Supplementary Information

Grain rotation and lattice deformation during perovskite spray coating and annealing probed in-situ by GI-WAXS

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GI-WAXS Setup Illustration. The annealing chamber mounted on the diffractometer is shown without the top lid. $(\hat{l}_{x'}, \hat{l}_{y'}, \hat{l}_z)$ are the versors of the laboratory reference system, 0 is the origin of the laboratory and sample reference system, α_i is the out-of-plane incident angle, and $2\theta_h$ is the position of $2\theta_h$ diffractometer circle. An illustration of the sample position with respect to the laboratory reference system is shown in green colour. For more details see ref.¹.



Video 1 | **Diffraction image sequence during isothermal deposition at 60 °C (spray coated sample).** Figure shows snapshots from <u>https://youtu.be/yxrqEi4Suxs</u>. When viewing the videos please select 1080p HD quality.



Video 2 | **Diffraction image sequence during isothermal annealing at 110** °C (spray coated sample). Figure shows snapshots from <u>https://youtu.be/Qsjmy-oZAm0</u>.

In-situ GI-WAXS on spin coated perovskite films. We conducted a series of in-situ annealing GI-WAXS measurements on films spin coated from MAI:PbCl₂ (3:1 mol in DMF) on Si/SiO2 substrates coated with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate PEDOT: PSS. The precursor solution was the same as the one described in the manuscript. We employed substrates spin coated with ~30nm of PEDOT: PSS to achieve precursor/perovskite nucleation conditions similar to the ones encountered in the preparation of ITO/PEDOT:PSS/Perovskite/PC₇₀BM/Ca/Al solar cells (see Fig. S1 and Tab. S1). We prepared the samples listed in the following Tab..

Spin-coated samples investigated by in-situ annealing GI-WAXS. We investigated a combination of perovskite films annealed at different temperatures and at different ambient conditions.

		Annealing Temperature		
		80°	90°	110°
Atmosphere	Air (RH ~ 40%)	S 1	S2	S3
	Helium	S4	S5	S6
	Wet Helium	S7	S8	S9

The Si/SiO₂ substrates coated with PEDOT: PSS were placed on a hotplate at 90°C for a few minutes, rapidly transferred to the spin coater chuck, and spin coated in air (relative humidity $\sim 40\%$). This is the procedure that we normally use in the spin coating of MAI:PbCl₂ for \sim 12% efficient air processed solar cells. The coated substrates were transferred to the GI-WAXS annealing chamber within one minute. Note that for these measurements we employed a different version of the hotplate from the one described in the manuscript, which did not display any remarkable thermal expansion. Samples S1, S2, S3 were annealed in air (relative humidity ~40%). Sample S2 was annealed under conditions that are similar to the ones employed for the fabrication of $\sim 12\%$ efficient solar cells, with the exception that the optimum relative humidity for high efficient solar cells during the anneal is $\sim 30\%$. Samples S4, S5, S6 were annealed in a helium atmosphere (very low levels of oxygen and water vapour). Samples S7, S8, S9 were annealed in a wet helium atmosphere. This condition was obtained by bubbling helium through a water container. The resulting atmosphere had high water vapour concentration but low oxygen concentration. We are unable to provide the exact oxygen and water vapour concentration inside the chamber. The thickness of these films, measured after the anneal, was ~350nm. The rate at which diffraction patterns were recorded (1 image every \sim 53s) for this dataset differs from the one described in our manuscript (1 image every \sim 17s). The as-coated samples were placed on the hotplate in the GI-WAXS annealing chamber and the temperature was rapidly increased to the target annealing temperature. The sample-detector distance for this dataset (~ 223 mm) was larger than the one described in our manuscript (~ 203 mm), which resulted in a broader visible reciprocal space on the detector in the second case. The initial phase of the anneal is also different. As described in the manuscript, the spray coated sample was placed on a 110°C warm hotplate. However, for the samples described here the temperature was rapidly increased from room to the set point temperature. The other measurement details correspond with the ones described in the manuscript. The following are videos of the diffraction patterns of the spin coated films measured during the in-situ annealing:

Video 3 | Spin coated sample S1, Air, 80°C: https://www.youtube.com/watch?v=8neSIkUWNEM.

Video 4 | Spin coated sample S2, Air, 90°C: https://www.youtube.com/watch?v=iLy1U5zobXQ.

Video 5 | Spin coated sample S3, Air, 110°C: https://www.youtube.com/watch?v=CxgPBeNzEqA.

- Video 6 | Spin coated sample S4, He, 80°C: https://www.youtube.com/watch?v=AHT6bG7wmpk.
- Video 7 | Spin coated sample S5, He, 90°C: https://www.youtube.com/watch?v=cUCwkif1leQ.
- Video 8 | Spin coated sample S6, He, 110°C: <u>https://www.youtube.com/watch?v=VJFeYKUYTVE.</u>
- Video 9 | Spin coated sample S7, Wet He, 80°C: <u>https://www.youtube.com/watch?v=f_GIvmQh3SE.</u>
- Video 10 | Spin coated sample S8, Wet He, 90°C: https://www.youtube.com/watch?v=d02868bohng.

Video 11 | Spin coated sample S9, Wet He, 110°C: <u>https://www.youtube.com/watch?v=q_G2d28iHBM.</u>

Note that the actual sample temperature is 3°C lower than the one indicated in the videos. Note also that there is some temperature overshoot, and that the sample temperature stabilizes within 3-5min.



Fig. S1 | Spin coated solar cell current vs voltage measurements. The precursor solution was prepared as described in the manuscript. Device fabrication details are available elsewhere^{2, 3} and are here summarized. The solar cell device layer stack was ITO/PEDOT:PSS/CH₃NH₃PbI_{3-x}Cl_x/PC₇₀BM/Ca/Al. The precursor solution was spin coated at 4000rpm on ITO substrates coated with PEDOT: PSS. The films were annealed at 90°C for 90 min. The devices were completed with a spin coated layer of PC₇₀BM, followed by Ca and Al evaporation, and encapsulated. The relative humidity during the spin coating and the annealing was ~ 30%. Current-voltage measurements were performed under a solar simulator (AM1.5 spectrum at an intensity of 100 mW/cm²) with an aperture mask defining a device area of 0.025cm². The measurements reported below were performed after light soaking the devices under the solar simulator for ~20 min, both with reverse and forward voltage sweeps.

Tab. S1 | Spin coated solar cells performance. Average and standard deviation values measured on a sample of 12 solar cells excluding the poorly performing ones (located at the edge of the substrate). The power conversion efficiency (PCE) value under brackets indicates the record efficiency.

	PCE [%]	J _{SC} [mA/cm2]	V _{OC} [V]	FF [%]
Forward sweep	11.6±0.6 (12.5)	17.8±0.2	0.898±0.022	72.8±1.8
Backward sweep	11.8±0.6 (12.8)	17.8±0.2	0.904±0.024	73.7±1.4



Fig. S2 | **Number of detected tracks vs time for the spin coated samples listed in Tab. Sabove.** We performed a qualitative analysis on the spin coated films measured by GI-WAXS (see Tab. Sabove) to demonstrate that grain rotation occurs also in spin coated samples. Here we show plots of the number of detected tracks vs time. This plot is analogous to the one in Fig. S2c in the manuscript. Note here that here the tracks were not manually sorted as discussed in the Methods. The plots clearly show that the number of detected tracks decreases as the annealing temperature increases. The lowest amount of detected tracks is measured when the sample is measured under dry He.



Video 12 | Detected tracks during isothermal deposition at 60 °C (spray coated sample). Figure shows snapshots from <u>https://youtu.be/bcnMLHoI7RY</u>.



Video 13 | **Detected tracks during isothermal annealing at 110 °C (spray coated sample)**. Figure shows snapshots from <u>https://youtu.be/YPzBwhG1rr0.</u>



Fig. S3 | Number of detected tracks as a function of the deposition time (td), during isothermal deposition at 60 °C. Tracks detected here belong to the precursor phase.



Fig. S4 | Statistics on the maximum azimuthal displacement of 529 precursor (black) and 72 perovskite (red) tracks during the anneal. 42.7% of precursor tracks rotate clockwise, 57.3% rotate counterclockwise. 41.6% of perovskite tracks rotate clockwise, 58.3% rotate counterclockwise. The absence of values around zero is due to the tracks selection criteria described in Methods.



Fig. S5 | Statistics on T_{start} , T_{end} , T_{rise} of 529 precursor (black) and 72 perovskite (red) tracks during the anneal. T_{start} is the time at which the track starts, T_{end} is the time at which the track ends, T_{rise} is the time that takes to the azimuth to increase/decrease from 10% to 90% of its last final value.



Fig. S6 | Statistics on the mean instantaneous velocity ($\Delta \chi/\Delta t$) of 529 precursor (black) and 72 perovskite (red) tracks during the anneal. The mean of the mean $\Delta \chi/\Delta t$ for precursor tracks rotating counterclockwise (negative velocity) is -0.17±0.12 ° min⁻¹, and 0.17±0.11 ° min⁻¹ (positive velocity). The same for perovskite tracks rotating counterclockwise is -9.0±3.7 × 10⁻³ ° min⁻¹, and 7.6±3.8 × 10⁻³ ° min⁻¹.



Fig. S7 | Statistics on the mean χ of 529 precursor (black) and 72 perovskite (red) tracks during the anneal. The statistic does not show any preferential orientation for the detected diffraction spots.



 Δq and $\Delta \chi$ correlation coefficient

Fig. S8 | Statistics on the correlation coefficient (ρ) between $\Delta \chi$ and Δq of 529 precursor (black) and 72 perovskite (red) tracks during the anneal. A $\rho = 1$ indicates that the two vectors are correlated, while a $\rho = -1$ indicates that the two vectors are negatively correlated. The mean ρ for positively correlated $\Delta \chi$ and Δq is 0.55±0.26 and 0.54±0.27 for precursor and perovskite tracks respectively. The mean ρ for negatively correlated $\Delta \chi$ and Δq is -0.54±0.28 and 0.44±0.30 for precursor and perovskite tracks respectively.



Fig. S9 | Statistics on the correlation test (pval) between $\Delta \chi$ and Δq of 529 precursor (black) and 72 perovskite (red) tracks during the anneal. The correlation coefficient is calculated with the Matlab function 'corr', which also returns *p*-values for Pearson's correlation using a Student's t distribution for a transformation of the correlation. If this value is below 0.5 the correlation is high.



Fig. S10 | Statistics on the spectral coherence between the power spectrum of $\Delta \chi$ and Δq of 529 precursor (black) and 72 perovskite (red) tracks during the anneal. The power spectral density is estimated with the Matlab function 'periodogram'. This is used for the calculation of the squared spectral coherence. The Matlab function 'mscohere' finds the magnitude squared coherence estimate of the input signals using Welch's averaged, modified periodogram method. Values close to 1 indicate highly coherent spectra.



Fig. S11 | Self-Organizing Map (SOM) trained for the discrimination of precursor tracks during the anneal. a, Matlab representation of the self-organizing map. The input vectors $[\chi_1 q_1 \chi_2 q_2 \dots \chi_{Ni} q_{Ni}]$ representing each track (see Methods) are 200 element long. The network consists of a layer of $4 \times 4 = 16$ neurons or clusters and is trained 5 times (1000 epochs) with the default algorithm (trainbu). b, When a track vector is inputted to the SOM, the SOM returns one of the 16 clusters. Each of the 16 subplots represents a cluster of tracks. The abscissa represents $\Delta \chi$ (from -5 to 5°), while the ordinate represents Δq (from -0.03 to 0.03 Å⁻¹). c, Tracks are further manually classified based on the Cartesian quadrant where they are located. d, Another representation of the SOM with the number of hits (tracks) per cluster.



Fig. S12 | Self-Organizing Map (SOM) trained for the discrimination of the perovskite tracks during the anneal. a, Matlab representation of the self-organizing map. The network consists of a layer of $2 \times 2 = 4$ neurons or clusters and is trained 5 times (1000 epochs) with the default algorithm (trainbu). b, When a track vector is inputted to the SOM, the SOM returns one of the 4 clusters. Each of the 4 subplots represents a cluster of tracks. The abscissa represents $\Delta \chi$ (from -5 to 5°), while the ordinate represents Δq (from -0.03 to 0.03 Å⁻¹). c, Another representation of the SOM with the number of hits (tracks) per cluster.



Fig. S13 | **SEM images on spray coated and spin coated samples (see Tab. S1) annealed for different periods of time.** Zoom 1. SEM images were taken with an FEI Inspect F. We used a 5 kV incident beam and a secondary electron detector.



Fig. S14 | **SEM images on spray coated and spin coated samples annealed for different periods of time.** Zoom 2 (images are taken at higher magnification on the same area displayed in the previous Fig.).



Fig. S15 | **SEM images on spray coated and spin coated samples annealed for different periods of time.** Zoom 3 (images are taken at higher magnification on the same area displayed in the previous Fig.).

Video 14 | Spray coated film probed in-situ on the same film area during the anneal by an optical microscope in reflection mode: <u>https://www.youtube.com/watch?v=GUeY2E3K49c</u>. The measurements were performed with a commercial hotplate placed under an Axioskop 2 MAT mot Zeiss Optical Microscope with a 32x magnification lens and an Axio Cam HRc. The spray coated film (spray coated as described in the manuscript) was annealed at 110°C for 95 min.

Video 15 | **Precursor tracks, cluster 1**: <u>https://youtu.be/wvsURc_-Xzc</u>. The first part of the video shows the sequence of diffraction images recorded during the annealing phase. The coloured markers indicate the detected diffraction spots location ('o' is the first location, '*' is the current location). The second part of the video shows image sequences of each moving spot with graphs of $\Delta \chi$, Δq , $\Delta \chi$ vs Δq , spot area, spot line profile and its full width at half maximum (FWHM), which is used in the Scherrer equation. The straight line in the image sequence indicates the range of scattering vector values used for extracting the line profile. The yellow contour represents the diffraction spot contour. The red arrows a field lines represent the velocity vectors of the moving spot.

Video 16 | Precursor tracks, cluster 2 (spray coated sample): <u>https://youtu.be/b_xBObOV6tQ</u>. See Video 5 caption.

Video 17 | Precursor tracks, cluster 3 (spray coated sample): <u>https://youtu.be/CeXT4aXQD5I</u>. See Video 5 caption.

Video 18 | Precursor tracks, cluster 4 (spray coated sample): <u>https://youtu.be/8ZIX5Zr8Fog</u>. See Video 5 caption.

Video 19 | Precursor tracks, cluster 1 (spray coated sample): <u>https://youtu.be/1QLHIEmbJhY</u>. See Video 5 caption.

Video 20 | Perovskite tracks, cluster 2 (spray coated sample): <u>https://youtu.be/TQPhJPoU1Ak</u>. See Video 5 caption.

Video 21 | Perovskite tracks, cluster 3 (spray coated sample): <u>https://youtu.be/aWyTpoGGyi0</u>. See Video 5 caption.

Video 22 | Perovskite tracks, cluster 4 (spray coated sample): <u>https://youtu.be/EEdfapUI9cA</u>. See Video 5 caption.

References

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