Supporting Information

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The necessity of gas-flow quenching for vacuum-dried high-quality perovskite films

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Abstract: Controlling the nucleation and crystal growth in solution-processed metal halide perovskite (MHP) thin films is the pivotal point in fabricating homogenous and pinhole-free films. Using scalable coating and printing techniques vacuum and gas flow-assisted drying processes turn out to be the most promising methods to induce nucleation and crystallization. Yet, the exact interplay and nature of these processes are unclear. In our work, we optically monitor these processes in-situ. For the first time, we can show that a controlled venting of the vacuum chamber and the use of a subsequent gas flow are key to achieve homogenous nucleation. Utilizing this gas flow-assisted vacuum drying process, we find that regular, optically dense and pinhole-free MHP layers can be fabricated via inkjet printing, which yield solar cells with a power conversion efficiency of 16%, as compared to 4.5% for vacuum drying.

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Experimental Procedures

Materials

The solvents dimethyl formamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), and γ-Butyrolacetone (99.8%) were purchased from Sigma-Aldrich. Lead (II) bromide ($PbBr_2$, 99.99%) and lead (II) iodide (PbI_2 ,99.99%) were purchased from TCI Deutschland GmbH. Cesium iodide (CsI) was also purchased from Sigma-Aldrich. Methylammonium bromide (MABr) and formamidinium iodide (FAI) were purchased from Dyenamo. [2-(9*H*-carbazol-9-yl)ethyl]phosphonic acid (2PACz) was purchased from Tokio Chemical Industry (TCI). Patterned indium tin oxide (ITO) glass substrates (25x25 mm, resistivity = 15 Ω sq-1, nominal ITO thickness = 150 nm) were purchased by Automatic Research GmbH. C_{60} (99.99%) and BCP were purchased from Sigma Aldrich, Cu shots from Alfa Aesar.

Perovskite precursor solution

PbI_2 (1.5 M) was dissolved in 0.8 ml DMF and 0.2 ml DMSO, $PbBr_2$ (1.5 M) dissolved in 0.16 ml DMF and 0.04 ml DMSO. These two solutions were stirred overnight at 60°C in an inert atmosphere. FAI powder was mixed into the prepared PbI_2 solution (1:1.09 molar ratio) and MABr powder was mixed into the prepared $PbBr_2$ solution (1:1.09 molar ratio). The solutions were shaken for few minutes until the organo-halide powders were fully dissolved. These solutions were mixed to form $(MA,FA)Pb(I,Br)_3$ precursor solution. CsI (1.5 M) was dissolved in 1 ml DMSO stirred overnight at 60 °C in the inert atmosphere. The “Triple cation” perovskite precursor solution was prepared by adding 5 vol.% of the CsI solution to the $(MA,FA)Pb(I,Br)_3$ precursor solution. The resulting precursor solution should hence have a stoichiometry of $Cs_{0.05}MA_{0.16}A_{0.79}PbBr_{0.51}I_{2.49.}$

Solar cell fabrication

Patterned ITO glass substrates were cleaned sequentially for 15 min with a 2% Mucasol solution in water (Schülke), water, acetone, and isopropanol at ~ 40 °C in an ultrasonic bath. After that, directly before HTM deposition, the substrates were treated in an UV-ozone cleaner for 15 min. All subsequent procedures were done in a nitrogen-filled glovebox (MBRAUN).

SAM powders were dissolved in anhydrous ethanol at a concentration of 3 mmol/l and put into an ultrasonic bath for 15min (30-40 °C) before using. 2PACz powder (molar weight 335.3 g/mol) was stored in a nitrogen glovebox, The SAMs were prepared by spin-coating. 100 µl of the solution was uniformly released onto the middle of the substrate, the lid was closed and after ~ 5 s resting, the spin-coating program (30 s at 3000 rpm) was started. After spin-coating, the substrates were heated at 100 °C for 10 min.
The stock perovskite precursor solution was diluted prior to the printing process to 0.42M with a solvent ratio of 60:15:25 (DMF:DMSO:GBL).
The perovskite ink was printed onto the substrate using an LP50 inkjet printer (Meyer Burger) equipped with a Spectra SE128 printhead (Fujifilm) inside a nitrogen-filed glovebox. The ink temperature was held at 30 °C during the printing process. The drops (80pL) were created with a single bias pulse at a width of 8 µs and peak voltage of 80 V. All films were printed at a resolution of 300 dpi. After printing, the substrates were transferred to a vacuum chamber (@20 mbar 0.16 L/s), followed by thermal annealing at 100 °C for 60 minutes.
After perovskite deposition, 23 nm C_{60} and 8 nm BCP were thermally evaporated in a MBRAUN ProVap3G at a base pressure of 10^{-6} mbar with an evaporation rate of 0.1-1.0 Å/s. For completing the device, 100 nm Cu was thermally evaporated through a shadow mask. The overlap of the substrate’s ITO with the Cu stripe defines the active area of 0.16 cm².

Thin film characterization

X-ray diffraction (XRD) measurements were done in air with a Bruker D8 Advanced machine using a CuKα (λ = 1.5406 Å) source in Bragg-Brentano geometry. Scanning electron microscopy (SEM) images were recorded with a Hitachi S-4100 and 5 kV acceleration voltage system. The resulting film thickness was verified by profilometry (Bruker Dektak).

Optoelectronic characterization

J-V scans were performed as 4-point measurements with a Keithley 2600 SMU controlled by a measurement control program written in LabView. The voltage values are swept in 20 mV steps with an integration time of 40 ms per point and settling time of 20-40 ms after voltage application.

In-situ-setup

A modified layout from the introduced setup by Merdasa et al was used.[1] Ocean Insight part QR400-7-UV-BX reflectance probe is used to collect the optical signals, and is placed at ~1 cm from the substrates. Ocean optics Flame FLMS12200 spectrometer is used to detect these signals at an integration time of 300 ms. As excitation source, a 415 nm line of a filtered fiber-coupled tungsten-halogen light source (Thorlabs’ SLS201LM) was used.

Contact angle measurement

Contact angles of the perovskite ink are measured via the sessile drop method on a Kruss DSA100 system at ambient conditions. The surface energies of the SAM layers are calculated by The OWRK-method, using dispersive and polar solvents.

Results and Discussion

Video S1: Drying behavior of 300 s vacuum-dried sample. The sample dries first from the outside to the inside of the wet film.
Video S2: Drying behavior of GAVD sample. The film dries first, where the N_2-flow hits the sample first.
(https://box.hu-berlin.de/d/21d88a19d291432bac55/)

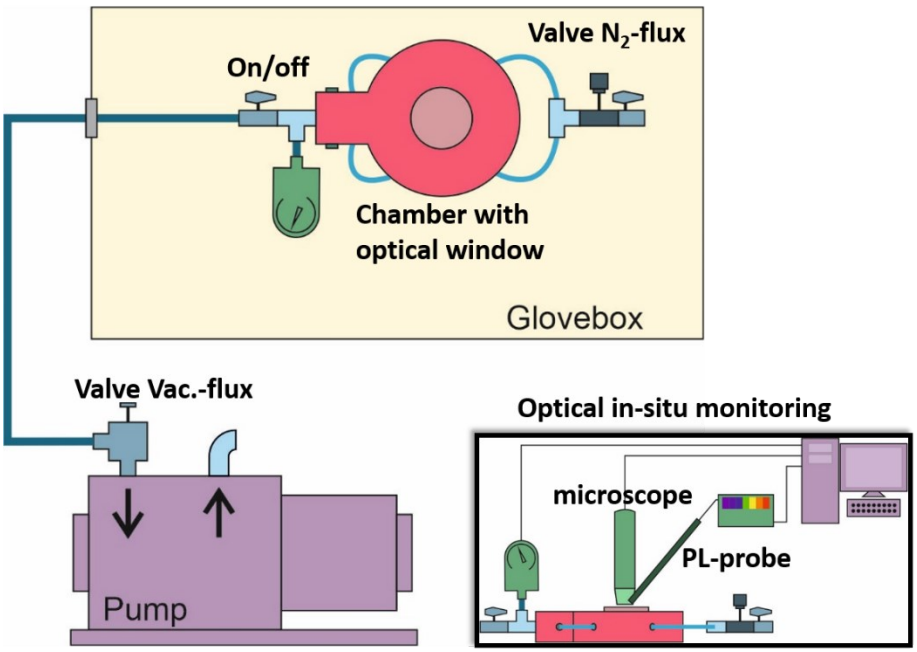

Figure S1: Schematic of the vacuum chamber and Insitu-PL setup with PL-probe and microscope to monitor the perovskite formation during the GAVD process.

GAVD process:

The chamber consists of two parts. The sample is placed on the bottom part. After printing (~ several seconds for 1cm² print area) the cover with the optical window is placed on top and the whole chamber is vacuumed. Nitrogen from the glovebox is introduced into the chamber through a ball-valve and the flow is controlled with an additional needle-valve. In the case of the vacuum condition, the inlet valves were kept closed at all times so that the pressure inside of the chamber during the 300 seconds of experiment was kept below 1 mbar. Finally, the printing process is performed directly on the bottom half of the vacuum chamber. The printing process itself requires the substrate to be immobilized, and this is done on a specially made substrate holder. On the other hand, the GAVD and vacuum processes do not require the substrate to be held, however, the substrate is already fixed on the bottom of the vacuum chamber when these processes are performed

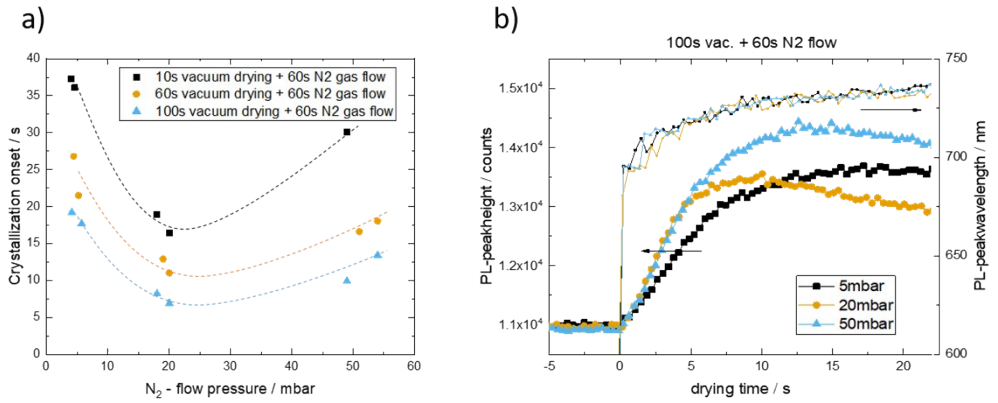

Figure S2: a) Crystallization onset of at different gas-flow rates corresponding to different chamber pressures. The additional usage of a controlled gas flow reduces the crystallization onset, compared to only vacuum dried samples (crystallization onset after ~200s). The dashed lines are only guidelines for the eye. b) Evolution of PL peak wavelength and peak height for different base pressures of GAVD samples. A similar strong increase of the PL signal occurs for the different base pressures.

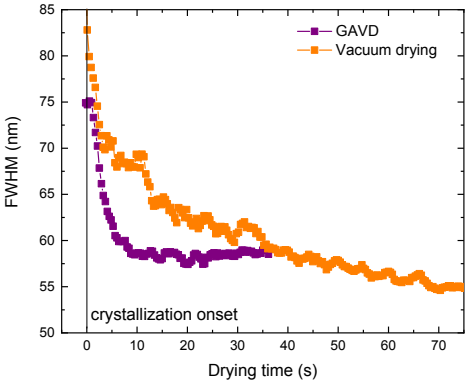

Figure S3: Evolution of Full width half maximum (FWHM) PL peak for GAVD and vacuum-dried samples. The FWHM value decreases strongly for the GAVD sample, whereas the vacuum dried sample shows a slower, but steady decrease over time.

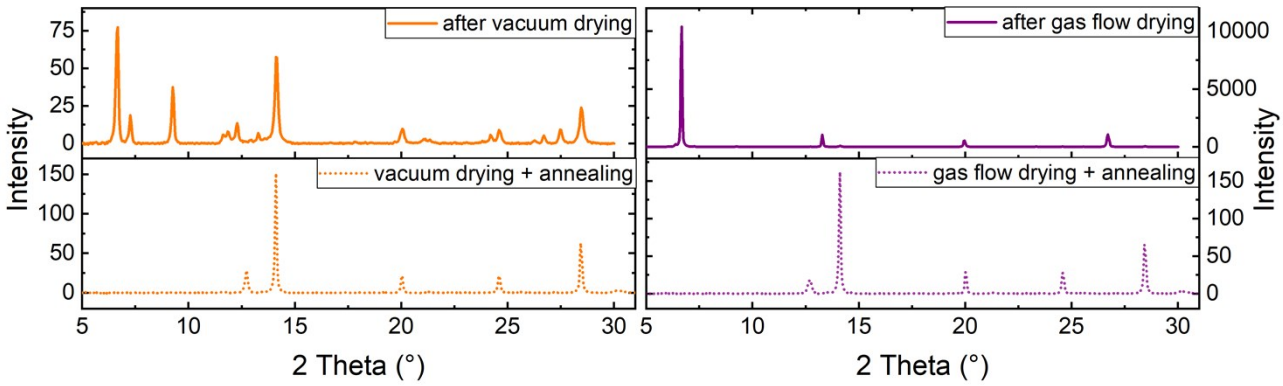

Figure S4: XRD diagram of samples dried with vacuum and GAVD with total counts The GAVD samples show much higher intensity and higher crystalline orientation.

Table S1: Allocation of the reflexes from Figure S3

2Theta GAVD	2Theta Vacuum- dried	Phase
6.55362	6.67	MA2DMSO2Pb3I8 - 002
7.191	7.27	MA2DMSO2Pb3I8 - 021
9.18281	9.26	MA2DMSO2Pb3I8 - 022
9.74052		PbI2·DMFpossible.
	11.65	delta- FAPbI3 (non perovskite)
11.77218	11.85	MA2DMSO2Pb3I8 - 023
	12.29	PbI2·DMF possible.
	12.96	MA2DMSO2Pb3I8 - 040
13.20628	13.28	MA2DMSO2Pb3I8 - 004
14.00301	14.12	3Cat – 001
19.85895	20.05	3Cat - 111
	21.33	MA2DMSO2Pb3I8
24.0816	24.20	MA2DMSO2Pb3I8 - 124/142
24.44013	24.59	3Cat - 201
	26.27	delta- FAPbI3 (non perovskite)
26.59129	26.71	3Cat - 211
27.38801	27.46	MA2DMSO2Pb3I8 - 160
28.26441	28.46	3Cat - 220

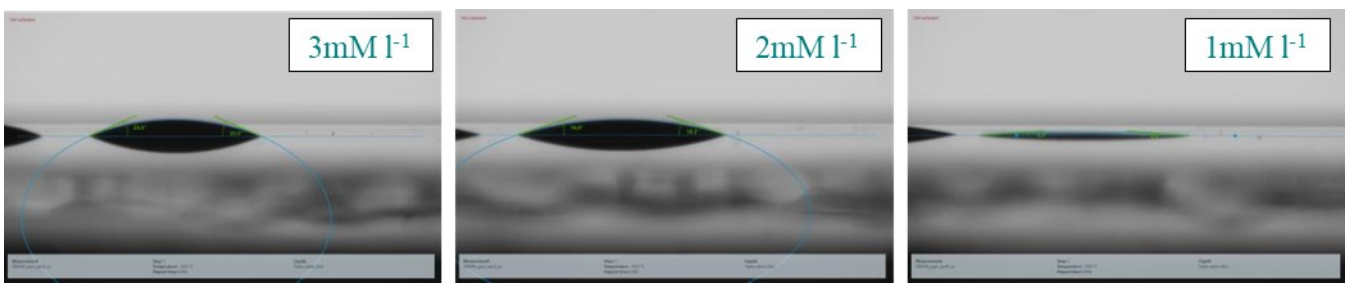

Figure S5: Pictures of contact angles of perovskite solution on 2PACz-SAM fabricated in different concentrations..

2PACz concentration / mM l^{-1}	Contact angle of 3CAT / °	Total Free Surface Energy / mN m^{-1}	Dispersive Surface Energy / mN m^{-1}	Polar Surface Energy / mN m^{-1}
1	23.5 ± 1.2	59.2	44.7	14.5
2	16.7 ± 1.6	60.3	44.4	16.0
3	10.3 ± 1.3	64.0	44.7	19.3

Table S2: Measured contact angle of perovskite solution on 2PACz- SAM and calculated surface energy, using the OWRK-method.

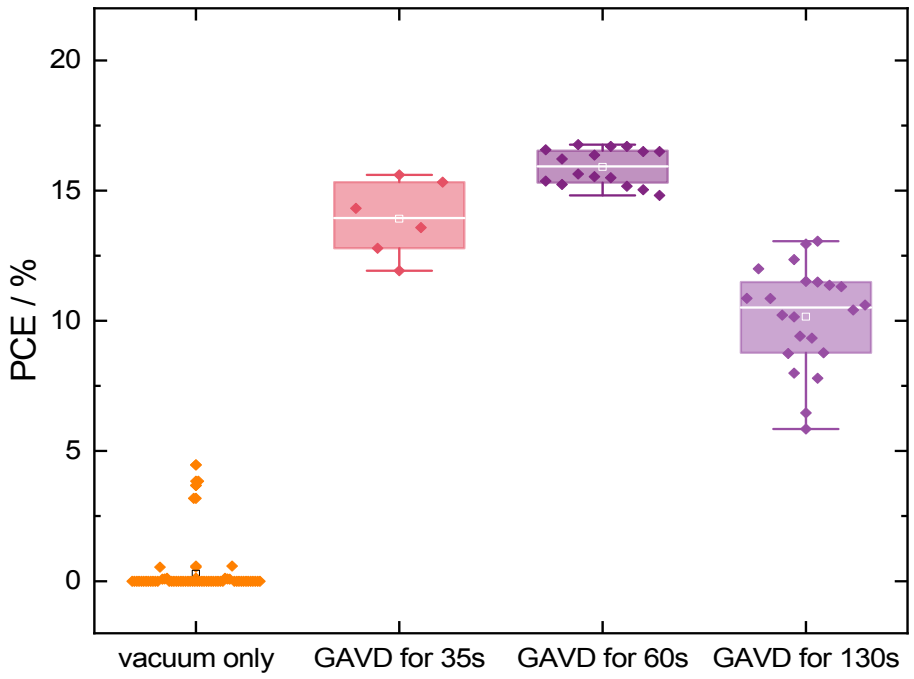

Figure S6: Statistics of solar cells made by only vacuum drying and different times under GAVD treatment. The active cell area is 0.16cm² in a p-i-n structure on 2PACz-SAM. The number of cells pero parameter are 12,6,16, and 22 respectively.

Literature

[1] A. Merdasa, C. Rehermann, K. Hirselandt, J. Li, O. Maus, F. Mathies, T. Unold, *Res. Sq.* **2020**, DOI 10.21203/rs.3.rs-102041/v1.

Author Contributions

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Edgar Nandayapa[‡]: data curation, formal analysis, investigation, validation, writing of original draft

Gopinath Paramasivam: investigation (material and sample preparation, device data)

Carolin Rehermann: investigation (XRD data), work on final manuscript

Vincent R. Schröder: investigation (XRD data), work on final manuscript

Mohammad Fadi Al Rayes: investigation (material and sample preparation, in-situ data, device data), work on manscript

Emil List-Kratochvil: project administration, funding acquisition, data interpretation, work on final manuscript

Eva Unger: project administration, funding acquisition, data interpretation, work on final manuscript