Electronic Supplementary Information (ESI) for

Formation and evolution of the unexpected PbI_2 phase at interface during the growth of evaporated perovskite films

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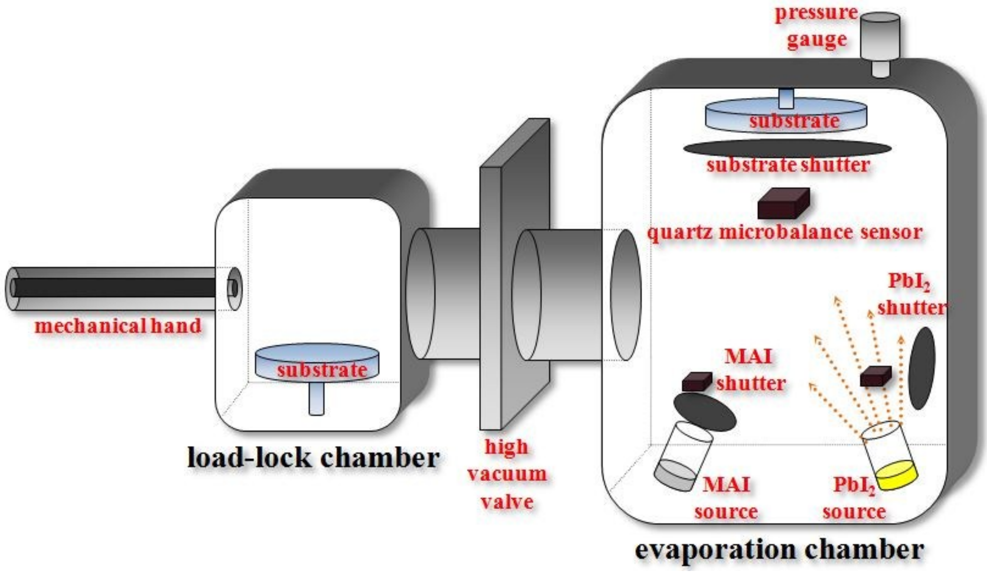

Fig. S1 Schematic diagram of dual-source evaporation system.

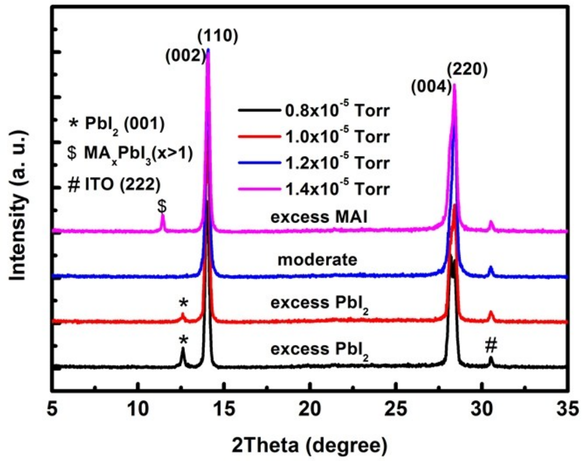

Fig. S2 X-ray diffraction patterns of perovskite films deposited under different MAI partial pressure.

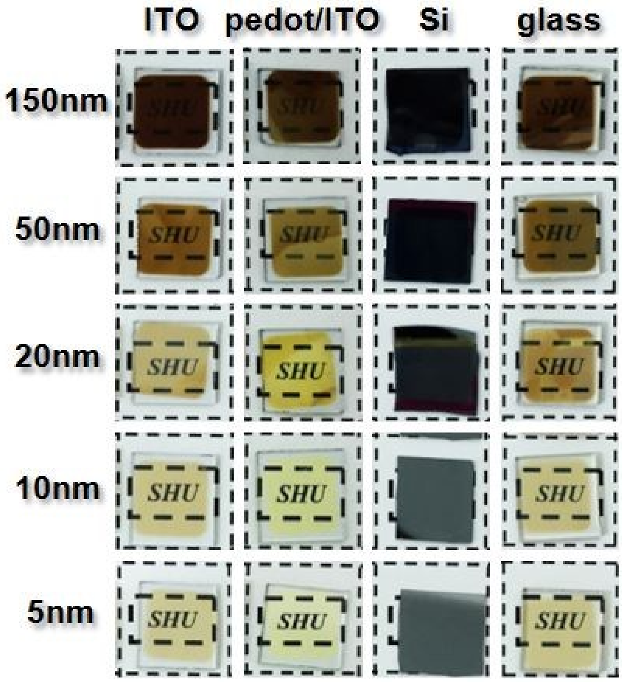

Fig. S3 Images of the perovskite films with different thickness deposited on different substrates.

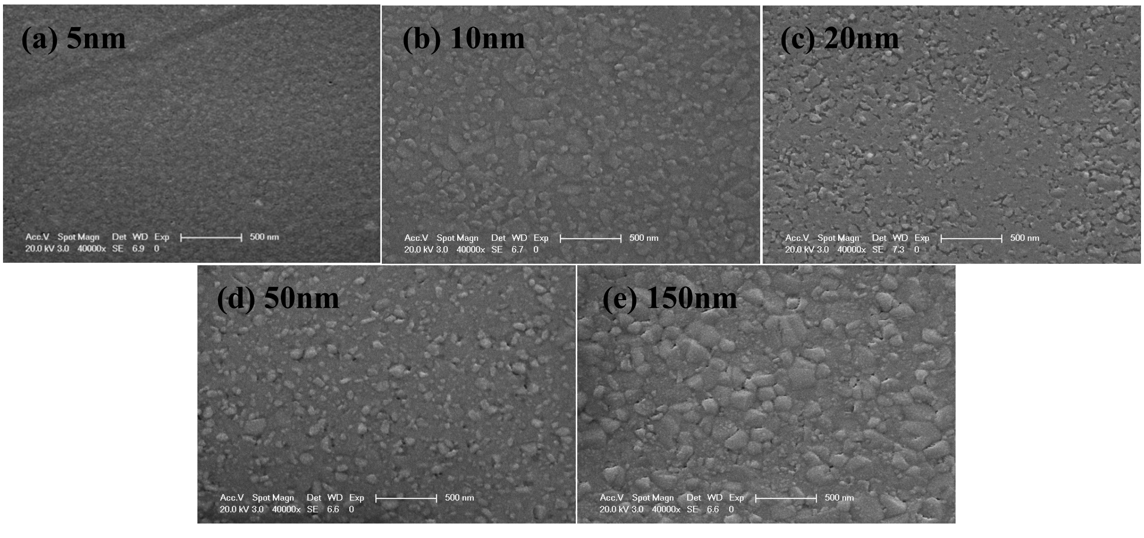

Fig. S4 Surface SEM images of perovskite films with different thickness deposited on ITO substrates. The scale bar is 500 nm.

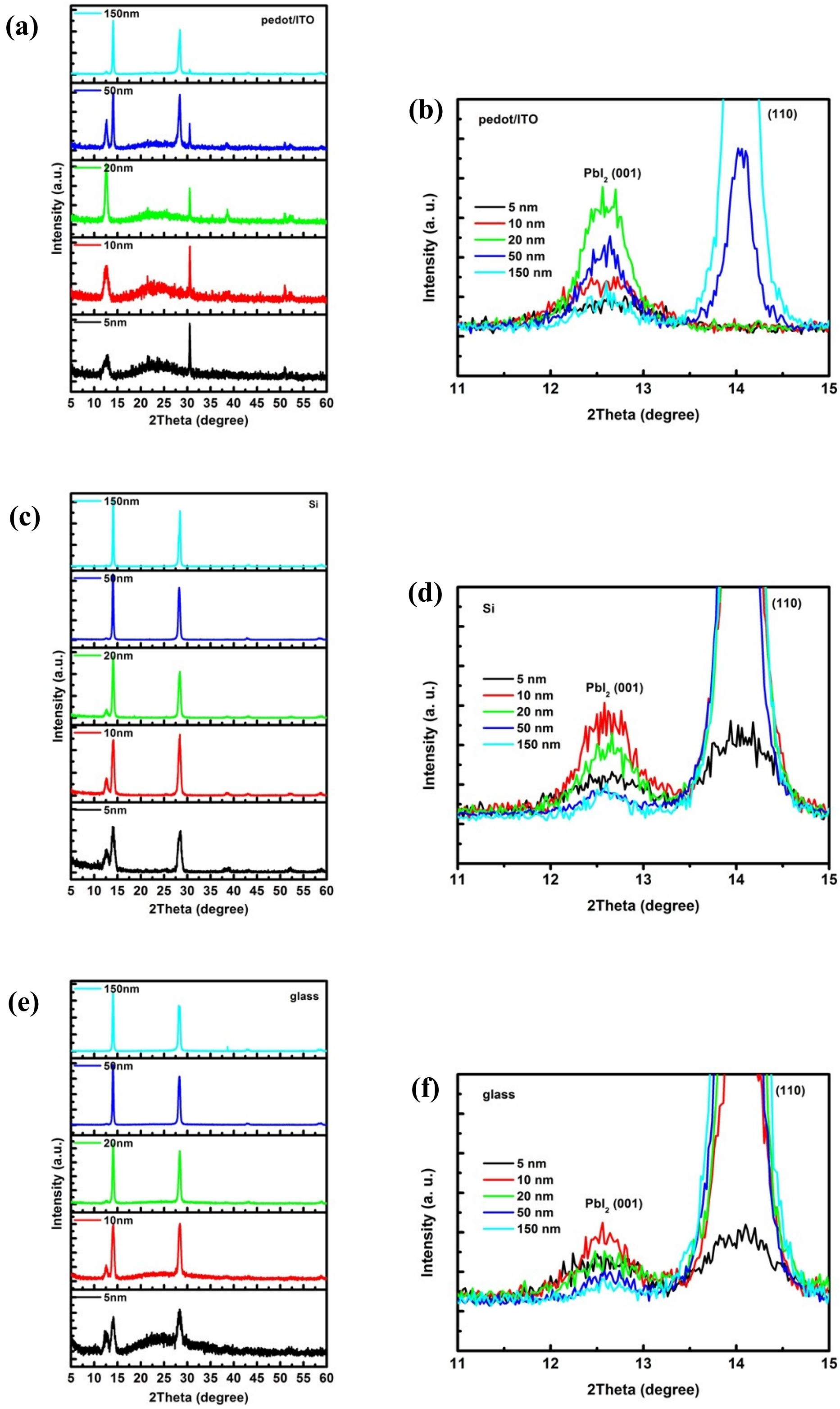

Fig. S5 X-ray diffraction patterns of perovskite films with different thickness deposited on (a) pedot/ITO, (c) Si and (e) glass substrates. X-ray diffraction patterns of the peak of PbI_2 (001) planes in perovskite films with different thickness deposited on (b) pedot/ITO, (d) Si and (f) glass substrates.

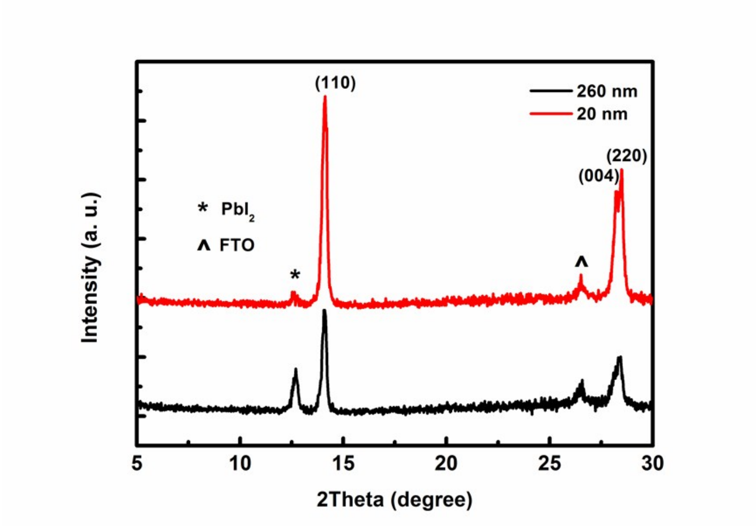

Fig. S6 X-ray diffraction patterns of perovskite films with thickness of 20 nm and 260 nm deposited on FTO/TiO_2/PCBM substrates.

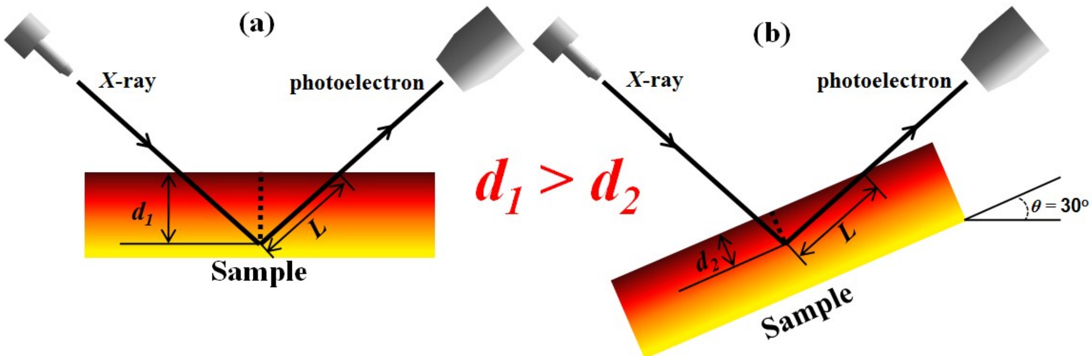

Fig. S7 The principle diagrams of XPS measurements under two different take-off angles. (a) normal take-off angle. (b) 30° take-off angle.

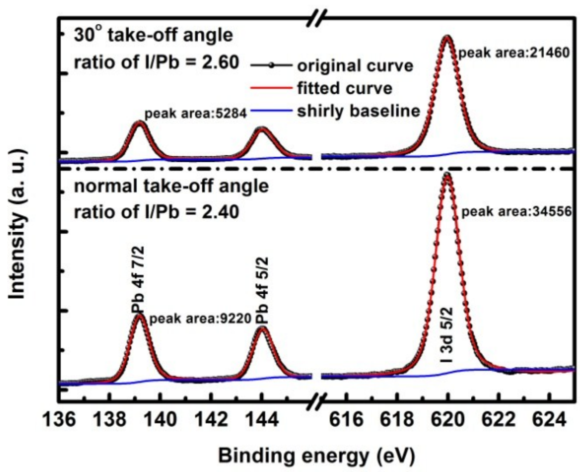

Fig. S8 High resolution XPS core level spectra of Pb 4f and I 3d 5/2 of the 10 nm-thick perovskite films under different take-off angle measurements. The bottom is under normal take-off angle and the top is under 30° take-off angle.

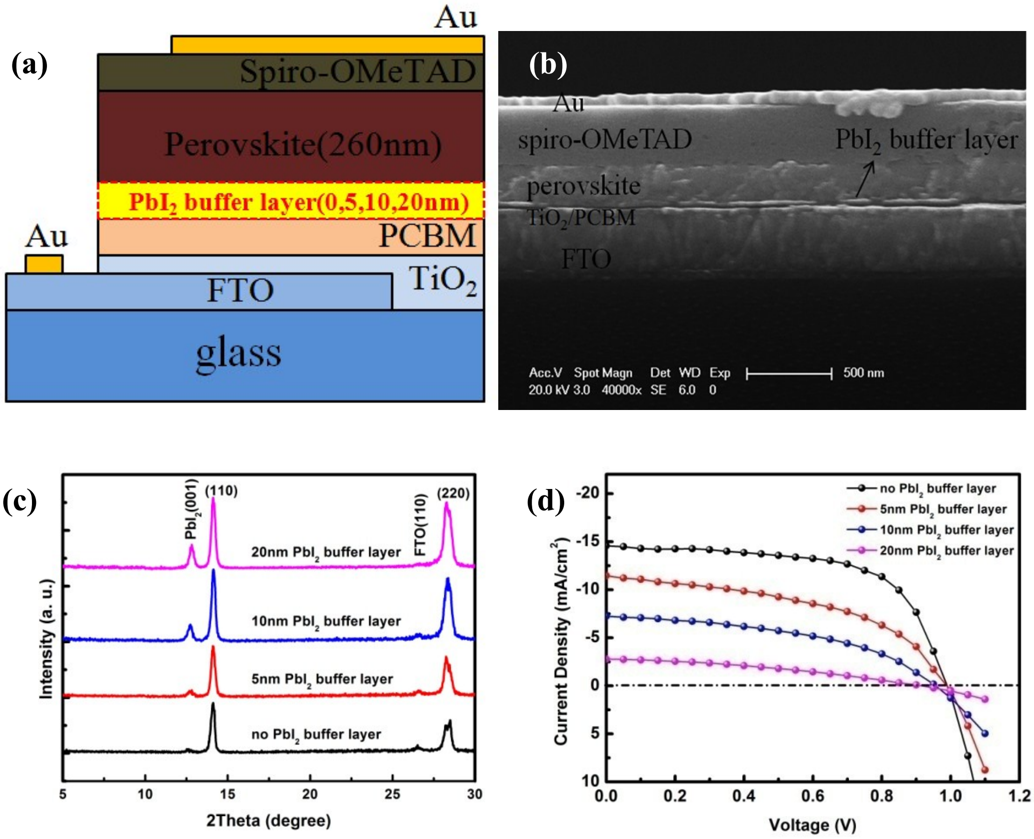

Fig. S9 (a) Device structure of designed perovskite solar cells (PSCs) to study the effect of PbI_2 phase at interface on device performance, a deliberately grown PbI_2 buffer layer with different thickness of 0, 5, 10, 20 nm was deposited on the FTO/TiO_2/PCBM substrates. (b) Cross-sectional SEM image of PSCs with a 20 nm-thick PbI_2 buffer layer. (c) XRD patterns of the perovskite films deposited on PbI_2 buffer layer with different thickness. (d) Current-density/voltage curves of the corresponding PSCs.

Table S1 Performance of most vacuum-based PSCs and solution-based PSCs with similar structure and sourse material to vacuum-based PSCs, which can be used to compare.

perovskite processing		source material	HTL	ETL	V_{OC} (V)	J_{SC} (mA/cm²)	FF (%)	PCE (%)	ref
vacuum	solution								
coevaporation	/	PbI_2+MAI	PEDOT:PSS/PolyTPD	PCBM	1.05	16.12	67	**12.04**	1
coevaporation	/	PbI_2+MAI	PEDOT:PSS/PolyTPD	PCBM	1.07	18.8	63	**12.7**	2
coevaporation	/	PbI_2+MAI	PEDOT:PSS/PolyTPD	PCBM	1.05	15.88	46	**7.73**	3
coevaporation	/	PbI_2+MAI	PEDOT:PSS/PolyTPD	PCBM	1.04	17.6	62	**11.4**	4
coevaporation		PbI_2+MAI	PEDOT:PSS/PCDTBT	PCBM/ LiF	1.05	21.9	72	**16.5**	5
coevaporation	/	PbI_2+MAI	spiro-MeOTAD	TiO_2	1.1	18	70	**13**	6
coevaporation	/	$PbCl_2$+MAI	PEDOT:PSS	PCBM	0.97	17.3	63	**10.5**	7
coevaporation	/	$PbCl_2$+MAI	spiro-MeOTAD	C60	0.78	14.4	69	**7.8**	8
coevaporation	/	$PbCl_2$+MAI	NiO	PCBM	0.79	14.2	65	**7.26**	9
coevaporation	/	$PbCl_2$+MAI	spiro-MeOTAD	TiO_2	1.07	21.5	68	**15.4**	10
hybrid deposition	/	$PbCl_2$+MAI	spiro-MeOTAD	TiO_2	1.09	17	54	**9.9**	11
hybrid deposition	/	$PbCl_2$+MAI	spiro-MeOTAD	TiO_2	1.01	12.82	66.	**8.64**	12
/	one-step	$PbCl_2$+MAI	spiro-MeOTAD	TiO_2	1.13	22.75	75	**19.3**	13
/	one-step (moisture)	$PbCl_2$+MAI	PEDOT:PSS	PCBM/ PFN	1.05	20.3	80.2	**17.1**	14
/	one-step	PbI_2+MAI	PEDOT:PSS	PCBM	1.1	20.9	79	**18.2**	15
/	one-step (hot-casting)	PbI_2+MAI	PEDOT:PSS	PCBM	0.94	22.4	83	**17.4**	16
/	one-step	PbI_2+MAI	PEDOT:PSS	PCBM	0.89	18.85	80	**13.37**	17
/	solvent engineering	PbI_2+MAI	NiO	PCBM	1.06	20.2	81.3	**17.3**	18

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