CPP 54: Hybrid and Perovskite Photovoltaics IV (joint session CPP/DF/DS/HL, organized by HL)

Time: Thursday 14:45–18:30 Location: H2

CPP 54.1 Thu 14:45 H2

Synthesis of perfectly oriented and micrometer-sized MAPbBr3 perovskite crystals for thin film photovoltaic applications — •Nadja Giesbrecht[1], Johannes Schlipf[2], Andreas Binek[1], and Pablo Docampo[1] — [1]Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU), Butenandtstr. 5-13, 81377 Muenchen,Germany — [2]Lehrstuhl fuer Funktionelle Materialien, Physik-Department, Technische Universitaet Muenchen, James-Franck-Str. 1, 85748 Garching, Germany

Wide band-gap perovskites such as methylammonium lead bromide (MAPbBr3) are interesting materials for photovoltaic applications due to their potentially high open-circuit voltage. However, the fabrication of high quality planar films has not been investigated in detail for this material. We report a new synthesis approach for the fabrication of bromide based perovskite planar films based on the control of the deposition environment. The correlation of photocurrent and perovskite crystal properties in photovoltaic devices is studied. We achieve dense layers with large and perfectly oriented crystallites, as confirmed with grazing incidence wide angle X-ray scattering (GIWAXS). This represents the first solution-processed MAPbBr3 perovskite film with such a high degree of order. The current output was found to depend on crystal order in the perovskite film with internal quantum efficiencies approaching unity. Hence, our work not only gives a new pathway to tune morphology and crystal orientation, but demonstrates its importance for planar perovskite solar cells.

CPP 54.2 Thu 15:00 H2

Structural properties of hybrid perovskites from first principles — •Jingrui Li[1], Jari Järvi[1,2], Hugo Levard[1], and Patrick Rinke[1] — [1]Aalto University, Helsinki, Finland — [2]University of Helsinki, Finland

Hybrid perovskites have received rapidly growing interest in recent years as promising photoactive materials in emergent photovoltaic technologies. We present a first-principles analysis of the atomistic structure of the methylammonium lead triiodide ($CH_3NH_3PbI_3$) perovskite in this work, with a particular focus on the orientation of $CH_3NH_3^+$ cations and its interplay with the inorganic matrix. Relativistic density functional theory calculations were performed using the all-electron local-atomic-orbital code `FHI-aims`. Our results indicate that (i) the lattice constants obtained by incorporating the long-range van der Waals interactions (using the Tkatchenko-Scheffler method) in the PBE exchange-correlation functional agree well with experiments; (ii) hydrogen bonding between the ammonium group and the I^- anions plays the decisive role in the position of the $CH_3NH_3^+$ cation and the shape of the PbI_3^{2-} framework; (iii) the reorientation of $CH_3NH_3^+$ is limited due to the high barriers (~ 80 meV). Based on these findings we establish a self-consistent multiscale model, in which the energetically favorable alignment of $CH_3NH_3^+$ dipoles in the material is determined by combining classical electrostatics and statistics with structure relaxation in DFT. Our procedure produces representative "pseudo random" methylammonium lead triiodide supercells that will form the basis of further first-principles work.

CPP 54.3 Thu 15:15 H2

Micrometer size grains of hybrid perovskite through rapid melting procedure — •Oleksandra Shargaieva, Felix Lang, Jörg Rappich, Carola Klimm, Manuela Klaus, Bernd Rech, and Norbert Nickel — Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Kekuléstr. 5, 12489 Berlin (Germany)

Interest in hybrid perovskites as an absorber has flared since the first successful attempts in dye solar cells (DSCs) and continues to grow as a promising material for solar cells application. The usage of such compounds is often associated with the opportunity to substitute existing materials due to the remarkable simplicity of the production process and its low costs. On the other hand, solution based processing of solid perovskite layers often includes difficulties with crystallization, which could result in the formation of grain boundaries. This type of crystalline defect has a strong impact on the performance of devices and tends to lower the power conversion efficiency.

In our work, we propose a new solvent-free approach to produce perovskite type compounds based on its melting process. This simple technic allows to obtain bulk material with grain sizes of several micrometers. Melting process enables the control of the crystallization of hybrid perovskite and by that suppresses grain boundaries formation. Furthermore, the procedure was optimized and successfully introduced into thin-film fabrication. Consequently, melting of perovskites gives a possibility to decrease non-radiative recombination and therefore, can improve the performance of the device.

CPP 54.4 Thu 15:30 H2

J-V Hysteresis Observed in Methylammonium Lead Halide Perovskite Films at Different Voltage Scales — •Martina Stumpp, Raffael Ruess, Jonas Horn, Jan Tinz, Christoph Richter, and Derck Schlettwein — Justus-Liebig-Universität Gießen, Institut für Angewandte Physik, Heinrich-Buff-Ring 16, D-35392 Gießen, GERMANY

Hysteresis in the current-voltage curves of methylammonium lead halide films deserves detailed investigation because it can affect their applicability in perovskite solar cells. In the current study, J-V hysteresis of $CH_3NH_3PbI_3$ and $CH_3NH_3Pb(I_{0.95}Br_{0.05})_3$ prepared via different established deposition techniques was studied in a symmetric contact geometry of microstructured gold electrode arrays on SiO_2/Si wafers. The measured J-V characteristics showed a different behavior of hysteresis depending on the applied voltage range. Residual currents at zero applied bias were observed following positive or negative poling showing persistent polarization of the perovskite films. At higher bias voltages, additional inverted hysteresis loops were measured pointing at a decrease in barrier height and width at blocking perovskite/metal contacts, presumably caused by migrating iodide ions. The net J-V characteristics in this voltage range can be simulated by two diodes operated back-to-back. Time-dependent studies were performed to analyze the decay of the different observed polarization phenomena in the films during either short-circuit or continuous sweeping of the bias.

CPP 54.5 Thu 15:45 H2

Water infiltration in methylammonium lead iodide: fast and inconspicuous — •Christian Mueller[1,2,3], Bernd Epding[2,3], Tim Helder[2,3], Michael Sendner[2,3], Annemarie Pucci[2,3], Wolfgang Kowalsky[1,2,3], and Robert Lovrincic[1,3] — [1]IHF, TU Braunschweig, Germany — [2]KIP, Universität Heidelberg, Germany — [3]InnovationLab, Heidelberg, Germany

Extensive research efforts over the last few years led to a significant increase in power conversion efficiency of organometal-halide perovskite (such as $CH_3NH_3PbI_3$) solar cells up to over 20%. However, our understanding of physical/chemical processes in the material lags behind device progress. For instance, the impact of water on $CH_3NH_3PbI_3$-based devices, despite being well documented, is still not well understood and as such remains controversial.

Herein we use IR spectroscopy in controlled atmosphere to demonstrate that water infiltration into $CH_3NH_3PbI_3$ occurs much faster and at much lower humidity than previously thought. We show that the exposure of $CH_3NH_3PbI_3$ to ambient environment leads to an increase of the photocurrent by more than one order of magnitude in lateral devices. Based on transient photocurrent measurements we speculate that the effect is associated with enhanced proton conduction when light is combined with water and oxygen exposure. Our results suggest that water infiltration plays an important role in the optoelectronic properties of $CH_3NH_3PbI_3$ based devices, well beyond the known water triggered degradation processes[1].

[1] C. Mueller et al., Chem. Mater., 27 (22), p. 7835-7841, 2015

CPP 54.6 Thu 16:00 H2

Graphene on Hybrid Solar Cells: from Silicon and Perovskite towards Tandem Solar Cells — •Felix Lang, Matthias Zellmeier, Marc A. Gluba, Steve Albrecht, Jörg Rappich, Lars Korte, Bernd Rech, and Norbert H. Nickel — Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium Photovoltaik, Kekuléstr. 5, 12489 Berlin, Germany

A variety of hybrid solar-cell architectures require the deposition of a highly transparent and conductive contact. However, deposition techniques for conventional transparent conductive oxides typically degrade the topmost organic layers. A non-destructive wet transfer process of large area graphene from the growth substrate onto the desired sample is the clear choice to tackle this challenging problem.

Here, we present for the first time the implementation of graphene on hybrid crystalline silicon/P3HT solar cells. Despite identical V_{OC} and superior external quantum efficiency, device performance is limited by graphene sheet resistance. To overcome this limitation we combined in-situ graphene doping with an absorber with a higher band gap. Both measures reduce the impact on the device performance.

Implementation of graphene on the perovskite $\mathrm{CH_3NH_3PbI_3}$ therefore enabled a semi-transparent device concept showing superior internal quantum efficiency compared to conventional Au-contacted solar cells. The graphene contact enabled an optical sub-band gap transmission of around 60 % for the complete device. This paved the way for the development of a four terminal crystalline silicon/perovskite tandem solar cell with a power conversion efficiency of 13.2 %.

CPP 54.7 Thu 16:15 H2

GW for transition metal perovskites — •Zeynep Ergonenc, Bongjae Kim, Peitao Liu, Georg Kresse, and Cesare Franchini — University of Vienna, Faculty of Physics and Center for Computational Materials Science

The ab initio calculation of quasiparticle (QP) energies beyond density functional theory is a technically and computationally challenging problem. In condensed matter physics the most widely used approach to determine QP energies is the GW approximation. The GW method has been widely applied to many elemental and binary semiconductors, but its application to more complex compound such as perovskites is less abundant. In this work we apply the GW technique to transition metal perovskites with different occupancies of d orbitals. We show that much care must be taken to obtain converge QP band structure in terms of number of unoccupied orbitals and k-points sampling. Accurate extrapolation procedures to the infinite-basis-set limit and infinite-k-point limit are necessary.

30 min. Coffee Break

CPP 54.8 Thu 17:00 H2

Controlling the optical properties of organic/inorganic halide perovskites by means of size and composition — •Verena A. Hintermayr, Lakshminarayana Polavarapu, Alexander S. Urban, and Jochen Feldmann — Chair for Photonics and Optoelectronics, Department of Physics, Ludwig-Maximilians-Universität (LMU), Amalienstaße 54, 80799 Munich, Germany

Organic/Inorganic halide perovskites display a huge potential for not only photovoltaic, but also light emitting applications. In order to improve the efficiency and functionality of applications based on this material a better control of their optical properties is desirable. Here, we present a general colloidal synthesis method for the preparation of hybrid organic/inorganic halide perovskite nanocrystals (NCs) with different size and composition. We have prepared highly stable perovskite NCs that show strong quantum confinement and NCs that exhibit bulk like optical properties. We additionally investigate the tunability of the optical properties of the NCs by systematically modifying their halide content (I, Br and Cl). This work opens up a simple synthetic route for the preparation of perovskite NCs with controllable dimensionality and composition.

CPP 54.9 Thu 17:15 H2

Dynamics and nature of photo-excited carriers in $\mathbf{(CH_3NH_3)PbI_3}$ organic-inorganic perovskite — •Daniel Niesner[1,2], Haiming Zhu[1], Tyler J. S. Evans[1], Bryan J. Kudisch[1], Prakriti P. Joshi[1], Kiyoshi Miyata[1], M. Tuan Trinh[1], Manuel Marks[1], and X.-Y. Zhu[1] — [1]Department of Chemistry, Columbia University, New York, NY 10027, USA — [2]Festkörperphysik, FAU Erlangen-Nürnberg, D-91058 Erlangen, Germany

Thin film solar cells based on organic-inorganic perovskites are the rising star in photovoltaics. The photophysics and transport mechanism behind the outstanding device performance remain a matter of debate. I will present the results of a study on carrier dynamics in vapor-deposited thin films of $\mathrm{(CH_3NH_3)PbI_3}$, combining time-resolved two-photon photoemission, transient absorption, and photoluminescence.

After optical excitation with sufficient photon energy (≥ 2.15 eV), highly excited electrons relax quickly (≤ 0.3 ps) to a region of the conduction band with a low density of states, located 0.3 eV above the band minimum. In parallel, polaron formation takes place on a time scale of 0.28 ± 0.04 ps, matching the time scale of cation motion. Polaronic screening suppresses further energy relaxation and thermalization. The polaron maintains a significant excess energy for more than 60 ps.

The excess energy can be utilized to overcome energy barriers at grain boundaries and contacts. Harvesting it directly would result in a solar cell with an efficiency exceeding the Shockley-Queisser limit.

CPP 54.10 Thu 17:30 H2

Infrared spectroscopic study of vibrational modes and water infiltration in methylammonium lead halide perovskites — •Michael Sendner[1,2], Christian Mueller[1,2,3], Tobias Glaser[1,2], Annemarie Pucci[1,2], Wolfgang Kowalsky[1,2,3], and Robert Lovrincic[2,3] — [1]Kirchhoff-Institut für Physik, Universität Heidelberg — [2]InnovationLab GmbH, Heidelberg — [3]Institut für Hochfrequenztechnik, TU Braunschweig

The interactions of the organic cation with the inorganic lattice in organo-metallic halide perovskites influence the vibrational properties of the cation which can be measured in the mid infrared (IR) spectral region. We determined the infrared optical properties of different methylammonium lead halide perovskite films ($\mathrm{CH_3NH_3Pb(I/Br/Cl)_3}$) and derived the full dielectric function [1]. The peaks of the vibrational modes are assigned by means of the comparison with MP2 calculated modes of the free methylammonium cation. The influence of the inorganic cage and the processing is discussed. Furthermore, we utilize IR spectroscopy to investigate the influence of water onto perovskite thin films. We show that the infiltration of water into $\mathrm{CH_3NH_3PbI_3}$ appears much faster and at much lower humidity than previously known [2]. We suggest a molecular picture of this infiltration where water molecules have a strong impact on the hydrogen bonding between the methylammonium cations and the surrounding Pb-I cage. [1] T. Glaser et al. J. Phys. Chem. Lett. 2015, 6 (15), 2913-2918 [2] C. Müller et al. Chem. Mater., 2015, 27 (22), 7835-7841

CPP 54.11 Thu 17:45 H2

Temperature and excitation density dependence of two-photon photoluminescence of perovskite CH3NH3PbBr3 — •Heiko Linnenbank[1], Michael Saliba[2], Lili Gui[1], Bernd Metzger[1], Giuseppe Nasti[2], Jeanette Kadro[2], Anders Hagfeldt[2], Michael Graetzel[2], and Harald Giessen[1] — [1]4th Physics Institute and Research Center SCoPE, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany — [2]Laboratory of Photonics and Interfaces, École polytechnique fédérale de Lausanne, Station 6, 1015 Lausanne, Switzerland

Recently solution processed organometallic halide perovskites have attracted much attention due to their simple processability, strong light absorption and favorable emission properties, which promises the realization of efficient on chip lasers. While several studies have been focused on one-photon excited luminescence processes like amplified spontaneous emission or lasing, only less attention has been paid to two-photon excited processes. In contrast to the usually expected quadratic dependence upon the excitation density in the case of two-photon photoluminescence, we rather measure a 4th power dependence at room temperature in the case of CH3NH3PbBr3. Such an excitation density dependence is a strong hint for a biexcitonic or exciton collision processes, which are rather unlikely at room temperature. To clarify the origin of the 4th power dependence, we investigate the form as well as the excitation density dependence of the photoluminescence spectra with respect to the sample temperature, revealing a suppression of the 4th power dependence with decreasing temperature.

CPP 54.12 Thu 18:00 H2

Dark field photoluminescence and scanning electron beam measurements on single organic/inorganic halide perovskites of varying geometry and composition — •Alexander Richter, Verena Hintermayr, Lakshminarayana Polavarapu, Alexander Urban, and Jochen Feldmann — Chair for Photonics and Optoelectronics, Department of Physics, Ludwig-Maximilians-Universität (LMU), Amalienstaße 54, 80799 Munich, Germany

During recent years organic/inorganic halide perovskites have become a promising candidate for photovoltaic applications and also show a huge potential for light emitting applications. In case of two dimensional crystals quantum confinement affects the optical properties. Here, we present results on individual nanocrystals. Perovskites fabricated with varying halide content and geometry are embedded in a polymer matrix film to prevent degradation. Dark field photoluminescence and scanning electron beam measurements on individual spots of the sample are carried out. This yields a direct link between shape, halide composition and photoluminescence of these particles.

CPP 54.13 Thu 18:15 H2

Luminescence blue-shift with decreasing size of perovskite needles. — •Amala Elizabeth and Katrin F.Domke — Molecular Spectroscopy Department,Max Planck Institute for Polymer Research, Mainz, 55128, Germany

Despite revolutionizing the photovoltaic industry by helping create highly efficient thin film solar cells, many intrinsic properties of organometallic halide perovskites still remain unknown. A complete understanding of the interplay of size, structure and electronic nature in determining the optical properties of thin film perovskites is crucial to fully exploit them for solar cell applications.

We studied methylammonium lead iodide perovskite thin films of ordered needles of varying submicron size. Energy-dispersive X-ray and IR spectroscopies reveal that the needles are chemically identical. While crystallinity is preserved in all samples, XRD and Raman spectra show a relative increase in the crystalline lead iodide content with decreasing needle size. Interestingly, we observe a blue-shift of 40 meV in both luminescence peak position and UV-vis absorption onset with decreasing needle size. Here, we discuss possible origins of the unexpected band gap increase with decreasing perovskite needle size, such as methyl ammonium cation orientational ordering [1] and lead iodide content [2].

References:

1. C. Quarti et al., J.Phys.Chem Lett. 5 (2014), 279-284.
2. Q.Shen et al., Nano Lett. 14 (2014), 4158-4163.