

AKJDPG 7: PhD Focus Session: In-situ probes toward better understanding of hybrid halide perovskites II (joint session CPP/AKJDPG)

Time: Friday 9:30–12:15

Location: ZEU 222

Invited Talk AKJDPG 7.1 Fri 9:30 ZEU 222

Time-resolved X-ray scattering to understand perovskite materials — OLIVER FILONIK¹, CHRISTOPHER GREVE², MEIKE KUHN², MICHAEL BUCHHORN², ADRIAN EBERT², RICHARD KELLNERBERGER², and •EVA M. HERZIG¹ — ¹MSE - Herzig Group, TU München, Lichtenbergstr. 4a, 85748 Garching — ²Dynamik und Strukturbildung - Herzig Group, Universität Bayreuth, Universitätsstr. 30, 95447 Bayreuth

The formation of perovskite thin films is of interest since this process determines the final material quality. In-situ X-ray scattering can help to learn more about the formation of perovskite crystals and how the crystallization is altered by the use of additives or other parameters. The film formation mechanism directly influences the performance of, for example, solar cells. We apply different techniques to extract time-resolved information and will show the opportunities and limitations of these in the quest for understanding formation-function relationships in perovskites.

AKJDPG 7.2 Fri 10:00 ZEU 222

In situ reflectometry and air flow control enables modeling of the drying process in blade coated hybrid perovskite solution films. — •SIMON TERNES^{1,2,3}, TOBIAS BÖRNHORST³, JONAS A. SCHWENZER¹, IHTEAZ M. HOSSAIN^{1,2}, ULI LEMMER¹, PHILIP SCHARFER^{2,3}, WILHELM SCHABEL³, BRYCE S. RICHARDS^{1,2}, and ULRICH W. PAETZOLD^{1,2} — ¹Light Technology Institute, Karlsruhe, Germany — ²Institute of Microstructure Technology, Eggenstein-Leopoldshafen, Germany — ³Institute of Thermal Process Engineering, Karlsruhe, Germany

In recent years, hybrid perovskite solar cells (PSCs) have been introduced to the field of thin-film photovoltaics, exhibiting not only a steep increase in power conversion efficiencies from 3.8% in 2009 to above 25% to date, but also opening the perspective toward low-cost, large-scale solution processing. However, in order to design industrial-scale printing machines for PSCs in an efficient manner, general modeling of the dynamic drying and crystallization processes in perovskite solution films is required. This modeling must extend beyond trail-and-error optimization and beyond the commonly used, non-scalable spin coating technique. In the work presented here, we demonstrate simultaneous exact drying control by a laminar air flow and in situ film thickness measurements by reflectometry on blade coated perovskite solution films. In this way, we derive a general model of the drying process in these solution films and correlate it with the evolving morphology, providing a strategy of optimal process transfer from spin coating to any industrial coating and drying technique.

AKJDPG 7.3 Fri 10:15 ZEU 222

The zero step for degrading perovskite solar cells: what atmosphere should we choose? — •RENJUN GUO¹, WEI CHEN¹, LENNART K. REB¹, MANUEL A. SCHEEL¹, STEPHAN ROTH², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching, Germany — ²Deutsches Elektronen-Synchrotron (DESY), Notkestrasse 85, 22607 Hamburg, Germany

The power conversion efficiency (PCE) of perovskite solar cells (PSCs) reached the champion value of 25.2 percent, making this technique competitive with commercial silicon solar cells. Despite such advantages, the application of PSCs is currently limited by combining high performance and operational stability because PCE of PSCs can degrade due to the presence of temperature, light, humidity, and oxygen. Besides, current degradation research on PSCs is carried out without standard protocol. Therefore, it is necessary to make the standard protocol for the long term degradation of PSCs. We investigated degradation processes of PSCs under both AM 1.5G and different atmosphere conditions with in-situ grazing incidence wide-angle X-ray scattering (GIWAXS) and grazing incidence small-angle X-ray scattering (GISAXS). With these approaches, we can follow the evolution of characteristic structures and of the inner morphology under the operational condition. After understanding the degradation mechanisms upon different atmosphere (nitrogen and vacuum), we can choose a reasonable atmosphere which allows for the standard aging routine to guide industrial development.

AKJDPG 7.4 Fri 10:30 ZEU 222

Growth of Methylammonium and Formamidinium Lead Halides by Co-Evaporation Analyzed with in situ X-ray Diffraction — •KARL HEINZE, THOMAS BURWIG, ROLAND SCHEER, and PAUL PISTOR — Martin-Luther-Universität Halle-Wittenberg, Halle an der Saale, Germany

Crystalline lead halide perovskite (e.g. Methyl Ammonium (MA) PbI₃), thin-film solar cells reach efficiencies far over 20%. These films are commonly prepared by solvent-based methods such as spin-coating, with limited scalability. An industrially attractive technique for the deposition of thin films is co-evaporation. Using a vacuum chamber with a built-in in-situ X-ray diffraction system, we are able to investigate the influence of varying processing conditions during the co-evaporation of MA lead halides (MAPbX₃, with X=I,Br,Cl) and formamidinium lead halides (FAPbX₃) on the film formation process and can cross-relate our findings to opto-electronic properties and solar cell performance. More specifically, we analyze the effect of different precursors flux rate ratios and substrate temperatures on the crystal growth and compare sequential to simultaneous co-evaporation. We find a strong impact of the processing temperature on crystal size and morphology and determine suitable process windows for optimal absorber compositions with small amounts of PbI₂ secondary phases. We note that processing conditions have also a strong impact on the crystal orientation of the films. This is especially pronounced for FAPbBr₃, where we were able to grow films with nearly complete orientation in either (100) or (111) direction.

AKJDPG 7.5 Fri 10:45 ZEU 222

Structural dynamics of halide perovskites via in-situ electron microscopy — •CHEN LI — Electron microscopy for Materials research (EMAT), University of Antwerp, Antwerp, Belgium

In-situ microscopy is a powerful tool to investigate dynamic transformations in materials. To observe such transformations the focused electron probe in scanning transmission electron microscope (STEM) can be used to both stimulate and image the movement of atoms [1]. Here we apply such dynamic STEM to directly observe ion migration in hybrid and inorganic halide perovskites.

Direct in-situ heating of samples can also be used inside electron microscopes to provoke phase changes with special heating holders [2]. We use in-situ heating in STEM to track the phase transitions in inorganic CsPbI₃ perovskites from an orthorhombic δ - phase to a cubic α -phase. An intermediate phase with layered configuration was observed during the transition.

[1] C. Li, Y. Y. Zhang, T. J. Pennycook, Y. L. Wu, A. R. Lupini, N. R. Paudel, S. T. Pantelides, Y. Yan and S. J. Pennycook, Column-by-column observation of dislocation motion in CdTe: dynamic scanning transmission electron microscopy, *Appl. Phys. Lett.* 2016, 109, 143107

[2] C. Li, E. S. Sanli, H. Strange, M. D. Heinemann, D. Greiner, R. Mainz, W. Sigle, D. Abou-Ras and P. A. v. Aken, Diffusion-assisted grain boundary migration in CuInSe₂. under review

15 min. break

AKJDPG 7.6 Fri 11:30 ZEU 222

Band structure and electronic properties of lead halide perovskites from photoemission studies — •FENGSHUO ZU^{1,2}, PATRICK AMSALEM¹, DAVID EGGER³, CHRISTIAN WOLFF⁴, RONGBIN WANG^{1,7}, MARYLINE RALAIARISOA¹, HONGHUA FANG⁵, MARIA ANTONIETTA⁵, DIETER NEHER⁴, LEEOR KRONIK⁶, STEFFEN DUHM⁷, and NORBERT KOCH^{1,2} — ¹HU Berlin — ²HZB Berlin — ³TU Munich — ⁴Universität Potsdam — ⁵University of Groningen, Netherland — ⁶Weizmann Institute of Science, Israel — ⁷Soochow University, China

Photovoltaic devices based on halide perovskites with outstanding optoelectronic properties have exhibited tremendous progress in performance. To understand the origin of these properties comprehensively, detailed knowledge on the underlying electronic band structure is required. Here, we present complementary results from low-energy electron diffraction, angle-resolved photoelectron spectroscopy, and density functional theory calculations for CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ single crystals. For both, sharp LEED patterns cor-

responding to the (001) surfaces of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ were observed together with well-resolved, dispersive valence band features. Furthermore, the fundamental differences between linear and logarithmic methods in determining the VB onset are discussed and addressed.[1] In addition, surface photovoltage effect, which has so far hardly been discussed in this context, is found to play significant effect in photoemission studies.[2] [1] Zu et al., J. Phys. Chem. Lett. 2019, 10, 601,[2] Zu et al., ACS Appl. Mater. Interfaces, 10.1021/ac-sami.9b05293.

AKjDPG 7.7 Fri 11:45 ZEU 222

Energy-Level Alignment of Formamidinium Tin Iodide with Organic Contact Materials — •JONAS HORN, PASCAL SCHWEITZER, and DERCK SCHLETTWEIN — Justus Liebig University Gießen, Institute of Applied Physics

The alignment of energy levels at the interfaces of a perovskite absorber with adjacent hole- and electron-transporting materials affects the formation of space-charge regions and interfacial recombination. These have consequences for charge transport in the layers and for the efficiency of devices. To analyze such alignment we used Kelvin-probe force microscopy (KPFM). This study is focused on formamidinium tin iodide (FASnI_3) as perovskite absorber, which avoids the toxicity problems of lead and is known to yield the highest power conversion efficiencies amongst all lead-free perovskite absorbers. The most common solar cell geometry for FASnI_3 implements C_{60} as electron-transporting material, which is prepared onto the perovskite by physical vapor deposition (PVD). Intermittently to PVD, we used KPFM to simultaneously monitor morphology and work function of C_{60} during its growth on FASnI_3 . We show that a sufficiently high deposition rate is needed to avoid island formation of C_{60} and obtain a homogeneously covering film with constant work function. We further show that the

width of the space charge layer in C_{60} is larger than the film thickness often implemented in perovskite solar cells. A band bending in the range of 300 meV is observed and consequences for prospective device operation are discussed.

AKjDPG 7.8 Fri 12:00 ZEU 222

Thermal decomposition dynamics of lead halide perovskite thin films — THOMAS BURWIG, KARL HEINZE, ROLAND SCHEER, and •PAUL PISTOR — MLU Martin-Luther-Universität Halle-Wittenberg

Despite the remarkable progress of lead halide perovskites, their low stability severely limits practical applications. To understand degradation pathways and pinpoint optimal compositions in terms of stability is therefore of utmost importance. Here we investigate the thermal stability of lead halide perovskite thin films grown by co-evaporation and analyze their thermal decomposition at elevated temperatures. Our approach allows to investigate the thermal decomposition by time-resolved in situ X-ray diffraction inside the vacuum growth chamber, without exposing the perovskite thin film to moisture or ambient air at any time. By applying fixed temperature ramps of 3-4 K/min. , we compare the onset of decomposition for a variety of different ABX_3 compositions and explore perovskites throughout the compositional space with $\text{A}=\text{MA,FA,Cs}$; $\text{B}=\text{Pb,Sn,(Ag,Bi)}$ and $\text{X}=\text{I,Br,Cl}$. We find an increasing decomposition temperature for the series MAPbCl_3 - MAPbI_3 - MAPbBr_3 , where the perovskite decomposes via degassing of MAX. The cation variation shows increased stability for CsPbBr_3 over FAPbBr_3 and MAPbBr_3 , mainly due to the increased sublimation temperature of CsX, which is even higher than that of PbX_2 . Finally, for the case of the most common and less stable MAPbX_3 perovskites, a series of time-resolved degradation experiments at constant temperatures provides detailed insights into the degradation kinetics of these materials.