Supplementary Information

Industrialization of Perovskite Solar Cell Fabrication:

Strategies to Achieve High-Throughput Vapor Deposition Processes

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Experimental section

Sublimation Setup

Sublimation experiments of perovskite precursor materials have been performed by M.Braun Inertgas-Systeme GmbH Dresden. The material is loaded into a Duran tube which is evacuated to reach a base pressure of ~10⁻⁴ mbar. Harvesting zones are defined by equidistant rings. An external cooling loop is placed before the outlet to the vacuum pump to collect any volatile species. Materials were used without further purification: FAI (GreatCell Solar, \geq 99.99%), MAI (GreatCell Solar, \geq 99.99%) and PbI₂ (TCI).

Nuclear magnetic resonance (NMR) spectroscopy

¹H-NMR spectra were recorded in dry DMSO-d₆ (Deutero GmbH) using a Bruker Advance III 300 spectrometer at a frequency of 300 MHz and a temperature of 298 K. Chemical shifts are reported in parts per million (ppm) relative to the present traces of d₅-DMSO(δ_{H} = 2.50 ppm, δ_{C} = 39.52 ppm) in the corresponding fully deuterated solvent.¹ All materials were weighed and dissolved under ambient conditions. Materials for this study were used after sublimation in a Duran tube setup, collecting material from different locations. Reference spectra of materials were obtained without further purification: NH₄I (Sigma-Aldrich, Lot# SZBD3010V), FAI (GreatCell Solar, ≥99.99%), MAI (GreatCell Solar, ≥99.99%).

Knudsen Effusion Mass Spectrometry (KEMS)

Knudsen effusion mass spectrometer used is the FINNIGAN MAT 271, housed at Forschungszentrum Jülich with detailed information given by Bischof et al.² This apparatus is composed of four main components: a Knudsen cell (KC), an electron impact ion source, a single-focusing magnetic sectorfield mass spectrometer, and a detection system consisting of a secondary electron multiplier with an ion counter and a multiplier.³ The sample to be analyzed is placed inside an alumina liner with a height of 8 mm, an outer diameter of 6.4 mm and a wall thickness of 0.5 mm, which in turn is placed in an iridium Knudsen cell consisting of a crucible measuring 8.5 mm in height, with an outer diameter of 7.8 mm and a wall thickness of 0.2 mm. The cell is covered with a lid that has a central orifice of 0.4 mm, allowing for the effusion of the molecular beam. The temperature was increased at a rate of 10 K/min for all materials. To maintain the desired temperature conditions, the KC is insulated by two nested heat shields made of tantalum. The tantalum shields are designed with openings to facilitate the effusion of a molecular beam along the cell's axis. Heating of the KC is achieved through radiation from a tungsten wire around the KC.^{3, 4} A W₉₇Re₃/W₇₅Re₂₅ thermocouple, integrated into the Knudsen cell holder, monitors the temperature. The entire setup is contained within a vacuum chamber maintained at approximately 10⁻⁶ mbar by a turbo molecular pump, and isolated from the mass spectrometer compartments, which are kept under ultra-high vacuum ($\sim 10^{-9}$ mbar) by ion getter pumps. The setup includes a shutter mechanism that allows for distinguishing between sample signals and background noise by blocking or allowing the molecular beam to pass. When the shutter is open, the molecular beam effuses from the KC through an aperture into the ion source, where ionization of the gaseous species occurs. Ionization is achieved via an electron beam generated by an incandescent cathode, operating at an electron energy between 60 and 70 eV with an emission current of 0.468 mA, which intersects the molecular beam perpendicularly. The detection system comprises a secondary electron multiplier and an ion counter, the former being used for analyzing smaller ion quantities and the latter for larger quantities. The ion-counting method, which reduces measurement errors through mass discrimination by the multiplier, was employed in the experiments conducted in this study.

About 60-100 mg of powder under study was loaded into the cell. The cell, along with its contents, was weighed. Upon identifying a sufficiently intense signal the KC's position was adjusted to maximize the signal. Two types of measurement series were conducted: isothermal and polythermal. The isothermal series involves measuring vapor species at a fixed temperature over a specified period, while the polythermal series includes isothermal measurements taken at discrete temperature intervals.

Materials for this study were used without further purification: FAI (GreatCell Solar, \geq 99.99%), PbI₂ (TCI, 99.99%, trace metals basis), CsI (TC, \geq 99.0% (titration))

Inductively coupled plasma optical emission spectroscopy (ICP-OES)

A stock solution (Inorganic Ventures) was prepared with the following concentrations: Pb:I (500 µg/mL Pb, 100 µg/mL I in a 1% [v/v] triethanolamine (TEA from Sigma-Aldrich®, BioUltra, \geq 99.5%) and 0.07% [w/v] of ethylenediaminetetraacetic acid (EDTA from Merck Millipore, Supelco®)). The PbI₂ solids were digested using a solution of 1% (v/v) TEA and 0.07% (w/v) EDTA in Milli-Q water: approximately 2-4 mg of PbI₂ was digested into 40 mL of matrix, and ultrasonicated for 2 hours at 50 °C to ensure complete dissolution. Linear calibrations of both Pb and I were generated using five calibration standard concentrations, resulting in R² \geq 0.999. Lead and iodine concentrations were determined with inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Thermo iCAP 7000 Dual View instrument. Iodine and lead were measured in both radial and axial views using wavelengths 178.276 nm for iodine and either 220.353 nm or 216.999 nm for Pb, respectively, with radial view determined to yield the best results for both. Procedural blanks were analyzed for both Pb and I, yielding <0.001% and <0.01%, respectively, of the reported sample concentrations. The relative standard deviation (RSD) obtained over the sample measurement period was generally 1% and < 1% for I and Pb, respectively.

Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC)

TGA/DSC measurements of PbI₂ (TCI, 99.99%, trace metals basis) were performed by NETSCH company using a STA 449 F3 Jupiter[®] setup equipped with a SiC furnace and a temperature rate of 10 K/min. The material was weighed in a 85 μ L Al₂O₃ crucible. For measurements under reduced pressure, a rotary vane pump was attached to achieve a pressure of ~10⁻² mbar. For measurements under high vacuum, a turbomolecular pump was added to reach a pressure of ~10⁻⁴ mbar. We note that this setup does not measure under equilibrium conditions, as material in the gas phase is constantly removed by pumping.

Determination of layer thickness

For FAI, thicknesses were determined through white light interferometry using a Bruker ContourGT-X. Layer thicknesses of PbI_2 and CsI were determined with a Bruker Dektak XT Profilometer. At HZB, layer thickness of PbI_2 were determined by ellipsometry with a JA Woolam M-2000 with a motorized stage to map M6-size wafer sized samples with a measurement spot size of 0.5 mm and a spot spacing of 25 mm. Prior to ellipsometry mapping, the modelled thickness was validated with a Bruker Dektak XT Profilometer.

Thermal sublimation setups used within this study

At Karlsruhe Institute of Technology (KIT): Physical vapor deposition of perovskite precursor materials was performed in a nitrogen glove box integrated PEROvap system (M.Braun Inertgas-Systeme GmbH Dresden). Individual QCMs were used to measure the rate of each material independently. A cooling inner surface, surrounding all sublimation sources, was set to 25 °C. Prior to the heating process, the system was evacuated for 60 min, with a standard base pressure at start of heating of $3.3 \cdot 10^{-6}$ mbar. For each process, the sublimation rate of each material was kept constant by manually adjusting the source temperature. Substrate temperature (18 °C) was kept constant for all experiments. Sublimation characteristics were investigated in an experimental setup featuring a 300 mm vertical distance between the sublimation source and the substrate. The point source and the center of the substrate are positioned off-axis, approximately 165 mm apart without a tilt towards the substrate. Emission characteristics were determined without rotating the substrate, under a base pressure of around 10^{-6} mbar. The film thickness was around 300 nm for all materials. Deposition rates during sublimation were FAI=1.0 Ås⁻¹, PbI₂=13.5 Ås⁻¹ and CsI=10.0 Ås⁻¹. The lateral distance to source of the QCM is 75 mm which is used for scaling from thickness distribution to static deposition rate profile. For all experiments, cylindrical 10 cm³ crucibles are used with material filling of 3 g for PbI₂ and CsI and 2 g for FAI. Materials for this

study were used without further purification: FAI (GreatCell Solar, ≥99.99%), PbI₂ (TCI, 99.99%, trace metals basis), CsI (TCI, ≥99.0% (titration))

At Helmholtz Center Berlin (HZB) (HySPRINT Photovoltaics Laboratory): Physical vapor deposition of perovskite precursor materials was performed in a nitrogen glove box integrated PEROvap system (M.Braun Inertgas-Systeme GmbH Dresden). Individual QCMs were used to measure the rate of each material independently. A cooling inner surface, surrounding all sublimation sources, was set to 25 °C. Prior to the heating process, the system was evacuated for 60 min, with a standard base pressure at start of heating of 3.3 · 10⁻⁶ mbar. For each process, the sublimation rate of each material was kept constant by programmatically adjusting the source temperature. Substrate temperature (20 °C) was kept constant for all experiments. Static deposition rates during sublimation was 1 Ås⁻¹ for PbI₂.

At Helmholtz Center Berlin (HZB) (KOALA): Physical vapor deposition of perovskite precursor materials was performed in a nitrogen filled glove box integrated PEROvap system (M.Braun Inertgas-Systeme GmbH Dresden) integrated in a VON ARDENNE cluster system CS400ESA. Sources where optimized at HZB or replaced by sources from Luxel Inc. (Radak II). Individual QCMs were used to measure the rate of each material independently. A cooling inner surface, surrounding all sublimation sources, was set to -30 °C. Outer chamber walls are stabilized to 23°C. QCM temperatures were stabilized to -20 °C. Prior to the heating process, the system was evacuated overnight, with a standard base pressure at start of heating of $4 \cdot 10^{-7}$ mbar. For each process, the sublimation rate of each material was kept constant by adjusting the source temperature with a PID controller (Siemens). Substrate temperature (23 °C) and substrate rotation speed (0 rpm) were kept constant for the vapor cloud shape experiments. Static deposition rate during sublimation was 1.4 Ås^{-1} for PbI₂ depositions.

Complementary data on analysis of thermal stability of MAI



Fig. S1 ¹H, ¹³C, and ³¹P NMR spectra of the materials collected from the crucible residue, main fraction, and volatiles deposited under active cooling at increasing temperatures. Characteristic signals are annotated. Ammonium (-NH₃, 7.49 ppm) and methyl (-CH₃, 2.36 ppm) groups were detected in the ¹H NMR spectra, with the methyl group also observed in the ¹³C NMR spectra at 25 ppm. Additionally, small quantities of methylammonium hypophosphite were detected, as indicated by additional signals in both the ¹H NMR (7.83 and 6.21 ppm) and ³¹P NMR (-2.3 ppm) spectra.



Fig. S2 Optical photographs of material collected from the crucible residue, the main fraction and volatiles deposited under active cooling for MAI. A red-colored material of unknown composition was observed in the crucible residue. In contrast, the visual appearance of the materials collected from the main fraction and the volatiles deposited under active cooling remained unchanged. For a temperature of 240 °C all material sublimed from the crucible, leaving no residue to be analyzed.

Complementary data on analysis of thermal stability of FAI



Fig. S3 Optical photographs of material collected in the crucible residue, the main fraction and volatiles deposited under active cooling for FAI. Discoloration of crucible residue from colorless to off-white and finally to grey/black was observed. The color of material collected from the main fraction barely changes with only slightly being off-white at 260 °C. Volatiles deposited under active cooling display discoloration to orange at 260 °C.

A reference ¹H-NMR spectrum of ammonium iodide (\geq 99%, Sigma-Aldrich) was recorded to investigate the origin of additional signals observed in sublimed FAI. A singlet peak with chemical shift of 7.09 ppm was detected, being consistent with previous observations.



Fig. S4 ¹H-NMR spectrum of ammonium iodide (NH₄I) in DMSO-d₆ at 300 MHz and 298K.



Fig. S5 A Polythermal KEMS measurements of FAI were conducted over a temperature range of 120–150 °C. The characteristic species were identified and annotated. **B** Isothermal KEMS measurements at 150 °C showed that the intensities of all species increased steadily for approximately 3 hours, after which they stabilized. After 10 hours, a decline in the measured intensities was observed, attributed to the depletion of the material in the crucible.





Fig. S6 ICP-OES measurements of PbI_2 . For comparison, the raw PbI_2 exhibited an I/Pb ratio of 2.02. In the crucible residue, the I/Pb ratio decreases slightly from 2.05 to 2.02. This is, however, expected to be non-significant considering the reported analytical uncertainty of the measurement. The I/Pb ratio in the main fraction remained constant within measurement accuracy without a clear trend. The volatiles deposited under active cooling displayed a higher I/Pb ratio compared to the raw material, with a slight increase observed with increasing temperature.



Fig. S7 A TGA and DTG analysis of PbI_2 performed under different pressures: ambient pressure under nitrogen atmosphere, 10^{-2} mbar, and 10^{-4} mbar. The TGA data indicate a mass loss occurring after reaching a specific temperature threshold. The maximum mass loss rates (DTG) were observed at 596 °C, 347 °C, and 362 °C for ambient, 10^{-2} mbar, and 10^{-4} mbar conditions, respectively. **B** DSC measurement showing an endothermic melting process at 403 °C.



Fig. S8 A Measured deposition rate at QCM (*e.g.* at a tooling factor of 100%) as a function of temperature for PbI₂. For each temperature a 5 min waiting time was used to reach equilibrium conditions. At temperatures above 280 °C no equilibrium could be reached and the static deposition rate was continuously rising. Therefore, 270 °C was chosen as the maximum temperature achieving a stable rate. The temperature is measured by a thermocouple attached to the bottom of the crucible. **B** Log-linear regression of the static deposition rate of PbI₂ and extrapolation of the static deposition rate up to 450 °C. This temperature range was chosen as ICP-OES measurements of the collected material did not indicate decomposition.



Fig. S9 A Polythermal KEMS measurements of PbI_2 were conducted over a temperature range of 200–325 °C. The characteristic species were identified and annotated. **B** Isothermal KEMS measurements at 270 °C showed that the intensities of all species increased steadily for approximately 3 hours, after which they stabilized shortly. After 3 hours, a rapid decline in the measured intensities was observed, attributed to the depletion of the material in the crucible which is completed after 5 hours.



Fig. S10 A Polythermal KEMS measurements of CsI were conducted over a temperature range of 380–470 °C. The characteristic species were identified and annotated. **B** Extracted intensities of identified species as a function of temperature. A higher oligomer of $Cs_2I_3^+$ was detected above a temperature of 420 °C.

Supplementary Note 1: Derivation of expression to fit thickness gradient of static deposition The intensity $I(\theta)$ is proportional to $cos^n(\theta)$, as expressed by the cosine law:

$$I(\theta) \propto \cos^n(\theta)$$
.

On a horizontal substrate holder, the angle θ is related to the distance x along the substrate holder and the height of the holder x_h using the tangent function:

$$\theta(x) = \arctan\left(\frac{x}{x_h}\right).$$

Substituting $\theta(x)$ into the cosine law relates the intensity to the effective angle at each point:

$$\cos^{n}(\theta(x)) = \cos^{n}\left(\arctan\left(\frac{x}{x_{h}}\right)\right).$$

Additionally, intensity decreases with the distance from the source (inverse square law), where the intensity decreases with the square of the distance from the source. The distance R from the source to a point x on the substrate is given by:

$$R = \sqrt{x^2 + {x_h}^2}.$$

Thus, the intensity at a given point x becomes:

$$I(x) = \frac{\cos^{n}\left(\arctan\left(\frac{x}{x_{h}}\right)\right)}{R^{2}} = \frac{\cos^{n}\left(\arctan\left(\frac{x}{x_{h}}\right)\right)}{x^{2} + x_{h}^{2}}$$

Assuming the thickness t(x) is proportional to the corrected intensity I(x), we introduce a proportionality factor A:

Complementary data on analysis of thermal stability of CsI

$$t(x) = A \cdot \frac{\cos^{n}\left(\arctan\left(\frac{x}{x_{h}}\right)\right)}{R^{2}} = A \cdot \frac{\cos^{n}\left(\arctan\left(\frac{x}{x_{h}}\right)\right)}{x^{2} + x_{h}^{2}}$$

This expression is used to fit the thickness gradient experimentally determined from static depositions.

Table S1 Measured film thicknesses distribution over radius (no rotation) of different perovskite precursor materials and setups.

	FAI @	PbI_2 @	CsI @	PbI ₂ @		PbI_2 @	
	KIT	KIT	KIT	HZB		KOALA	
Lateral	Film	Film	Film	Lateral	Film	Lateral	Film
distance	thickness	thickness	thickness	distance	thickness	distance	thickness
to	[nm]	[nm]	[nm]	to	[nm]	to	[nm]
source				source		source	
[mm]				[mm]		[mm]	
75.7	375	639±7	475±32				
103.9	380	456±16	436±5	60	513	87.4	994
132.2	250	387±7	358±3	70	319	120.9	866
160.5	210	361±6	301±1	10.7	292	154.5	703
188.8	190	240±9	243±3	11.7	241	188.0	685
217.1	115	187±5	197±3	15.5	167	221.5	573
245.4	90	143±6	162 ± 2	16.5	139	255.1	351
						288.6	296

Table S2 Fitting parameters and static deposition rate at the position of the QCM.

Material	Static	A [arb. u.]	Exponent n	FWHM	Static rate
	QCM rate			distance	at FWHM
	[nm/s]			[mm]	[nm/s]
FAI @ KIT	0.10	4.34·10 ⁷	4.33	112	0.14
PbI ₂ @ KIT	1.35	6.84·10 ⁷	4.59	145	0.83
CsI @ KIT	1.00	$5.04 \cdot 10^{7}$	2.93	170	0.58
PbI_2 @ HZB	-	-	9.91		
PbI_2 @	-	-	2.95		
KOALA					



Fig. S11 A-C Static deposition rate as a function of position relative to the source for FAI, PbI_2 , and CsI, respectively.



Fig. S12 A Static deposition rate as a function of position relative to source for different sublimation setups. Static deposition rates were calculated from QCM reading for the laboratory-scale setup and from deposition time and final film thickness for the KOALA setup, respectively. **B** Normalized static deposition rate.



Fig. S13 Spatial map of static deposition rates for a single point source and a conceptual linear source with 13 point sources spaced 50 mm apart of each other. A/B for PbI₂. C/D for FAI. E/F for CsI.



Fig. S14 Static deposition rate and cumulative film thickness as a function of the position relative to the source for **A** FAI, **B** PbI₂ and **C** CsI. The substrate speed was set to 1 m min⁻¹ in all cases such that the final thickness is equivalent to the dynamic deposition rate in nm m min⁻¹. The profile is extracted at x = 400 mm, the position of the central wafer in this case.

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