

Chloride-Improved Crystallization in Sequentially Vacuum-Deposited Perovskites for p-i-n Perovskite Solar Cells

Supporting information

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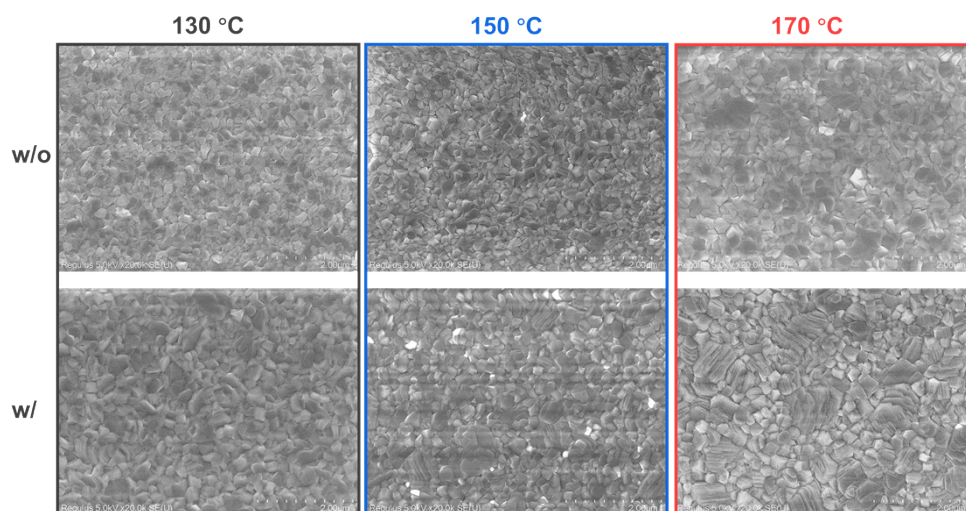


Figure S1 Top-view SEM of samples w/o and w/ PbCl₂ annealed at different temperatures.

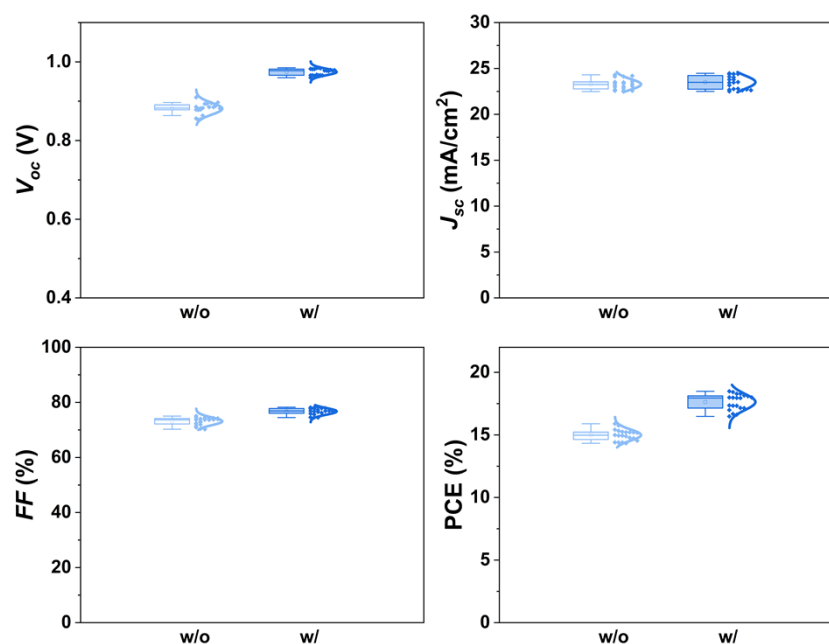


Figure S2 Statistical distribution of the photovoltaic parameters (V_{oc} , J_{sc} , FF , and PCE) of solar cells w/ and w/o

PbCl₂. Each condition includes 20 solar cells. All the samples were annealed with 150°C for 20 mins.

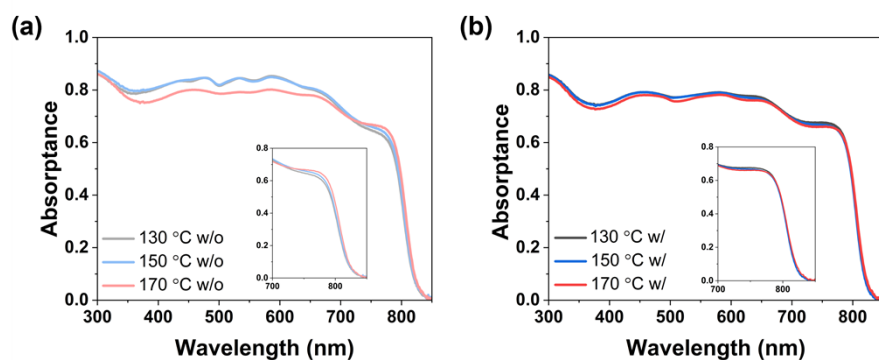


Figure S3 Absorbance spectra of samples (a) w/o and (b) w/ PbCl₂ annealed at different temperatures. The inset figures zoom-in the spectra in the wavelength range of 700-850 nm.

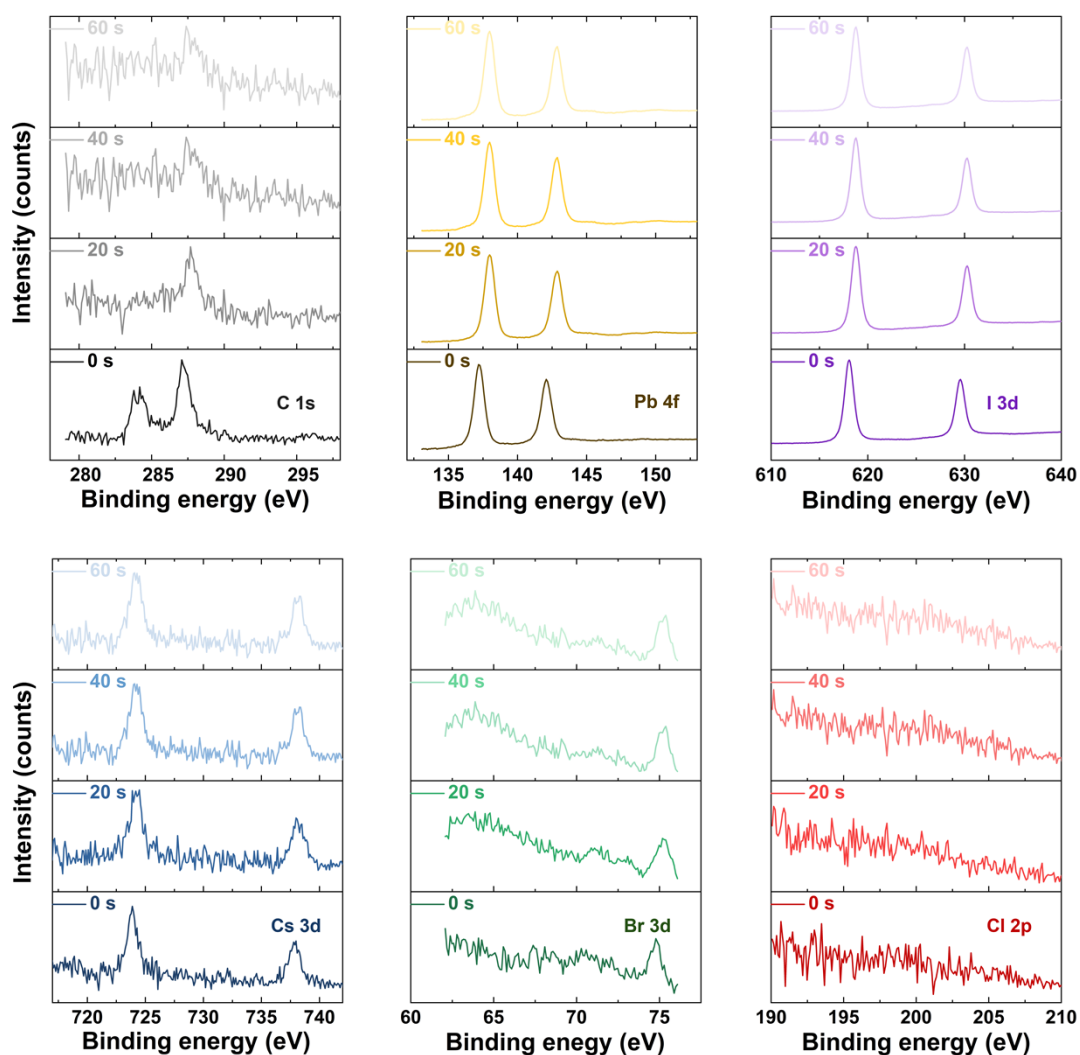


Figure S4 Fine XPS images of C 1s, Pb 4f, I 3d, Cs 3d, Br 3d, and Cl 2p peaks with different etching time (in-depth).

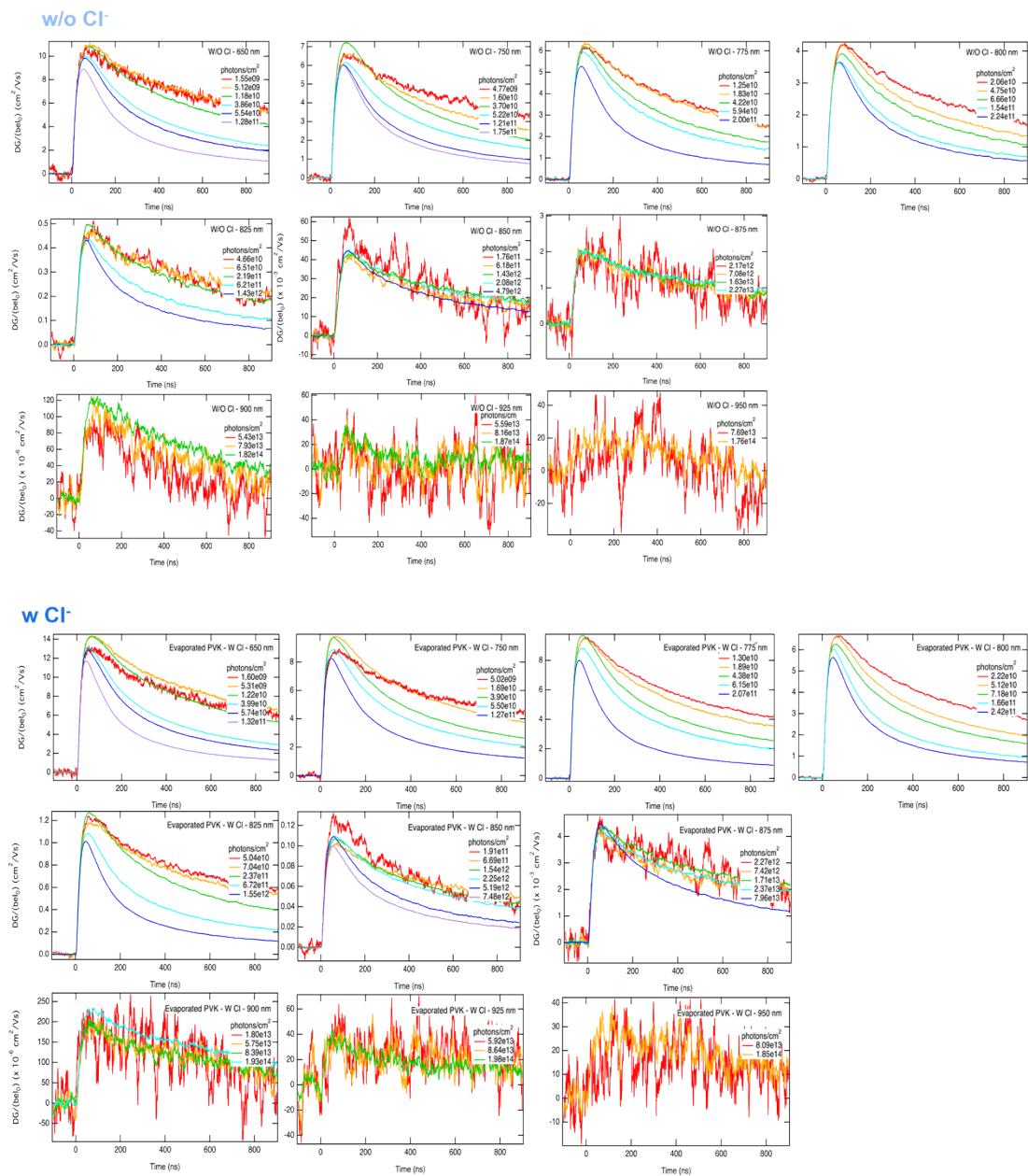


Figure S5 TRMC plots of both w/o and w/ PbCl_2 samples measured with different excitation wavelength and photon intensity.

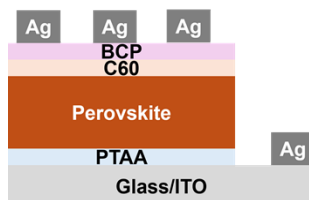


Figure S6 Schematic structure of the solar cell.

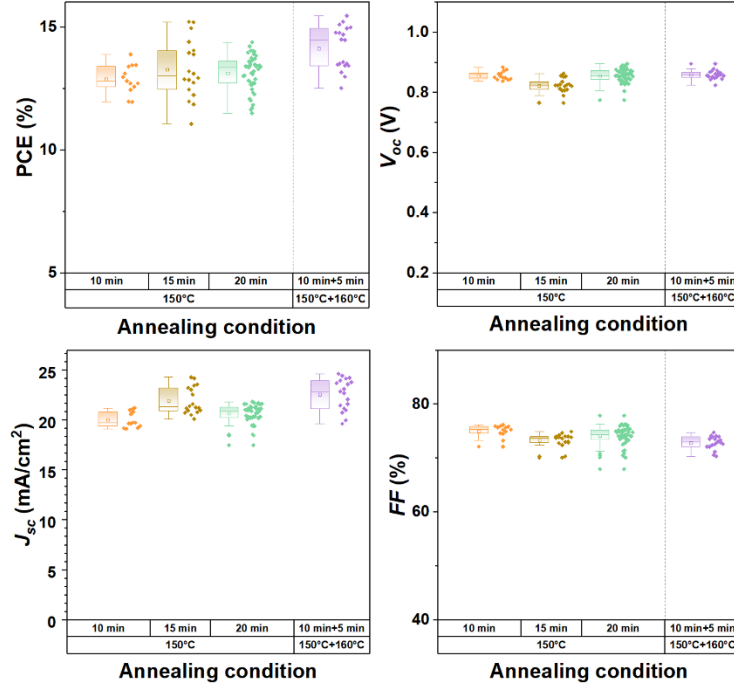


Figure S7 Statistical distribution of PSCs w/o PbCl₂ based on different annealing temperature and time. The purple distribution boxes mean that the related samples were annealed at 150 °C for 10 mins and afterwards at 160 °C for 5 mins.

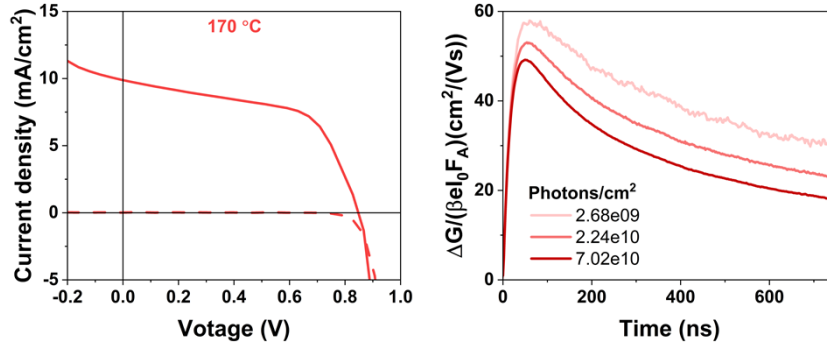


Figure S8 J - V curve of the cell and TRMC of the PVK films with 170 °C annealing for 10 mins.

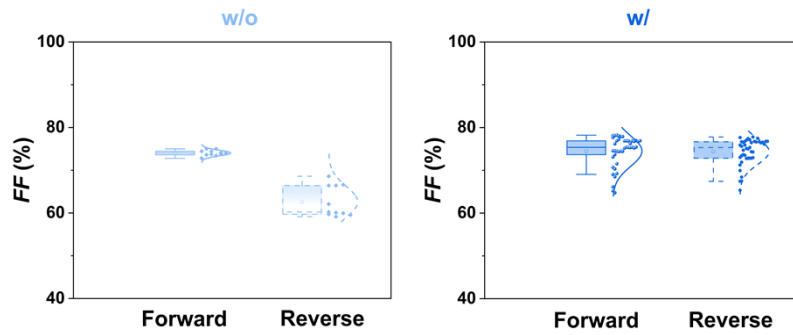


Figure S9 Statistical distribution of FF in forward and reverse scan modes of the samples (left) w/o and (right) w/ PbCl₂.



Figure S10 Photo of degraded samples (quartz/PVK) state in ambient air.

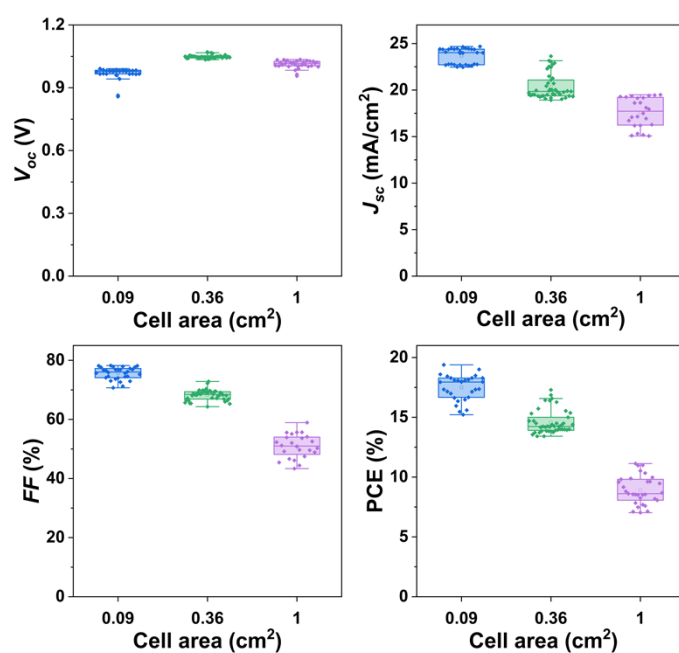


Figure S11 Distribution of external parameters (PCE , V_{oc} , J_{sc} , and FF) of PSCs as a function of cell area based on annealing condition of $150\text{ }^{\circ}\text{C}$ and 10 mins. Data of more than 20 cells are collected for each variation. The cells of 0.09 cm^2 and 0.36 cm^2 reported here are prepared in the same batch, while the 1 cm^2 cells are prepared in another batch with the same deposition parameters.

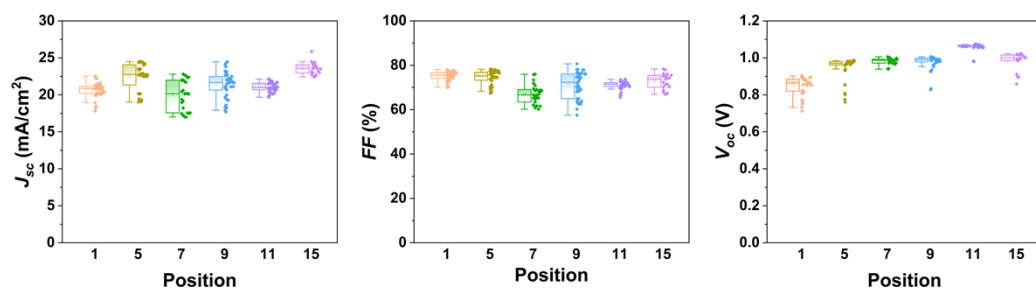


Figure S12 Statistical distribution of the V_{oc} , J_{sc} , and FF based on the samples at different position shown in Figure 5d.

Table S1 Processing parameters for different precursors.

Samples	Precursors			
	PbI ₂	FAI	CsBr	PbCl ₂
Temperature (°C)	202-236	160-180	310-330	150-170
Rate (Å/s)	1.8-2.0	1.8-2.4	0.08-0.10	0.08-0.15
Vacuum (mbar)	10 ⁻⁶ -10 ⁻⁷	10 ⁻⁶ -10 ⁻⁷	10 ⁻⁶ -10 ⁻⁷	10 ⁻⁶ -10 ⁻⁷

Table S2 Peak position of (100) for samples w/o and w/PbCl₂ annealed at different temperature from **Figure 1b**.

Annealing temperature	w/o PbCl ₂	w/ PbCl ₂
130	13.927	13.889
150	13.891	13.885
170	13.878	13.871

Table S3 Grain size statistics obtained from top-view SEM and crystallite size calculated using the Scherrer equation.

Sample	Top-view SEM grain size (nm)	D (nm)
w/ 130 °C	157	139.6
w/ 150 °C	225	170.3
w/ 170 °C	281	209.5

Table S4 Summary of best p-i-n PSCs based on sequential and co-thermally deposited absorber layer. PCE together with deposition methods, cell structure, and device parameters are reported.

Deposition approach	Cell Structure	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref
Sequential deposition	ITO/2T-NATA/MAPbI ₃ /C60/BCP/Ag	1.06	22.42	80.9	19.23	¹
	ITO/PTAA/CsPbI ₃ /PCBM/Al	1	15.5	66.0	10.2	²
	ITO/PTAA/MAPbI ₃ /C60/BCP/Agc	1.09	23.11	77.0	19.4	³
Co-deposition	ITO/TaTm:F6-TCNNQ/TaTm/MAPbI ₃ /C60/C60:PhIm/Ag	1.14	22.08	80.5	20.3	⁴
	TCO/MoO ₃ /TaTm/MAPbI ₃ /C60/BCP/Ag	1.077	21.7	82.5	19.3	⁵

ITO/NiO _x /MAPbI ₃ /C60/BCP/(Cu or Au)	1.03	20.6	79.0	16.8	6
ITO/McO-2PACz/MAPbI ₃ /C60/BCP/Cu	1.15	22.43	79.6	20.5	7
ITO/PTAA/FA _{1-y} CsyPb(I _{1-x} Cl _x) ₃ /C60/BCP/Ag	1.06	23	79.0	19.3	8
ITO/CuPc/FA _{0.83} Cs _{0.17} PbI ₃ /C60/BCP/Au	0.93	21.1	72.0	13.9	9

Table S5 The photovoltaic parameters and hysteresis index for the PSCs shown in **Figure 4a-c**.

Cell area (cm ²)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Hysteresis index
0.09_Foward	1.001	23.75	78.50	18.56	-0.05
0.09_Reverse	0.999	22.95	76.74	17.60	
0.36_Foward	1.07	23.34	68.32	17.06	-0.04
0.36_Reverse	1.07	22.75	67.14	16.35	

Reference

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