Universal Formation Mechanism of Halide Perovskite Thin Films

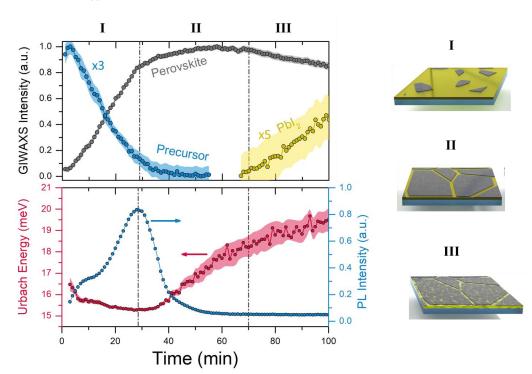
Martin Ledinsky*(1); Ales Vlk (1); Robert Hlavac (3); Lucie Landova (1); Antonin Fejfar (1); Monica Morales-Masis (2), Vojta Kliner (1. 2), Nada Mrkyvkova (3), Peter Siffalovic (3)

- (1) Institute of Physics of the Czech Academy of Sciences, Cukrovarnicka 10, 16200 Prague, Czech Republic.
- (2) MESA+ Institute for Nanotechnology, University of Twente, Enschede, 7500 AE, The Netherlands.
- (3) Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia.

Metal halide perovskites (MHPs) have gained significant scientific interest due to their outstanding optoelectronic properties and high efficiencies in solar cell photoconversion. There are many ways to prepare MHPs of reasonable quality, the solution process is still the best in this manner. But the vacuum-based methods, which are relevant for industry and large area deposition, are not lacking far behind. The final product is always the MHP thin film of similar morphology and structure. The only substantial difference is the dimension of the grains, which used to be larger for solution processed films. Therefore, logical question arises, what are the differences in the MHP film formation?

Recently, with the insight of in-situ photoluminescence (PL) and GIWAXS measurements, we have studied the MHP film deposition by solution processes. Based on the results depicted bellow, we divided the MHPs growth into three stages. In short, we see fast growth of MHPs grains from GIWAXS in the first growth stage, accompanied by proportional increase in PL signal. However, in the second stage the growth speed significantly decreases, and the PL signal is highly quenched. This observation means that the free grown grains (stage I) are of low defect densities, but once they start to connect (stage II) the grain boundaries are formed, where defects are concentrated. This leads to rapid decrease of the PL signal. The last stage documents partial degradation at long deposition times only. Surprisingly, very similar observation was done by in-situ measurement of evaporated MHPs² and films prepared by pizza oven deposition. Recent results shows the same tendencies for the pulsed laser deposited MPHs as well [4].

Deeper understanding to this universal formation mechanism of MPHs thin films give us a unique opportunity to enhance its optoelectronic quality. One critical aspect is formation of large grains, the second one is the passivation process mainly at the grain boundaries. In-situ PL characterization is able to guide us through these processes, defect passivation directly during the crystallization or growth process is controllable by this way. Direct defect passivation may lead to substantial V_{OC} increase in the finalised MHPs solar cell.



- [1] Mrkyvkova, N.; Held, V.; Nádaždy, P.; Subair, R.; Majkova, E.; Jergel, M.; Vlk, A.; Ledinsky, M.; Kotlár, M.; Tian, J.; et al. Combined in Situ Photoluminescence and X-ray Scattering Reveals Defect Formation in Lead-Halide Perovskite Films. J. Phys. Chem. Lett. 2021, 12 (41), 10156–10162. https://doi.org/10.1021/acs.jpclett.1c02869.
- [2] Held, V.; Mrkyvkova, N.; Nádaždy, P.; Vegso, K.; Vlk, A.; Ledinský, M.; Jergel, M.; Chumakov, A.; Roth, S. V.; Schreiber, F.; et al. Evolution of Structure and Optoelectronic Properties During Halide Perovskite Vapor Deposition. J. Phys. Chem. Lett. 2022, 13 (51), 11905–11912. https://doi.org/10.1021/acs.jpclett.2c03422.
- [3] Guesnay, Q.; Sahli, F.; Artuk, K.; Turkay, D.; Kuba, A.; Mrkyvkova, N.; Vegso, K.; Siffalovic, P.; Schreiber, F.; Lai, H.; Fu, F.; Ledinský, M.; Fürst, N.; Schafflützel, A.; Bucher, C.; Jeangros, Q.; Ballif, C.; Wolff, M.: Pizza Oven Processing of Organohalide Perovskites (POPOP): A Simple, Versatile and Efficient Vapor Deposition Method. Adv. Energy Mater. 2024, 2303423 https://doi.org/10.1002/aenm.202303423
- [4] Kliner, V.; Soto-Montero, T.; Nespoli, J.; Savenije, T.; Ledinsky, M.; Morales-Masis, M.: Pulsed Laser Deposition of Halide Perovskites with over 10-fold Enhanced Deposition Rates. Journal of Physical Chemistry Letters, accepted for publication

Acknowledgements:

We acknowledge the use of the CzechNanoLab research infrastructure supported by the MEYS (LM2023051 and LM2023039) and to the project number 9F23003 supported by the MEYS.