

Supporting Information

Vapor Transport Deposition of Methylammonium Iodide for Perovskite Solar Cells

Florent Sahli,^{†} Nathanaël Miaz,^{†‡} Niccolò Salsi,[†] Cédric Bucher,[†] Aymeric Schaffliützel,[†] Quentin Guesnay,[†] Léo Duchêne,[§] Björn Niesen,[†] Christophe Ballif,^{†‡} Quentin Jeangros.^{†*}*

[†] Photovoltaics and Thin-Film Electronics Laboratory, Institute of Microengineering (IMT), Ecole Polytechnique Fédérale de Lausanne (EPFL), Rue de la Maladière 71b, 2002 Neuchâtel, Switzerland

[‡] CSEM, PV-Center, Jaquet-Droz 1, 2002 Neuchâtel, Switzerland

[§] Laboratory Materials for Energy Conversion, Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

*F.S.: email, florent.sahli@alumni.epfl.ch.

*Q.J.: email, quentin.jeangros@epfl.ch.

KEYWORDS: organohalide deposition, chemical vapor deposition, organic vapor phase deposition, organic-inorganic perovskite, large-scale vapor deposition.

Vapor transport deposition setup

The vapor transport deposition setup consists in an evaporation unit (containing the crucible and its heating system, a gas inlet and outlet, and a thermocouple attached to the crucible) and the deposition chamber (featuring a temperature-controlled substrate holder and a showerhead at the gas inlet). The evaporator and chamber are connected by a gas transport line. The exhaust of the chamber is connected to a dry pump via a butterfly valve, which enables regulating the pressure of the system (from 3.7 to 12 mbar). In addition, a cold trap is placed before the butterfly valve to condense any residual organic vapors to protect the pump. The different components of the system are described briefly below.

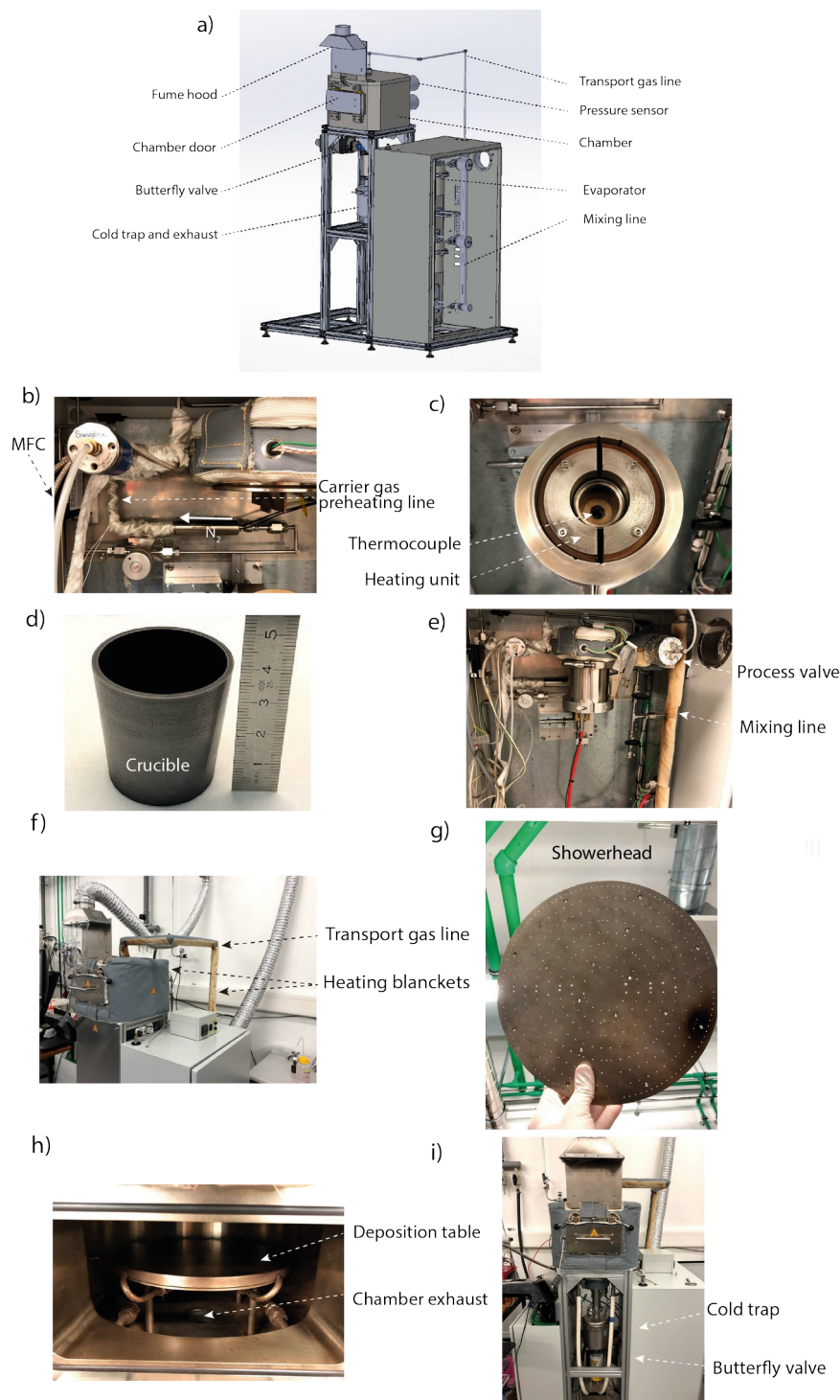


Figure S1: a) Overview of the setup. The CAD design was done using Solidworks, b) picture of the carrier gas preheating unit upstream of the evaporator, c) the evaporation unit, d) picture of the graphite crucible, e) overall picture of the carrier gas preheating unit, evaporator and mixing line, f) a side-view of the system with the gas transport line, g) picture of the showerhead, h) a view of the chamber with the deposition table and exhaust, i) the front of the VTD system with the cold trap and butterfly valve.

Carrier gas inlet: N₂ is used as a carrier gas to drive the evaporated organic vapors from the evaporator into the deposition chamber. A mass flow controller (MFC) regulates the carrier gas flow. A carrier gas preheating unit consisting in a tubular heating coil and thermal heating blankets enable modifying the temperature of the carrier gas upstream of the evaporator (up to a set point of 150 °C, Figures S1b and S4).

Evaporator: evaporation is carried out in a graphite crucible containing ~1 g of MAI. The temperature of the crucible is continuously monitored by a thermocouple directly in contact with the bottom of the crucible. The crucible heating unit consists in a cylindrical stainless steel tube that surrounds the crucible. The heating coil is placed inside the stainless steel tube. The upper part of the evaporator is enveloped in heating blankets to prevent organohalide condensation (Figure S1c,e).

Gas transport line: the pipes connecting the evaporator to the chamber can be heated up to 200 °C thanks to a heating blanket (Figure S1f). In addition to the gas transport line from the evaporator to the chamber, an additional gas line is added at the outlet of the evaporator unit. This mixing line is used to increase the carrier gas flow rate within the gas transport line during the cooling of the source to prevent organohalide condensation. This line also enables us to dilute the organohalide flow and to increase the working pressure of the chamber.

Chamber: organohalide vapors carried by N₂ are forced through a showerhead to improve the homogeneity of the deposition (showerhead at 170 °C when chamber walls are at 200 °C, Figure S1g). The temperature of the deposition table (Figure S1h) can be modulated via an oil circuit (from 25 °C to 180 °C, controlled by a thermocouple). The chamber walls can be heated thanks to a heating blanket (from 25 °C to 200 °C). When the blankets are set to 200 °C, the temperature measured on the inner side of the chamber reaches ~170 °C. The temperature of the heating blankets are set to 200 °C throughout this manuscript unless stated otherwise.

Exhaust: the exhaust of the chamber is directly located beneath the deposition table (Figure S1h) and a trap cooled by a water circuit is placed after the chamber to condense the residual organohalides (Figure S1i). A butterfly valve is placed after the cold trap to regulate the pressure of the system. Finally, a dry pump is attached to the system.

Table S1: FTIR main vibrational modes of MAI based on literature data and measured in this work.^{4,41} C-H and N-H bending at 1400-1500 cm⁻¹ could not be identified due to the presence of the H₂O vibration peaks.

Bond	Vibrational mode	From literature Wavenumber (cm ⁻¹)	This work Wavenumber (cm ⁻¹)
N-H ₃	stretching	3080 (asym)//2993 (sym)	3091
	bending	1486 (sym),1563 (as)	- (H ₂ O peaks)
C-H ₃ /N-H ₃	rocking	1252	1244
C-H	stretching	2963 (asym) // 2912 (sym)	2963 (asym)
	bending	1427 (sym), 1463 (asym)	- (H ₂ O peaks)
C-H ₃ /N-H ₃	rocking	912	915
C-N	stretching	990	990

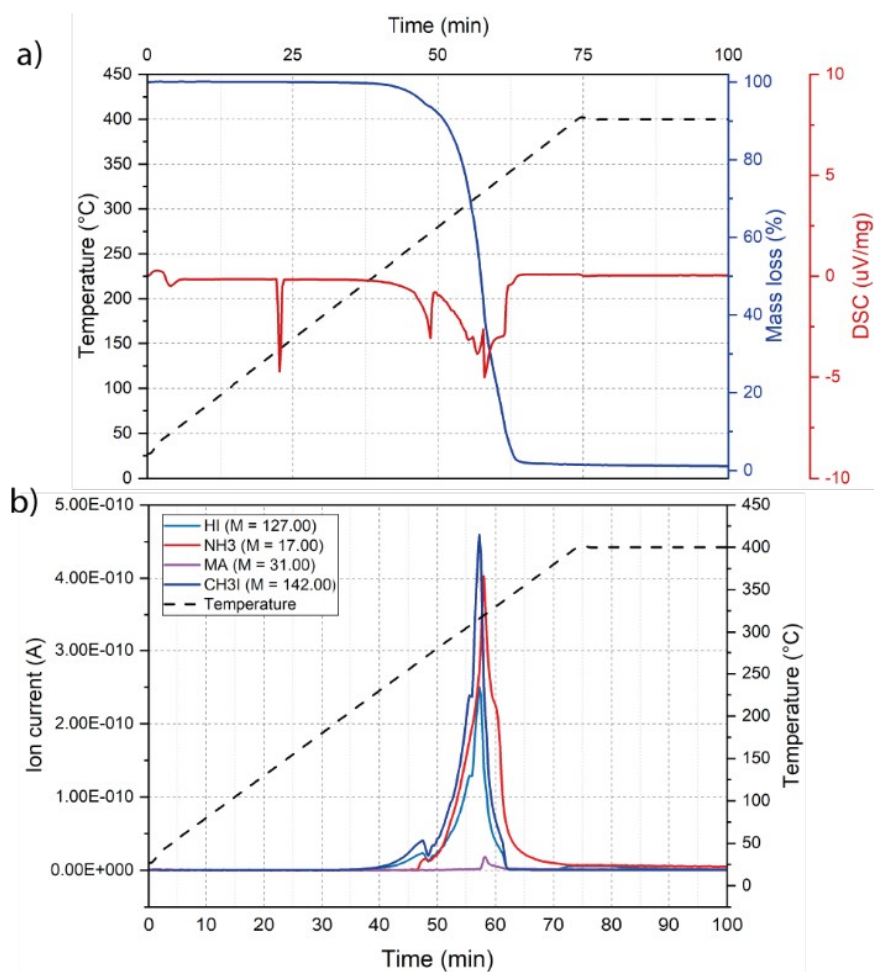


Figure S2: a) TGA and DSC analysis of MAI (25-400 °C), b) mass spectrometry analysis showing the major fragments observed during MAI evaporation (25-400 °C).

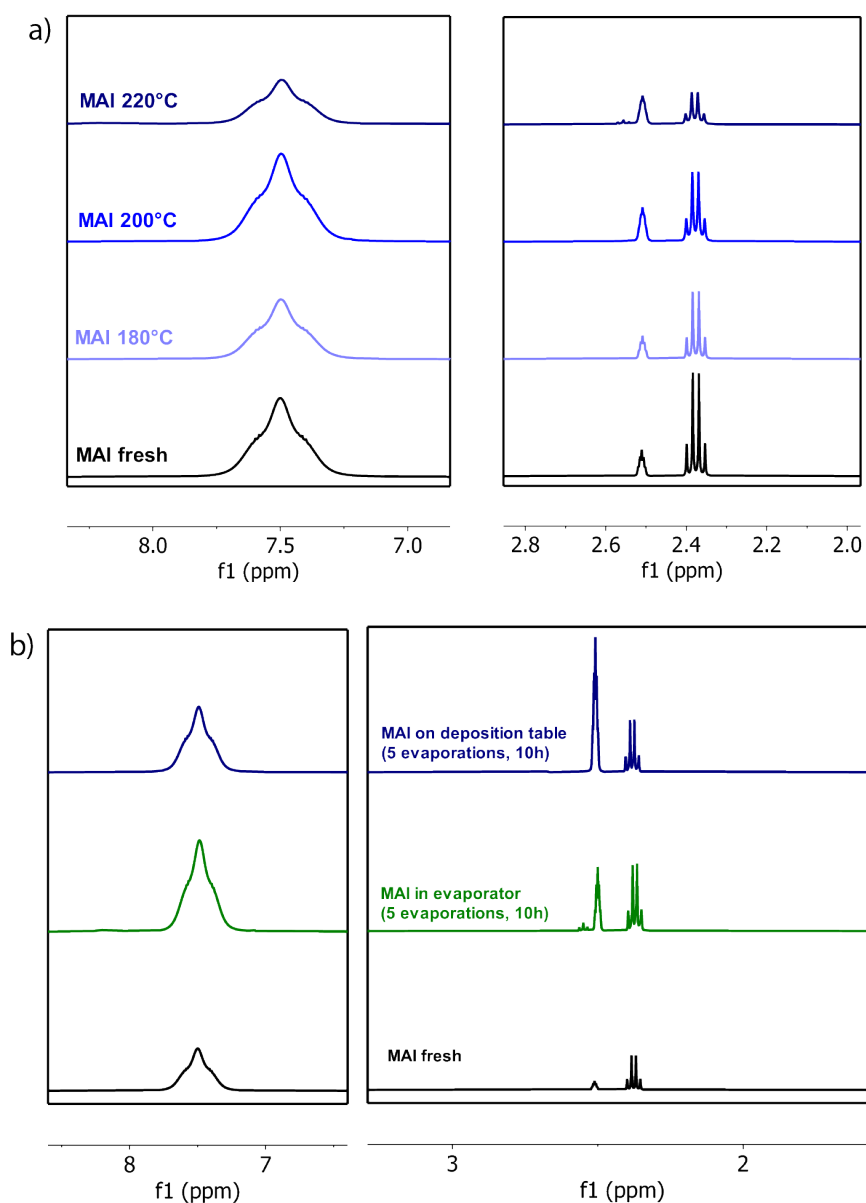


Figure S3: a) Liquid ^1H NMR of the MAI powder remaining in the crucible after a deposition at a carrier gas flow of 800 sccm and a working pressure of 4 mbar for 2 h with different T_{crucible} . A zoom on the NH_3 peak (7.5 ppm) is shown in the left insets, while CH_3 peaks (2.4 ppm, the peak at 2.5 ppm is the $\text{DMSO}-d_6$ peak) are shown in the right insets, b) Liquid ^1H NMR of the fresh MAI powder, MAI left in the crucible after 5 depositions with a T_{crucible} of 200 °C (carrier gas flow rate = 800 sccm, working pressure = 4 mbar, total duration >600 min) and the corresponding MAI deposited on the deposition table.

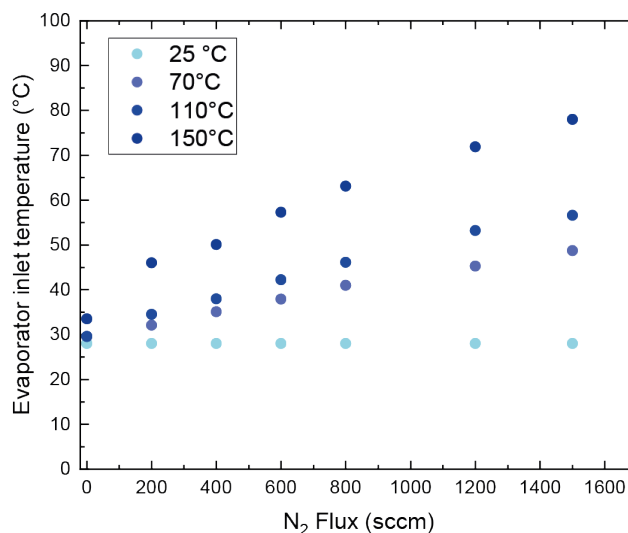


Figure S4: Evaporator inlet temperature as a function of the gas flow rate and temperature set point of the carrier gas preheating blanket ($T_{\text{preheating}}$). Note that these measurements were performed in atmospheric conditions (~ 1 bar), meaning that these values may differ from the operational temperatures (4-12 mbar).

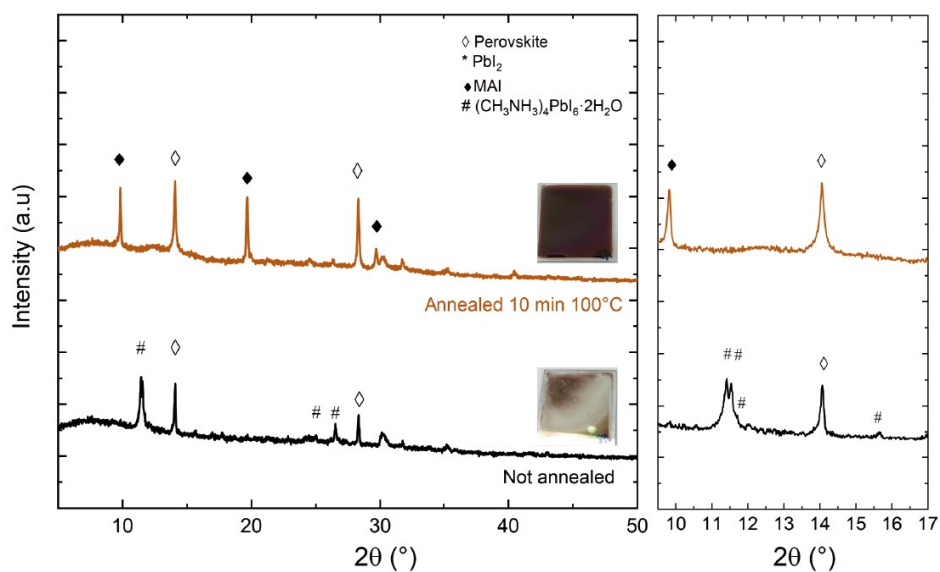


Figure S5: X-ray diffractograms of a PbI_2 layer oversaturated with MAI, leading to the formation of a hydrated $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ phase (bottom curve). Annealing the film for 10 min at 100 °C converts this hydrated phase to a mixture of perovskite and MAI phases (top curve). The inset on the right side provides a magnified view of the low diffraction angle range. Upon annealing, the hydrated film converts within seconds into a perovskite + MAI film, whereas the conversion of the perovskite + MAI film into the hydrated phase occurs at a slower rate (minutes to hours).

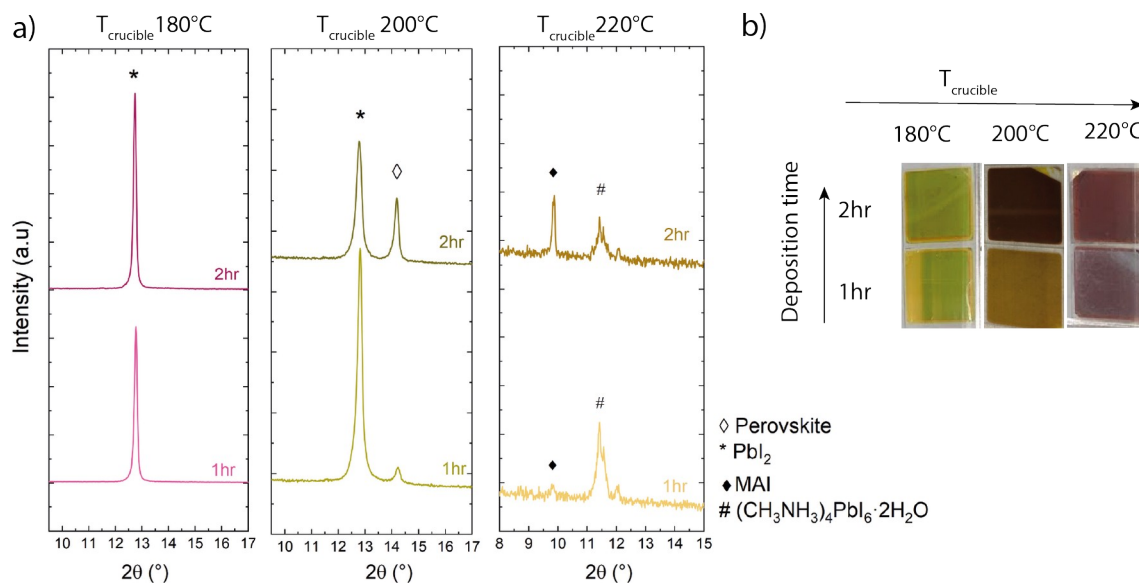


Figure S6: a) X-ray diffractograms of the PbI_2 templates at a $T_{\text{substrate}}$ of 70 °C and exposed to MAI vapors evaporated at different T_{crucible} (180 °C, 200 °C, 220 °C) and for different durations (1 to 2 h), b) pictures of the corresponding perovskite layers (carrier gas flow of 800 sccm, working pressure of 12 mbar).

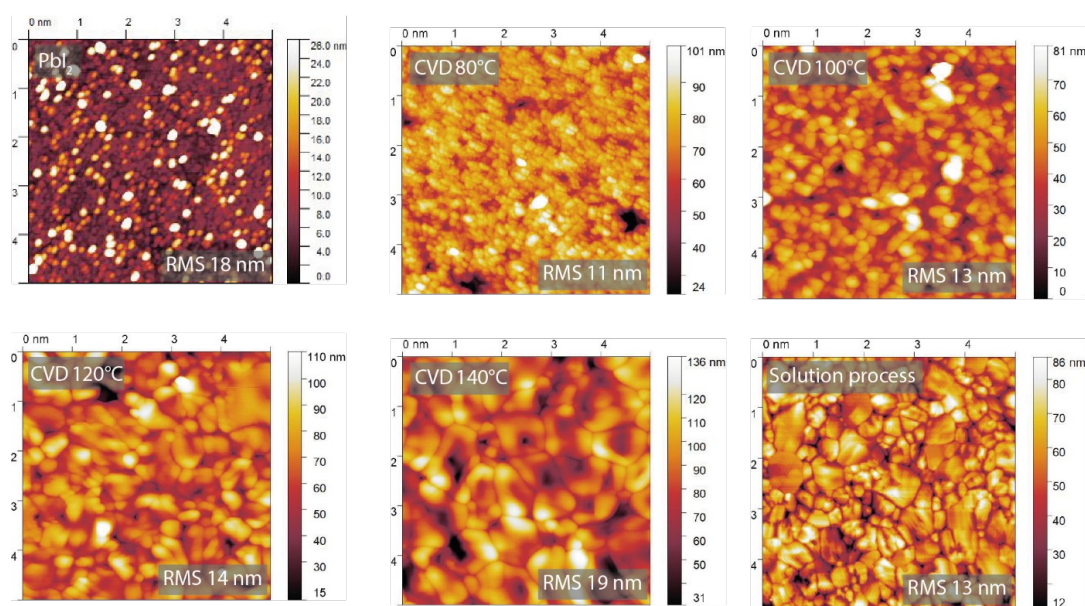


Figure S7: AFM scans of the PbI_2 and perovskite layers deposited by CVD at a $T_{\text{substrate}}$ of 80 °C, 100 °C, 120 °C, 140 °C, respectively. The last inset shows a perovskite layer, which was formed by spin coating MAI on the PbI_2 template and a subsequent annealing step.

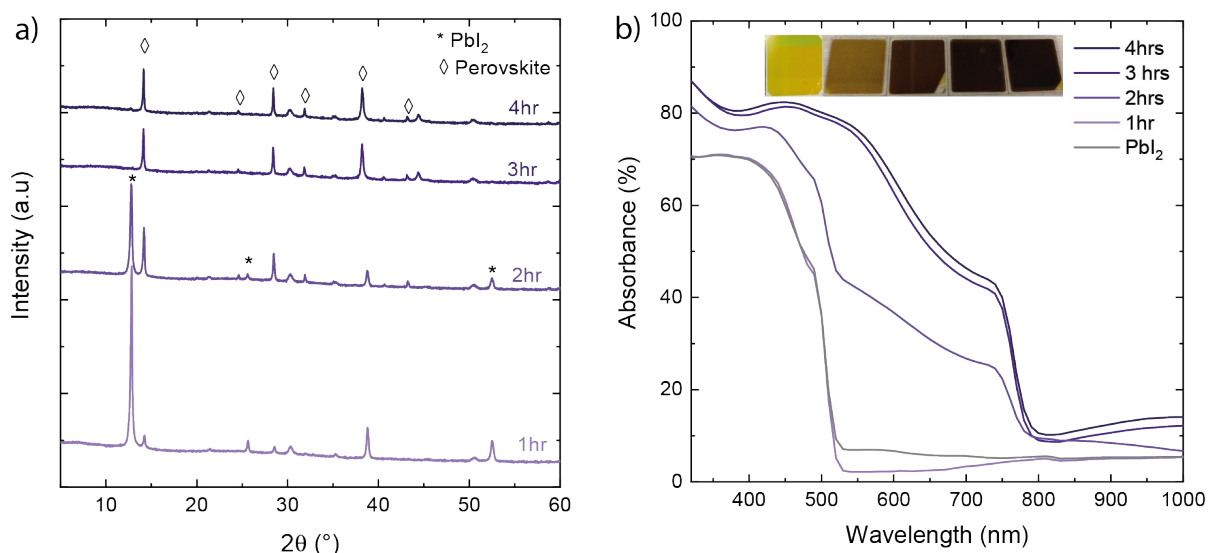


Figure S8 a) X-ray diffractograms of the perovskite formation with time, b) UV-vis-NIR absorbance of the corresponding layers. Deposition conditions: $T_{\text{substrate}}$ of 130 °C for different durations (1 to 4 h), T_{crucible} of 200 °C, carrier gas flow of 800 sccm, working pressure of 12 mbar.

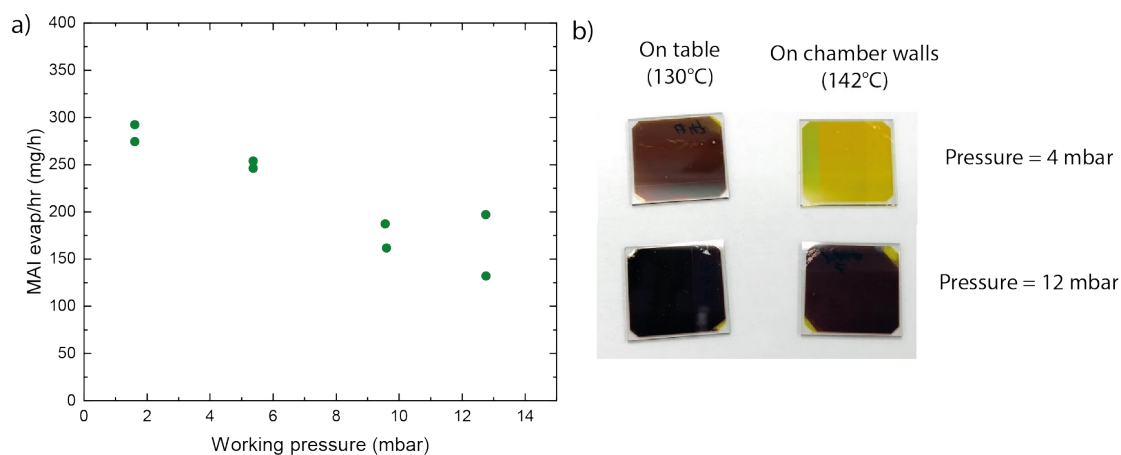


Figure S9: a) Mass loss (in mg/h) measured in the crucible as a function of the chamber working pressure. Deposition parameters are the following: carrier gas flow rate = 800 sccm, $T_{\text{preheating}}$ = 150 °C, evaporation duration \approx 120 min, T_{crucible} = 200 °C, for an initial mass of MAI in the crucible of 1 g. b) Pictures of the PbI_2 templates after their exposure to organohalide vapors when left on the deposition table ($T_{\text{substrate}}$ = 130 °C) or tapped on the chamber walls ($T_{\text{substrate}}$ = 142 °C) at working pressures of 4 mbar and 12 mbar. Note that the showerhead was removed during this experiment.

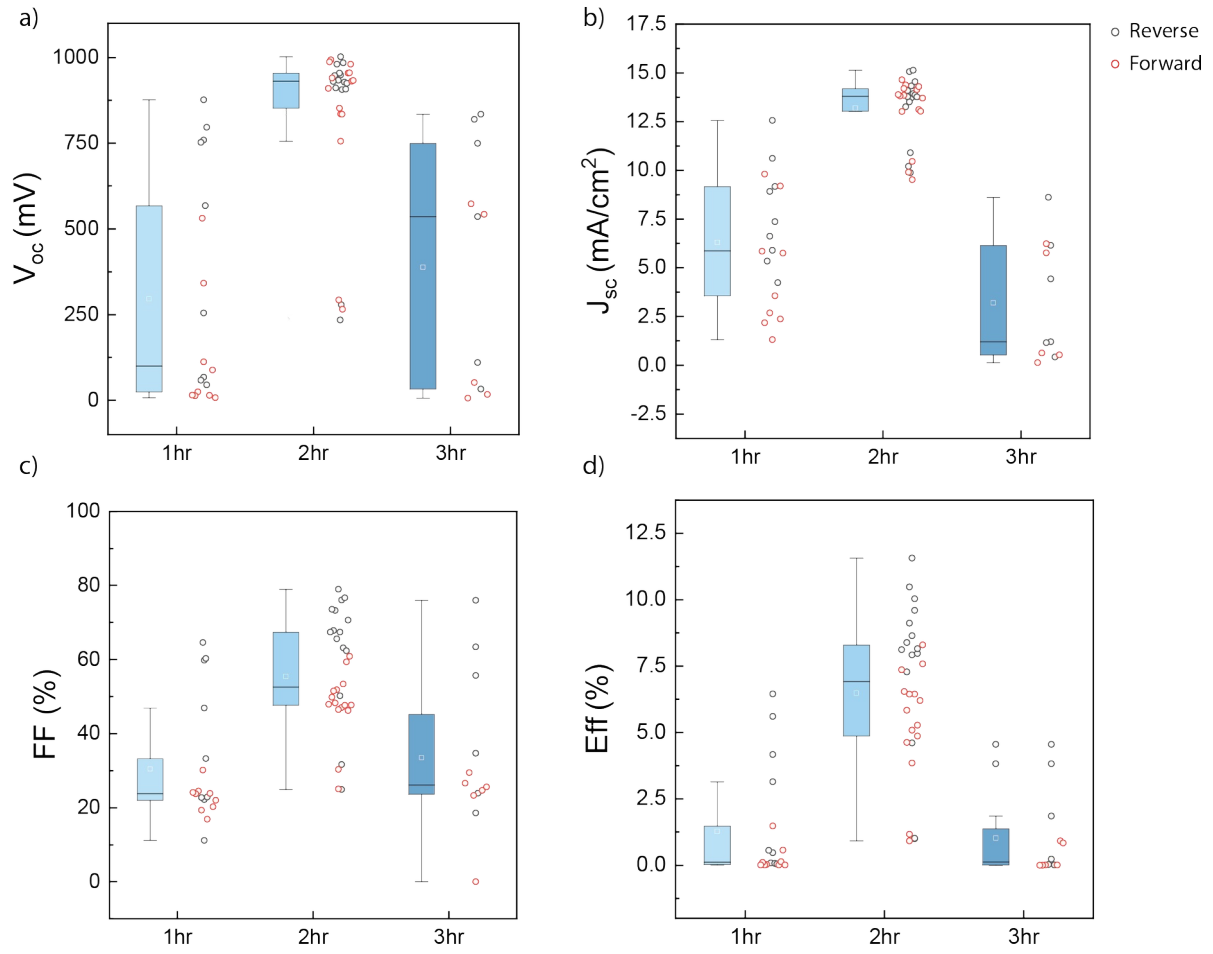


Figure S10: J - V parameters (9-12 cells per condition, reverse and forward scans are displayed) of cells produced by PVD/CVD with $T_{\text{crucible}} = 200\text{ }^{\circ}\text{C}$ and $T_{\text{substrate}} = 120\text{ }^{\circ}\text{C}$ for an evaporation duration of 1 to 3 h. a) Open-circuit voltage (V_{oc}), b) short-circuit current density (J_{sc}), c) fill factor (FF) and d) efficiency (Eff).

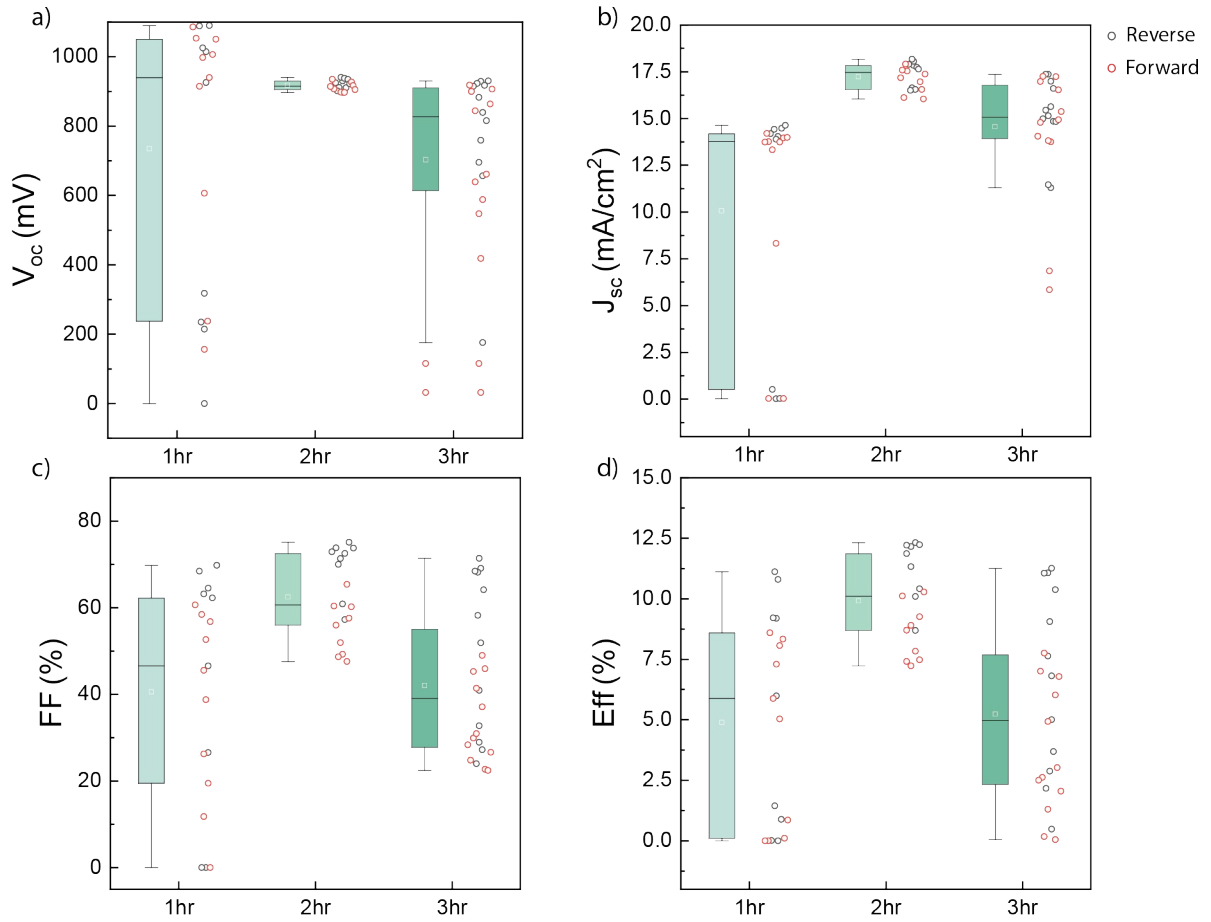


Figure S11: J - V parameters (9-12 cells per condition, reverse and forward scans) for PVD/CVD cell produced with $T_{\text{crucible}} = 210\text{ }^{\circ}\text{C}$ and $T_{\text{substrate}} = 140\text{ }^{\circ}\text{C}$ for an evaporation duration of 1 to 3 h. a) V_{oc} b) J_{sc} , c) FF and d) efficiency.

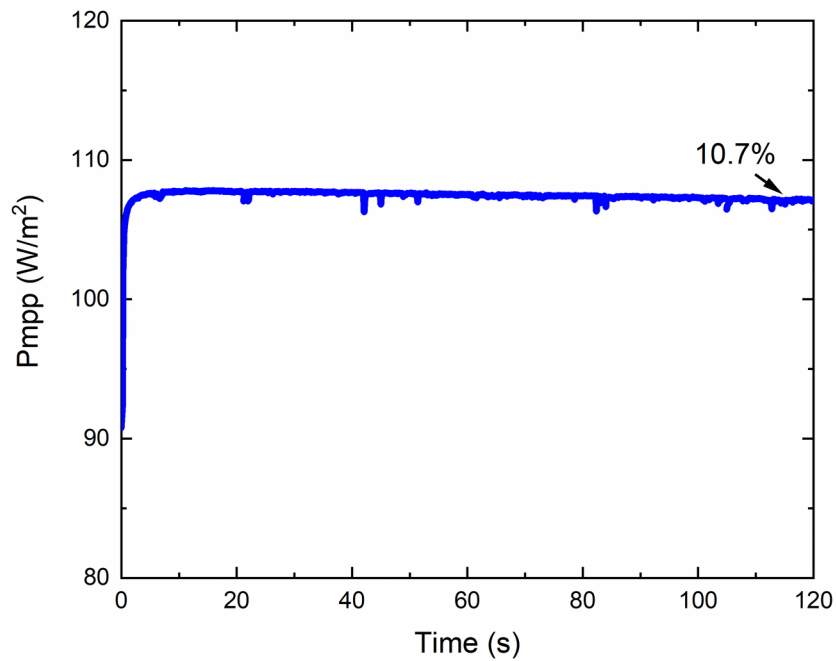


Figure S12: Maximum power point tracking for 120 s of a perovskite solar cell produced with the PVD/CVD technique with $T_{\text{crucible}} = 210\text{ }^{\circ}\text{C}$ and $T_{\text{substrate}} = 140\text{ }^{\circ}\text{C}$ for 2 h.

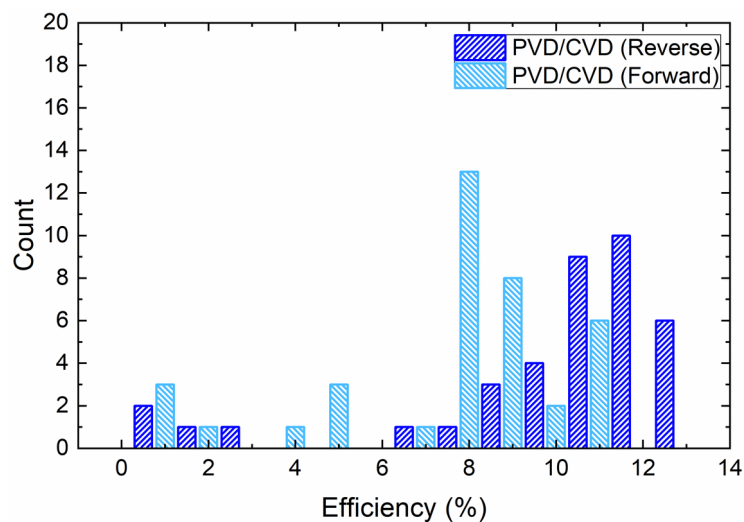


Figure S13: Statistical distribution of reverse and forward scans efficiencies of perovskite solar cells produced by the PVD/CVD method. The deposition conditions are: $T_{\text{crucible}} = 210\text{ }^{\circ}\text{C}$ and $T_{\text{substrate}} = 140\text{ }^{\circ}\text{C}$ for an evaporation duration of 2 h.

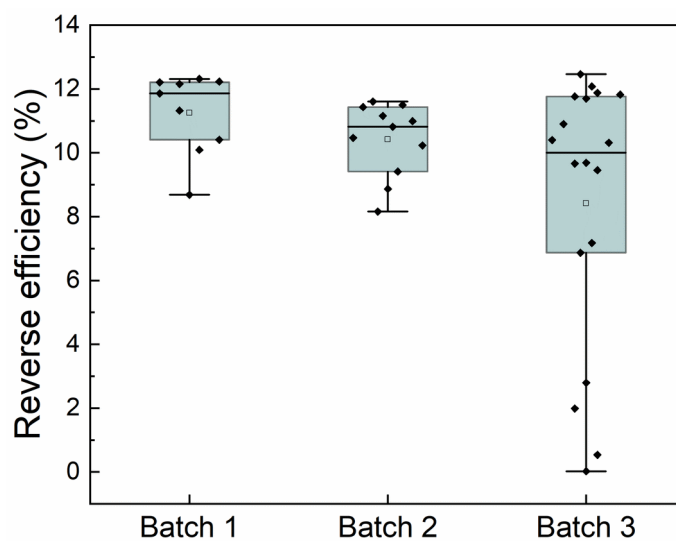


Figure S14: Statistical distribution of reverse scans efficiencies of perovskite solar cells produced by the PVD/CVD method from 3 different batches. The deposition conditions are: $T_{\text{crucible}} = 210\text{ }^{\circ}\text{C}$ and $T_{\text{substrate}} = 140\text{ }^{\circ}\text{C}$ for an evaporation duration of 2 h.

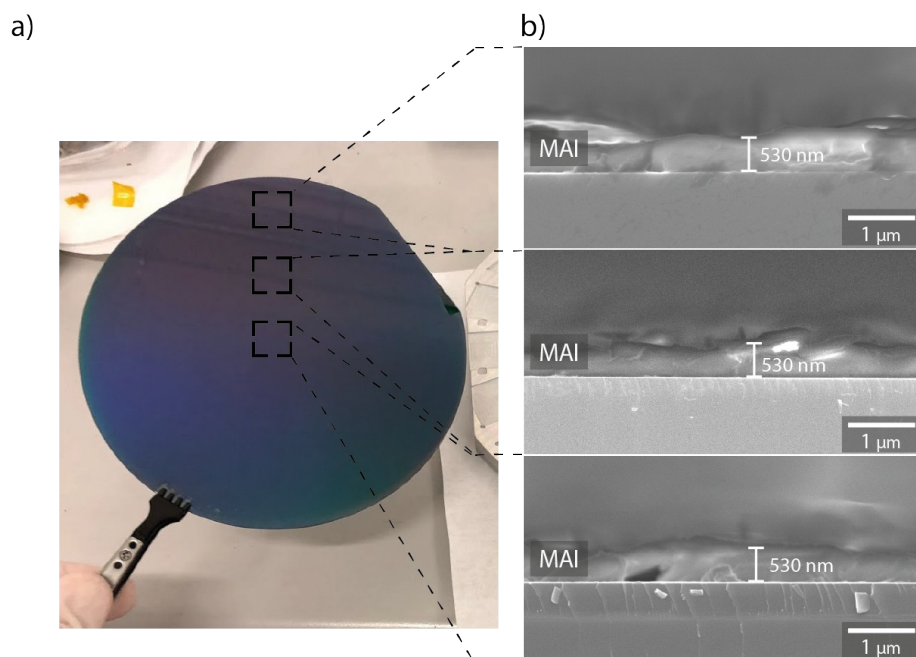


Figure S15: a) Picture of a 6 in. c-Si wafer coated with MAI ($T_{\text{substrate}}$ of 70 °C), b) cross-section SEM images taken at the centre (bottom), middle (middle) and edge (top) of the c-Si wafer.

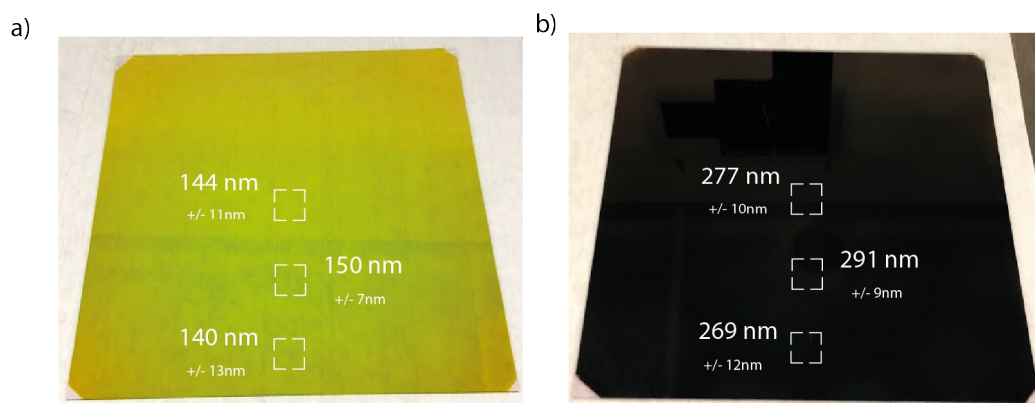


Figure S16: a) PbI_2 layer deposited by PVD on a $15 \times 15 \text{ cm}^2$ glass/ITO substrate and b) the same template coated with MAI and converted to the perovskite. Thicknesses are measured by profilometry.

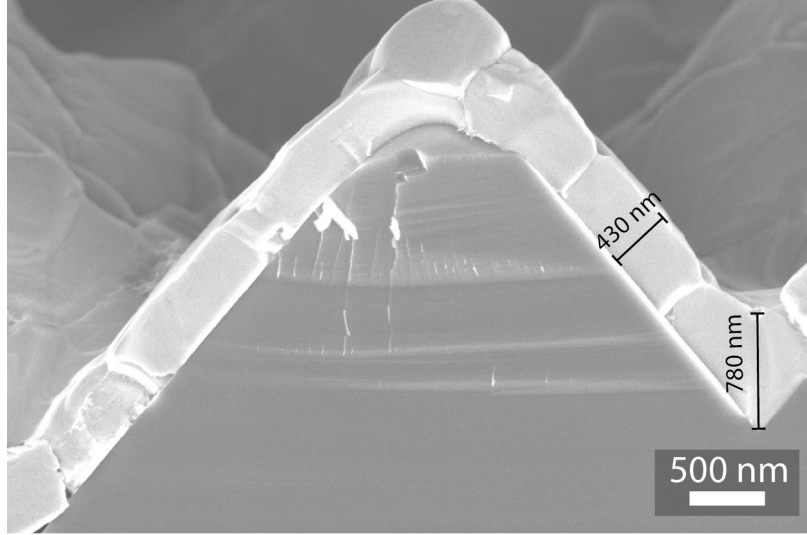


Figure S17: Cross-section SEM image of the perovskite layer produced with the PVD/CVD method on top a c-Si pyramid. Note that 400 nm of PbI_2 (flat surface equivalent) was deposited by thermal evaporation. The CVD deposition conditions for MAI are: $T_{\text{crucible}} = 200\text{ }^\circ\text{C}$ and $T_{\text{substrate}} = 120\text{ }^\circ\text{C}$ for an evaporation duration of 2 h. The perovskite thickness is 430 nm perpendicular to the pyramid edge and 780 nm from top to bottom at the valley.