

### Atomic layer deposition of Al<sub>2</sub>O<sub>3</sub> on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> for enhancement of perovskite solar cells stability

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Organic-inorganic perovskites like methylammonium lead triiodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) films represent a new paradigm for photovoltaics, which have the potential to overcome the performance limits of current technologies and achieve low cost and high versatility.[1-5] Although the power conversion efficiency of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-based perovskite solar cells exceeded already 21 %, a number of key issues must be solved before the widespread commercialization will be possible.

Typically, when exposed to the air or moisture hybrid perovskite films degrade within a couple of hours or days.[1,2] Moreover, the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite cannot sustain prolonged annealing at temperatures higher than around 85°C.[3,4] It also undergoes degradation upon applying electric field with the presence of moisture.[5] Improving and controlling perovskite stability along with understanding of degradation pathways are now deeply studied. By understanding how the material properties affect the performance of perovskite solar cells, further improvements for future applications will be possible.

The conformal coverage of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite film at low temperature with a thin metal oxide layer is very promising to protect it against degradation. The perfectly matching method to fulfill both requirements is the atomic layer deposition (ALD) [6]. In order to prevent thermal degradation of the perovskite a deposition at temperatures lower than 80°C is desirable.

In this paper, we present our X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) studies on the ALD growth of Al<sub>2</sub>O<sub>3</sub> on the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite film at room temperature. TMA and H<sub>2</sub>O were used as aluminium and oxygen precursors for ALD. The chemical and electronic changes occurred at the Al<sub>2</sub>O<sub>3</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface were firstly investigated using synchrotron radiation source XPS (SR-XPS) at the undulator beamline U49/2-PGM2 at BESSY-II in Berlin/Adlershof with the ASAM end-station. The photoelectrons were excited by X-rays with energies of 640 eV and recorded by the PHOIBOS-150 (SPECS GmbH) hemispherical electron analyzer equipped with a 1D delay line detector at take-off angle ( $\alpha$ ) of 45°. The topography measurements were performed at room

temperature by AFM using the Veeco CP-II AFM system operated in a contact mode.

The SR-XPS and AFM results of the Al<sub>2</sub>O<sub>3</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface indicate that Al<sub>2</sub>O<sub>3</sub> initially grows layer by layer up to approximately 12 ALD cycles (~0.6 nm) and then 3D islands start to form (see Fig. 1). After 50 ALD cycles the 2D Al<sub>2</sub>O<sub>3</sub> film is covered with approximately 86 % of Al<sub>2</sub>O<sub>3</sub> islands.

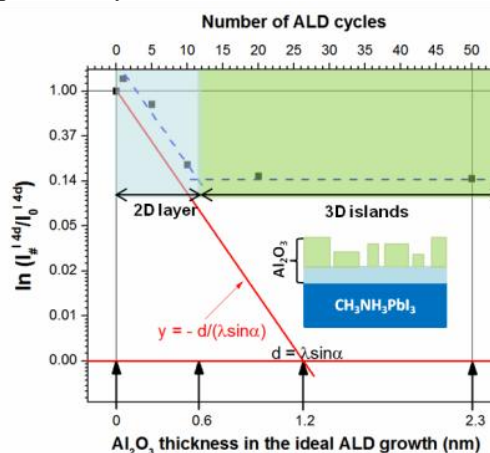


Figure 1. Growth model of Al<sub>2</sub>O<sub>3</sub> on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite at room temperature based on analysis of the I4d XPS signal attenuation versus number of complete TMA and H<sub>2</sub>O ALD cycles.

Moreover, XPS results have shown that oxygen is initially present in the perovskite film most probably due to not fully removed DMF solvent and it participates in the reaction with TMA precursor through adsorption on active sites during the few first ALD cycles.

The stability test upon air exposure of the alumina/perovskite system has shown that coating the perovskite film with an ultra thin Al<sub>2</sub>O<sub>3</sub> layer enhances its lifetime. This finding opens new possibilities to increase the stability of the perovskite solar cells where the low temperature processing is mandatory to protect the perovskite film against degradation.

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- [1] T. Leijtens, G. E. Eperon, S. Pathak, A. Abate, M. M. Lee, H. J. Snaith, *Nat. Commun.* **4** (2013) 2885.
- [2] J. A. Christians, P. A. Miranda Herrera, P. V. Kamat, *J. Am. Chem. Soc.* **137** (2015) 1530.
- [3] B. Conings, J. Drijkoningen, N. Gauquelin, A. Babayigit, J. D'Haen, L. D'Olieslaeger, A. Ethirajan, J. Verbeeck, J. Manca, E. Mosconi, F. D. Angelis, H.-G. Boyen, *Adv. Energy Mater.* **5** (2015) 1500477.
- [4] L.-C. Chen, C.-C. Chen, J.-C. Chen, C.-G. Wu, *Solar Energy* **122** (2015) 1047.
- [5] T. Leijtens, T. T. Hoke, G. Grancini, D. J. Slotcavage, G. E. Eperon, J. M. Ball, M. D. Bastiani, A. R. Bowring, N. Martino, K. Wojciechowski, M. D. McGehee, H. J. Snaith, A. Petrozza, *Adv. Energy Mater.* **5** (2015) 1500962.
- [6] G. Niu, W. Li, F. Meng, L. Wang, H. Dong, Y. Qiu, *J. Mater. Chem. A* **2** (2014) 705.