications - Insights from Density Functional Theory — •LINN LEPPERT^{1,2}, SEBASTIAN E. REYES-LILLO^{1,2}, and JEFFREY B. NEATON^{1,2,3} — ¹Molecular Foundry, Lawrence Berkeley National Laboratory — ²Department of Physics, University of California Berkeley — ³Kavli Energy NanoScience Institute at Berkeley

Efficiencies of solar cells based on hybrid halide perovskite absorbers have reached 22%, making them serious contenders to silicon solar cells. Nevertheless, the toxicity of lead, the material's instability, as well as pressing questions about the role of structural heterogeneities present challenges to its large scale fabrication and long term use. Recently it has been shown that photovoltaic properties vary significantly between different crystal facets of perovskite thin films, suggesting an appreciable effect of electric fields on the local electronic structure [1]. In this contribution, I will elucidate the coupling between electric polarization, which increases as a function of the macroscopic alignment of the organic moieties, and the band edge electronic structure. In particular the Rashba effect, an energy band splitting in k -space, increases with increasing polarization, indicating significant tunability with experimentally feasible applied fields. The effect can be tuned

further by chemical substitution of the organic molecule as well as by anisotropic strain, allowing for considerable Rashba splitting even in the absence of electric fields [2]. [1] S. Leblebinci, L. Leppert, et al., *Nature Energy* 1, 16093 (2016). [2] L. Leppert et al., *J. Phys. Chem. Lett.* 7, 3683 (2016).

DS 19.9 Tue 12:00 ZEU 222

Computational search for sulphide perovskites for solar energy conversion application — •KORINA KUCHAR, MOHNISH PANDEY, KRISTIAN SOMMER THYGESEN, and KARSTEN WEDEL JACOBSEN — Center for Atomic-scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK * 2800 Kgs. Lyngby, Denmark

Oxide perovskites are in general known to be wide band gap semiconductors which hampers their use for visible light absorption. However, recent experiments on the synthesis of inorganic sulphide perovskites, for example $BaZrS_3$ [1] and $SrZrS_3$ [2], with band gaps of 1.7 eV and 0.8-1 eV, respectively, show that sulphur is a possible substitution to oxygen in inorganic perovskites to lower their band gaps. Several binary, ternary and quaternary sulphides are already known to have relevant band gaps. We perform a systematic investigation of the class of ABS3 compounds in eight phases using Density Functional Theory (DFT). The screening procedure applied is based on simple criteria such as stability, band gap in the visible part of the solar spectrum, high charge mobility and small tendency of the material to form defects. Finally we report a set of sulphide perovskites we found to be stable and have interesting properties for use as solar energy conversion materials.

1. DOI: 10.1021/acs.chemmater.5b04213 2. DOI: 10.1016/j.solidstatesciences.2005.02.010

DS 19.10 Tue 12:15 ZEU 222

Towards a multiscale statistical description of hybrid perovskite materials — •JINGRUI LI¹, JARI JÄRV^{1,2}, and PATRICK RINKE¹ — ¹COMP Centre of Excellence, Aalto University, Finland — ²Department of Physics, University of Helsinki, Finland

Hybrid perovskites (HPs), in particular methylammonium lead iodide ($MAPbI_3$), have received enormous interest in recent years as promising photoactive materials in emergent photovoltaic technologies. An important feature of HPs is their structural complexity introduced by the organic cations (e.g., MA^+). At room temperature or above, the MAs will be oriented (quasi-)randomly, forcing HPs into disordered structures. The disorder affects important materials properties such as the stability and electronic structure that are crucial for the application of HPs in novel photovoltaic devices. Our previous density-functional theory (DFT) study reveals that hydrogen bonding leads to an anisotropic interaction between the MA cations and the inorganic cage. The deformed cage and the MA orientation are interdependent, analogous to a chicken-and-egg paradox [1]. From the insight of this single unit cell model, we derive a multiscale scheme for disordered $MAPbI_3$ structures, in which the interaction between neighbouring MA ions is described by a pair model. We show that the total number of relevant pairs can be reduced to only 86 and then analyse DFT results for large, geometry optimized $MAPbI_3$ supercell models in terms of their "pair-mode" distribution. With our model we can then describe disordered HPs on length scales beyond a few nanometers.

[1] J. Li and P. Rinke, *Phys. Rev. B* **94** 045201 (2016).