Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Influence of halide precursor type and its composition on the electronic properties of vacuum deposited perovskite films†

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Table S1. Elemental stoichiometry of the perovskite films obtained by XPS.

The XPS intensities are compensated by relative atomic sensitivity factors (RASFs) which are obtained by MAI and PbX_2. (RASF of Pb 4*f* 8.329, C 1*s* 0.296, N 1*s* 0.447, I $3d_{5/2}$ 7.000, Cl 2*p* 0.705, and Br 3*d* 1.080)

Deposition ratio	PbI_2 : MAI				$PbCl_2$: MAI				$PbBr_2$: MAI			
Element of perovskite	1 : 1	1 : 2	1 : 3	1 : 4	1 : 1	1 : 2	1 : 3	1 : 4	1 : 1	1 : 2	1 : 3	1 : 4
Pb	0.20	0.11	0.10	0.08	0.23	0.13	0.10	0.09	0.28	0.23	0.13	0.13
C	0.10	0.19	0.20	0.24	0.07	0.18	0.22	0.25	0.06	0.12	0.23	0.21
N	0.13	0.23	0.20	0.23	0.04	0.20	0.22	0.21	0.06	0.12	0.22	0.20
I	0.57	0.47	0.50	0.45	0.66	0.49	0.46	0.45	0.07	0.12	0.20	0.29
Br or Cl	none				<0.01 (less than 1%)				0.53	0.41	0.22	0.17
Ratio of C/(I+Br)	0.18	0.40	0.40	0.53	0.11	0.37	0.48	0.56	0.10	0.23	0.55	0.46
Excess MA^+ (C-Pb/Pb)	-0.50	0.73	1.00	2.00	-0.70	0.38	1.20	1.78	-0.79	-0.48	0.24	1.62

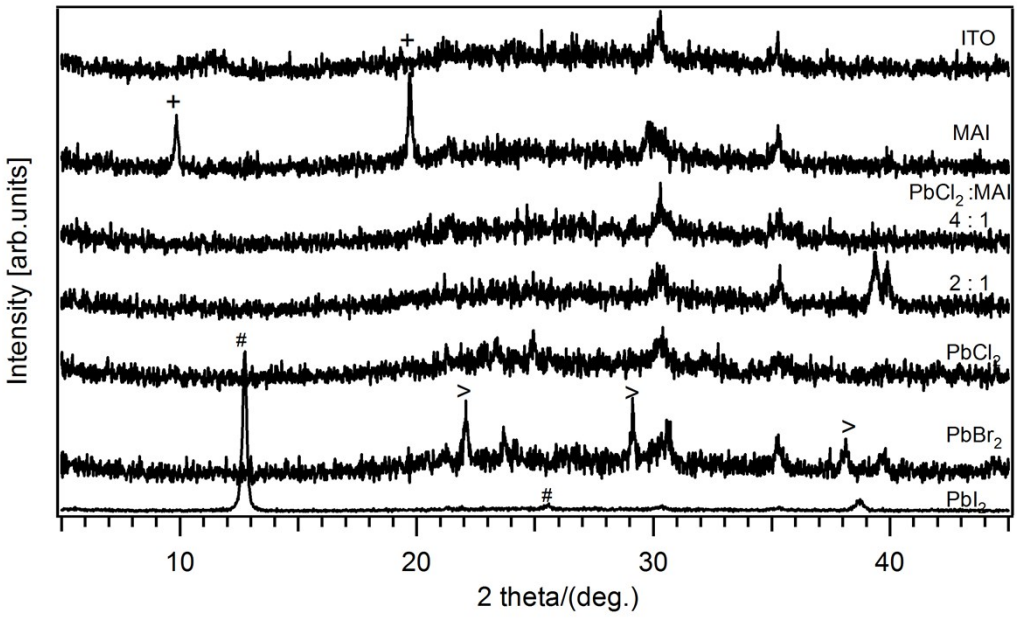

Fig. S1 XRD spectra for ITO, MAI, $MAPb(I_{1-y}Cl_y)_3$ formed under $PbCl_2$ rich condition, $PbCl_2$, $PbBr_2$, and PbI_2 films, respectively. Diffraction patterns assigned by #: PbI_2, +: MAI, >: $PbBr_2$.

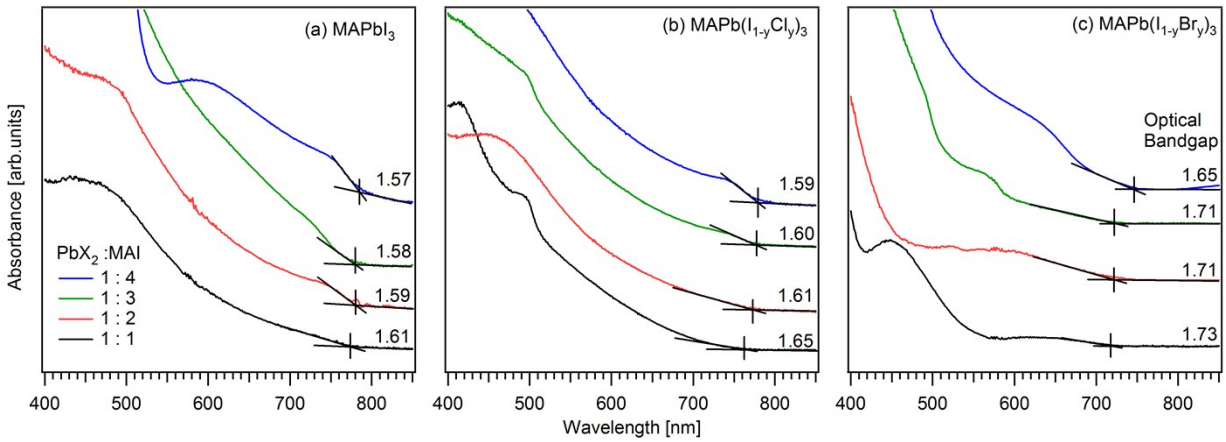

Fig. S2 UV-Vis absorption spectra of (a) $MAPbI_3$, (b) $MAPb(I_{1-y}Cl_y)_3$, and (c) $MAPb(I_{1-y}Br_y)_3$. From the bottom of each figure, precursor deposition ratio is varied from 1:1 to 1:4, respectively. Vertical bars indicate the absorption onsets and their corresponding values are optical bandgap (eV) of those materials: bandgap (eV) = 1240/cut-off wavelength (nm).

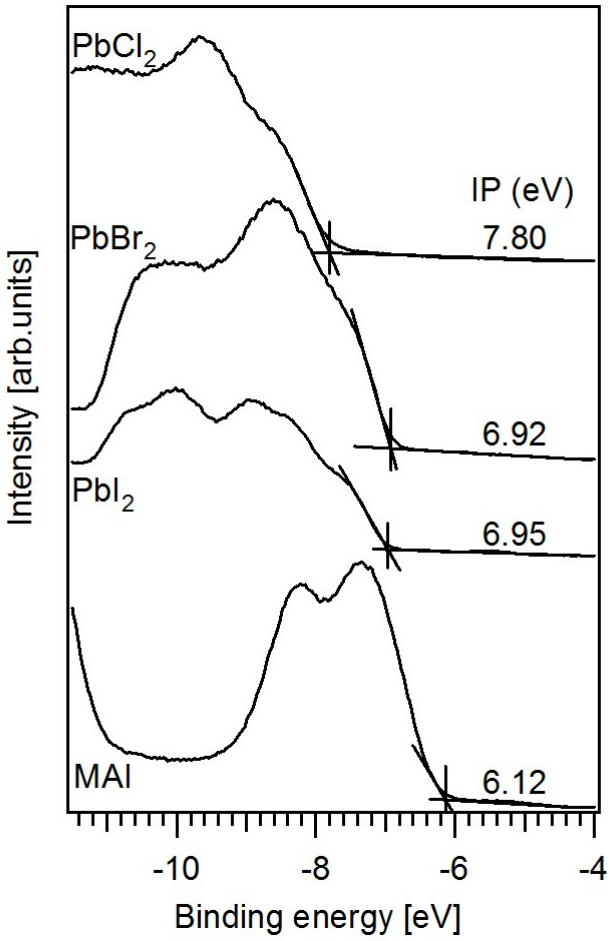

Fig. S3 UPS valence band spectra for pristine MAI, PbI_2, $PbBr_2$, and $PbCl_2$ from the bottom of the figure, respectively. Vertical bars indicate ionization potentials (IPs) of those materials.

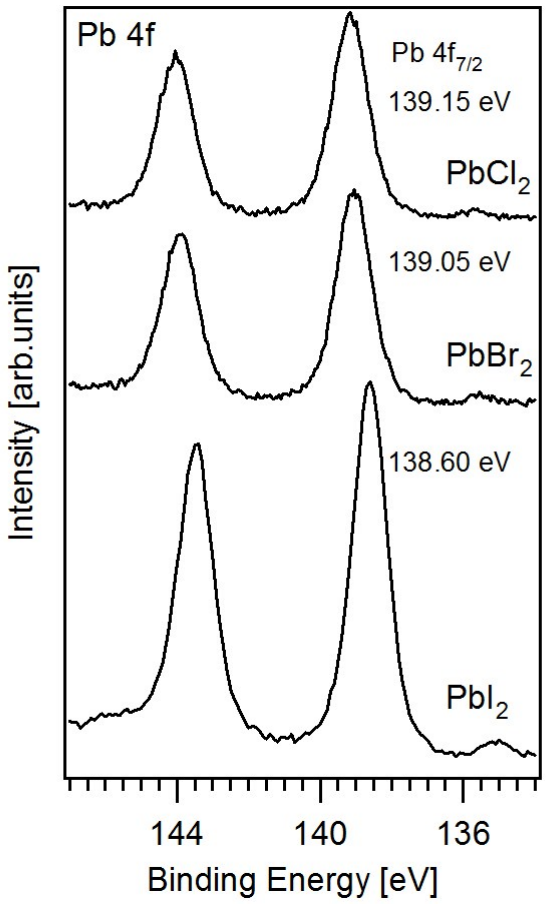

Fig. S4 Pb 4f core level spectra of lead halide precursors used for the perovskite formation. Each Pb $4f_{7/2}$ binding energy is noted.

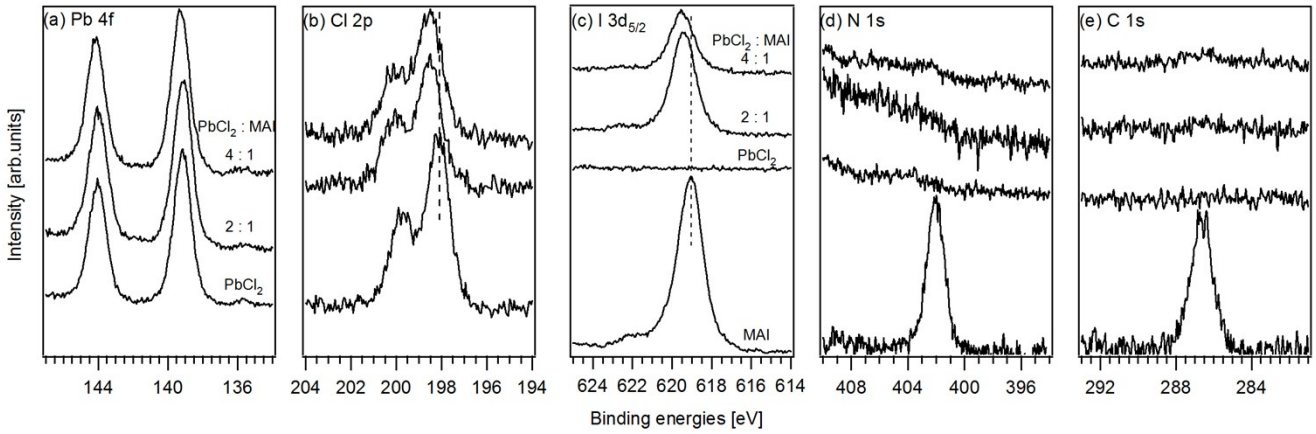

Fig. S5 XPS core level spectra for $MAPb(I_{1-y}Cl_y)_3$ deposited under $PbCl_2$ rich condition (4:1, and 2:1), $PbCl_2$, and MAI films.

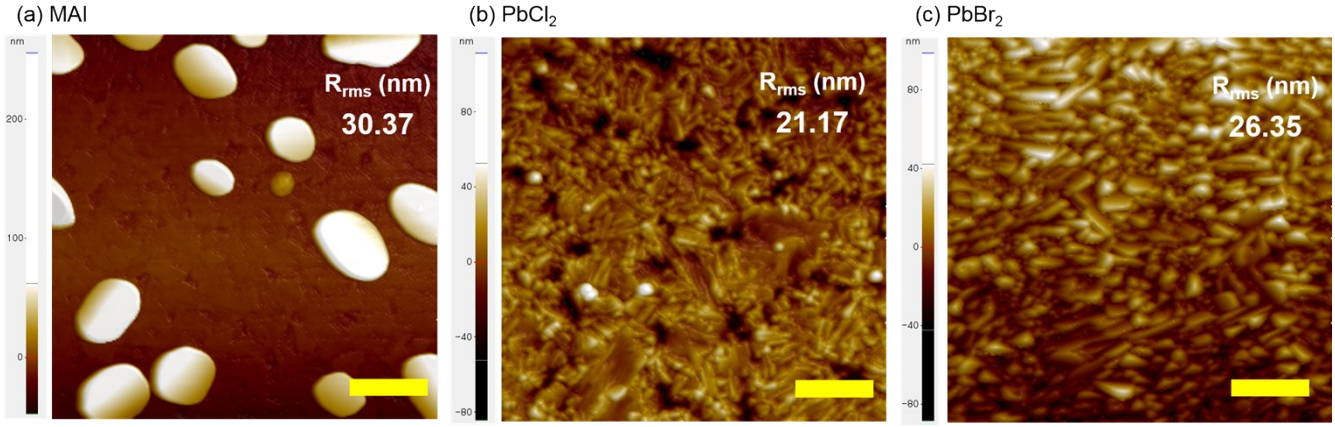

Fig. S6 AFM images of precursor-only films. (a) MAI, (b) $PbCl_2$, and (c) $PbBr_2$. Yellow bar indicates 1 µm.