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Supporting information

Band-gap tuning of lead halide perovskites using a sequential deposition process

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Experimental

Device fabrication

Fluorine doped tin oxide (FTO, < 14 ohm/square, 2.2 mm thick) substrates were etched (Zn powder & 4 M HCl) to form the desired pattern. The etched substrates were subsequently cleaned with decon soap solution, then deionized water, followed by ethanol. Then a thin compact layer of TiO_2 (80-100 nm, blocking layer) was deposited by aerosol spray-pyrolysis at 450^{o}C using ambient air as a carrier gas. For spray-pyrolysis, a solution of titanium diisopropoxide bis (acetylacetonate) (75 wt% in isopropanol) and absolute ethanol were used in a 1:9 ratio (V/V). These substrates were immersed in 40 mM of $TiCl_4$ solution for 30 min at 70 ^{o}C, followed by rinsing with deionized water and ethanol. A TiO_2 layer (~ 400-500 nm) composed of 20-nm-sized particles was then deposited by spin coating, and subsequently annealed at 500°C for 30 mins. An organic-inorganic perovskite $(CH_3NH_3)PbI_3$ was deposited by a sequential method as reported in the literature.[1] Lead iodide (PbI_2) (1M) was dissolved in N,N-dimethylformamide (DMF) overnight under stirring conditions at 70^{o}C. The solution was spin coated on the TiO_2 substrates at 6000 r.p.m for 5 s, followed by annealing at 70 ^{o}C for 30 mins. Subsequently the films were dipped in 10 mg/mL solution of CH_3NH_3I (*MA*I) and CH_3NH_3Br (*MA*Br) in 2-propanol for approx. 20 min. In order to form the mixed lead iodide and bromide perovskites, the *MA*I and *MA*Br solutions were mixed in the various volumetric ratios, keeping the final amount of mixed solution fixed. Based on composition of the mixed solvent, molar concentration of the Iodide and Bromide were calculated in the initial precursor solution. The films were then rinsed further with 2-propanol and dried at 70 ^{o}C for 30 min. An organic hole conductor namely spiro-OMeTAD (2, 2', 7, 7'- tetrakis-(N, N-di-p-methoxyphenylamined) 9, 9'-spirobifluorene) was dissolved in chlorobenzene (120 mg/mL) and spincoated on these substrates. Additives like Li $(CF_3SO_2)_2$ N (29 μL/ml from stock solution of 520 mg/ml), tert.-butylpyridine (29 μL) and FK102 dopant (24 μL, stock solution 300mg/ml) were added to the above solution. The subsequently masked (shadow masking) substrates were placed in a thermal evaporator for gold (Au) deposition (~80 nm). The active area was defined by the overlap of TiO_2 and Au (0.2 cm^2). During measurements, the samples were masked using a black tape, to prevent the stray currents generated away from the active area.

Characterization

Top view and cross-sectional images were recorded using a Field Emission Scanning Electron Microscope (FESEM, JEOL, JSM-7600F, 5 kV). Photocurrent-voltage(I-V) measurements were carried out using San-EI Electric, XEC-301S under AM 1.5 G. Incident photon to current conversion efficiency (IPCE) was determined using PVE300 (Bentham), with dual Xenon/quartz halogen light source, measured in DC mode with no bias light used. Incident light intensity was calibrated using a photodiode detector (silicon calibrated detector,Newport). UV-Vis absorption spectra were collected with a Shimadzu UV3600 spectrophotometer. Structural and phase characterization of the as-prepared film was achieved by X-ray diffraction (XRD). The XRD patterns were recorded using Bruker AXS (D8 ADVANCE) X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å) from 20^0 to 80^0.

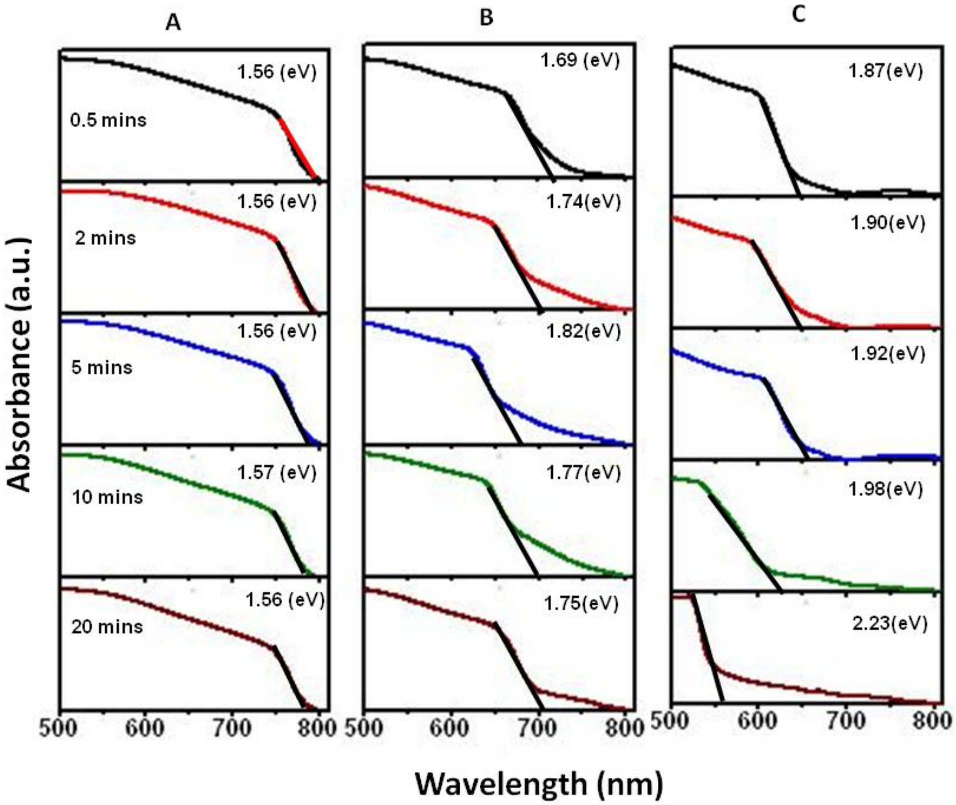

Fig. S1: Ex-situ UV-vis spectra of perovskite films formed by dipping PbI_2 films (on mp-TiO_2/bl-TiO_2/FTO substrate) at different time interval in: A) Methyl ammonium iodide (*MA*I), B) Mixture of Methyl ammonium iodide (*MA*I) & Methyl ammonium bromide (*MA*Br) (1:1), and) Methyl ammonium bromide (*MA*Br) solutions in isopropanol (IPA).

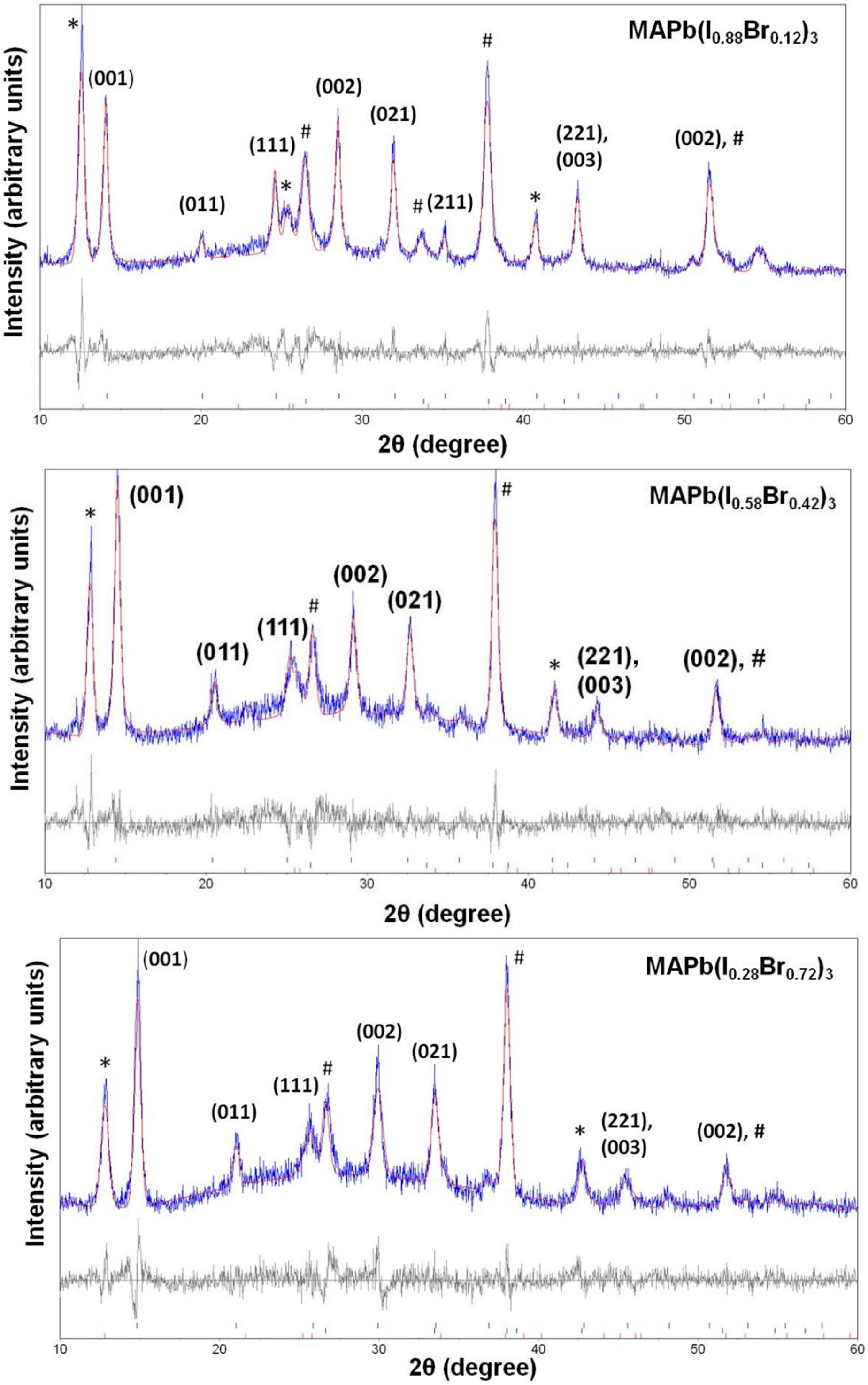

Fig. S2: Representative Pawley fits for the $MAPbI_{3-x}Br_x$ series: $MAPb(I_{0.88}Br_{0.12})_3$, $MAPb(I_{0.58}Br_{0.42})_3$ and $MAPb(I_{0.28}Br_{0.72})_3$. The blue line is the experimental pattern, the red line is the calculated pattern and the grey line is the difference between the experimental and calculated pattern. The * and # represent the Bragg reflections associated with PbI_2 (2H-polytype) and TiO_2 (anatase) respectively.

Br content (x) in mole	Lattice parameters (Å)

0	6.305(5)*
0.26	6.243(5)
0.41	6.197(5)
0.58	6.139 (5)
0.74	6.016(5)
0.85	5.977(5)
1	5.906(5)

Table S1: Lattice parameters of pseudocubic or cubic *MA*Pb($I_{1-x}Br_x$)$_3$ as a function of Br content (x). * The cubic lattice parameter for the undoped $MAPbI_3$ is the average of the pseudo-cubic lattice parameters of the tetragonal cell.

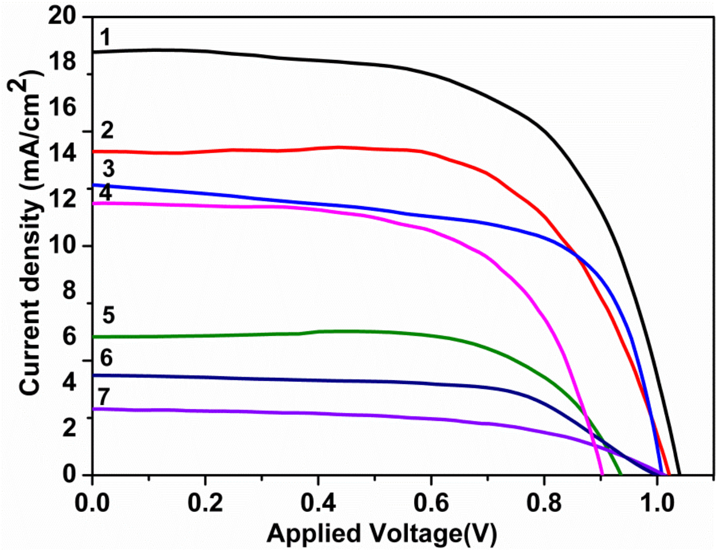

Fig.S3 : The characteristic J-V curves of the mixed lead halide perovskite devices. The number 1 to 7 represents the composition of the mixed halide. 1. $MAPbI_3$, 2. $MAPb(I_{0.88}Br_{0.12})_3$, 3. $MAPb(I_{0.74}Br_{0.26})_3$, 4. $MAPb(I_{0.58}Br_{0.42})_3$, 5. $MAPb(I_{0.41}Br_{0.59})_3$, 6. $MAPb(I_{0.28}Br_{0.72})_3$, and 7. $MAPb(I_{0.05}Br_{0.95})_3$.

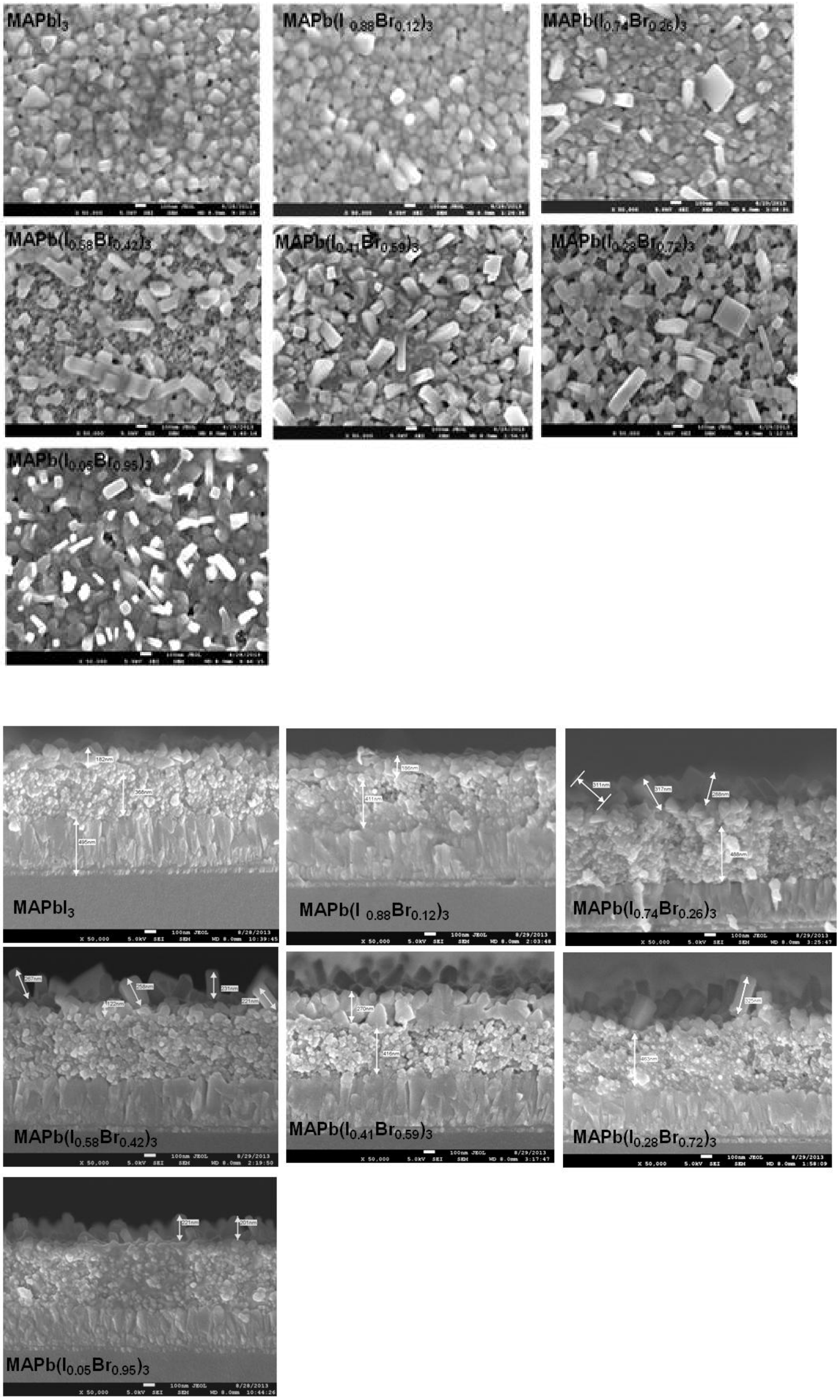

Fig. S4: Field emission microscopic (FESEM) images of the mixed halide perovskite films with different halide mixtures top & cross sectional view.