Supporting information

Analysis of the ALD processing over methylammonium lead iodide perovskite films

Perovskite layers were fabricated in a N_2 filled glove box (H_2O and O_2 < 0.1 ppm) by spin coating a precursor solution composed by 0.8 mM of lead acetate trihydrate (99.999% from Sigma Aldrich), 0.2 mM of lead chloride (99.99% form Alfa Aesar) and 3 mM methylammonium iodide (from Dyesol) in 1 ml of N,N-dimethylformamide (anhydrous, from Sigma Aldrich).[1] The solution was spin coated on the substrate at 3000 RPM for 60 seconds and the films were annealed on an hotplate at 130°C for 10 minutes to form the perovskite structure.

Fabrication of ALD layers: ALD processes were carried out on two remote plasma ALD reactors: Oxford Instruments FlexAL™ and OpAl™ for Al2O3, TiO_2, MoO_3 and ZnO processes while a home-built remote plasma reactor (Aldi-1) was used for NiO process. Their specifications are described elsewhere.[2–4] All the data about the ALD processes are reported in Table S2 for each metal oxide. The metal precursors $Al(CH_3)_3$, $Ti(OCH(CH_3)_2)_4$, $Zn(C_2H_5)_2$ and $Ni(C_5H_4CH_3)_2$ were purchased by Sigma Aldrich, while $(NtBu)_2(NMe_2)_2Mo$ by Strem Chemicals.

Table S2: The ALD process conditions for the metal oxides reported in this work.

	Al_2O_3	**Al_2O_3**	**ZnO**	**TiO_2**	**MoO_3**	**NiO**
Reactor	FlexAL™	OpAL™	OpAL™	FlexAL™	OpAL™	Aldi-I
Precursor	$Al(CH_3)_3$	$Al(CH_3)_3$	$Zn(C_2H_5)_2$	$Ti(OCH(CH_3)_2)_4$	$Mo(N^tBu)_2(NMe_2)_2$	$Ni(C_5H_4CH_3)_2$
$T_{substrate}$ *(°C)*	30-80	80-120	100-120	50-80	50-80	50
$T_{precursor}$ *(°C)*	25	25	25	45	50	55
Precursor dose(s)	0.04	0.04	0.05	4	4	3
Precursor purge (s)	3	5	5	5	4	5
H_2O dose(s)	--	0.1	0.1	--	--	--
O_2 plasma exposure(s)	3	--	--	12	4	3
Plasma power (W)	100	--	--	100	100	100
Oxidant purge (s)	3	5	6	3	4	5
Ar bubbling flow(sscm)	--	--	--	50	45	50

XPS characterization: the chemical compositions of the perovskite layers and the ALD films deposited on top of them were analysed by X-ray photoelectron spectroscopy (XPS Thermo Scientific K-Alpha KA1066, monochromatic Al Ka (hν =1486.6 eV), X-ray spot: 400 mm). In order to obtain information from the interface perovskite/ALD metal oxide, the nominal thickness of the ALD overlayer was maintained at 6 nm, lower than the escape depth of the electrons (almost 10 nm).

XRD characterization: The crystallinity of the pristine sample, thermally stressed, after co-reactant exposure, and after ALD metal oxide processes, were studied by X-ray diffraction (XRD; PanAlytical X'pert PRO MRD). The areas of the peaks relative to the perovskite structure at 14.1° and to the PbI_2 at 12.6° were obtained fitting the data with a gaussian function. In the manuscript, the areas are displayed normalized to the one of the pristine sample.

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