Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information:

Large, Formamidinium Lead Trihalide Perovskite Solar Cells Using Chemical Vapor Deposition with High Reproducibility and Tunable Chlorine Concentration

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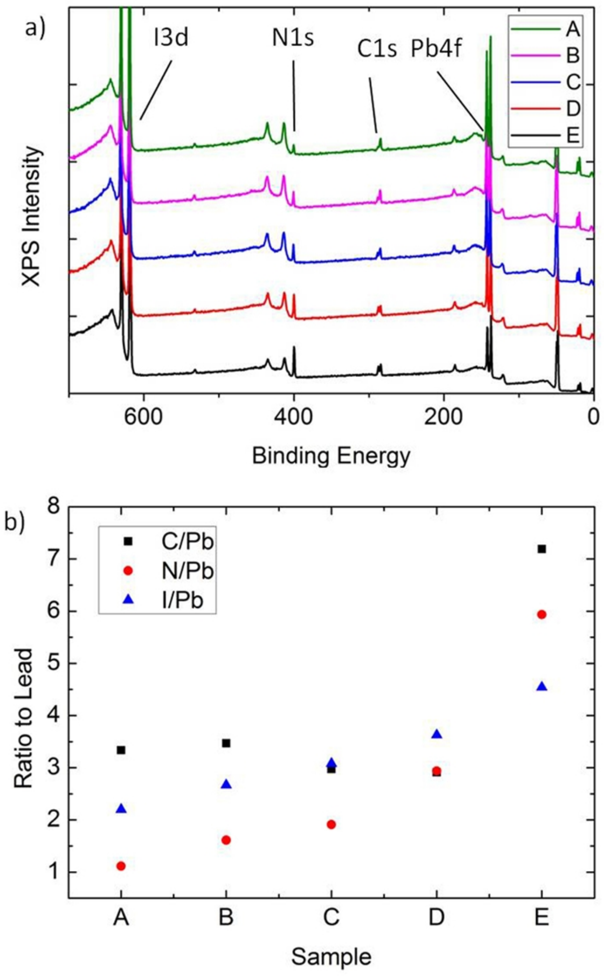

Fig. S1 FAI concentration gradients in low temperature CVD growth. The figure shows X-ray photoelectron spectra (XPS) of perovskite on FTO. Samples were prepared at 120°C using a CVD process and were loaded in positions 3 cm apart (also presented in Fig. 2 in the main text). The sample farthest from the FAI source was at position A and the sample closest to the FAI was position E. a) XPS spectra of the 5 samples. c) Concentration ratios of iodine, carbon, and nitrogen relative to lead. I3d, C1s, N1s, and Pb4f peak areas were used to measure relative concentrations, and were normalized with sensitivity factors. Iodine, carbon, and nitrogen peaks increase in intensity as samples approach the FAI source, while lead peaks decrease. This confirms that the different samples correspond to different concentrations of FAI, and that the concentration of FAI is responsible for the different phases.

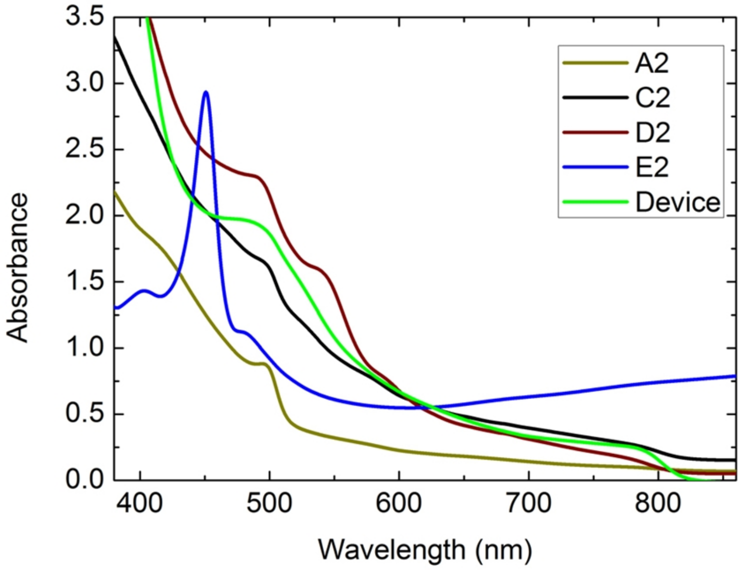

Fig. S2 Absorption spectra of different phases of perovskite. Ultraviolet-Visible spectroscopy from a working solar cell and perovskite samples from batch 2**.** The batch A2-E2 was measured with ToF-SIMS (Fig. 5) in the main text. Spectra were normalized using a glass slide or FTO/TIO2 glass. A defined absorption edge at ~830 nm begins to form when the film turns red (sample D2), and is clearly seen in the device. An absorption peak forms at ~450 nm when the film has turned yellow (sample E2). Sample E2 appears cloudy and has a significant amount of scattering.

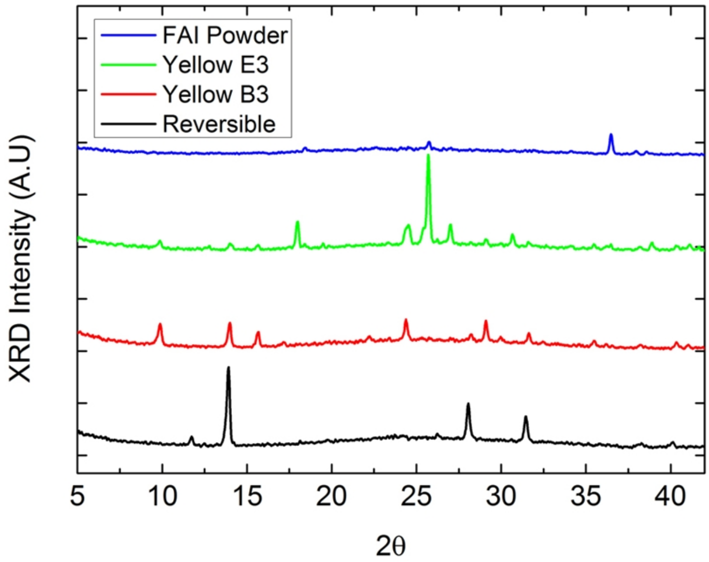

Fig. S3 Crystal structure of yellow phases and perovskite from the reversible formation process. The figure shows X-ray diffraction spectra of perovskite samples and FAI powder. Spectrum of a perovskite film showing that films formed by the reversible process can return to perovskite crystal structure with peaks at 13.8°, 28.0°, and 31.5° after turning to a yellow film similar to film E. XRD spectra of two yellow films grown at 150°C from locations B (9.9°, 15.7°, and 29.1°) and E (18.0°, 25.7°, 27.0°, and 30.7). FAI powder measured by XRD was found to have prominent peaks at 18.5°, 25.8°, 36.5°. It is possible that the prominent peak at 25.7° in yellow E3 originates from crystalline FAI, but no other peaks from yellow films are common to either perovskite or FAI powder. This suggests that there are at least two lead-FAI crystal structures that can be formed by CVD.

	FAI Time [180C]	Substrate Temp.	Orientation	V_{oc}	J_{sc} [mA/cm^2]	*FF*	*PCE* [%]
Highly Undersaturated	**6 min**	**30 min, 160 C**	**Vertical**	**0.9 +/- 0.03**	**17.2 +/- 2.4**	**51 +/- 5**	**7.8 +/- 1.3**
Undersaturated	**6 min**	**30 min, 160 C**	**Flat**	**0.97 +/- 0.01**	**19.5 +/- 1**	**56 +/- 3**	**10.5 +/- 0.7**
Saturated	**16 min**	**60 min, 160 C**	**Flat**	**0.97 +/- 0.02**	**21.6 +/- 0.8**	**62 +/- 2**	**13.0 +/- 0.2**
Oversaturated	**7 min***	**60 min, 160 C**	**Flat**	**0.99 /- 0.01**	**20.4 +/- 0.8**	**57 +/- 4**	**11.5 +/- 1.0**
Highly Oversaturated	**12 min***	**160 C-> 140 C, 60min**	**Flat**	**0.93 +/- 0.8**	**18.5 +/- 3**	**46 +/- 8**	**8.0 +/- 1.8**
PbI_2 ($PbCl_2$ “Undersaturated")	**6 min**	**30 min, 160 C**	**Flat**	**0.93 +/- 0.05**	**17.5 +/- 1.3**	**45 +/- 9**	**7.4 +/- 2.0**
PbI_2 Saturated	**4 min*, [175 C]**	**60 min 160 C**	**Flat**	**0.88 +/- 0.02**	**20.6 +/- 0.7**	**44 +/- 6**	**7.8 +/- 0.8**
Large Area 1 cm^2	**5 min***	**60 min 160 C**	**Flat**	**0.99 +/- 0.03**	**17.7 +/- 1.0**	**43 +/- 1**	**7.5 +/- 0.3**

Table S1 Summary of growth conditions and device performance from all batches of solar cells presented in the main text. Times marked with (*) had the FAI crushed prior to deposition to decrease deposition time and improve batch to batch reproducibility. The data table represents a total of 66 devices, where the average number of devices per batch was 9, excluding the large area batch, where only two devices were made.

Scan Condition	V_{oc}	J_{sc} [mA/cm²]	*FF*	*PCE* [%]
Nominal 0.4 Vs^{-1} Forward	1.03	20.9	66	14.2
Slow 0.06 Vs^{-1} Forward	1.03	19.6	58	11.7
Slow 0.06 Vs^{-1} Reverse	1.02	20.2	43	8.9

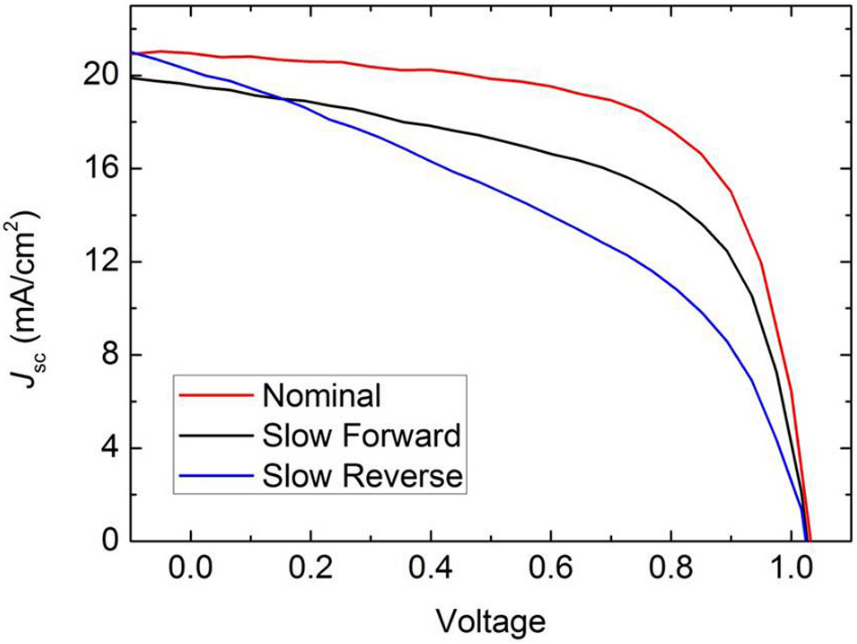

Fig. S4 Dwell Time affects J_{sc} but not hysteresis. The figure shows IV measurements from the highest-performance solar cell. The dwell time for solar cell measurements was increased from the nominal 10 ms per point with a 0.4 V/s sweep rate to 500 ms with 0.06 V/s. Increasing the dwell time impacts the J_{sc}, but does not appear to improve relative hysteresis. The above example is consistent with all cells measured in reverse bias, where the average efficiency was 62% +/- 8% of the same cell measured in forward bias. This decrease in efficiency when measured in reverse is primarily due to a decrease in fill factor by 65% +/- 7% of the cell's value measured in forward bias. This shows that hysteresis is present in FAI devices for fast and slow scan rates.

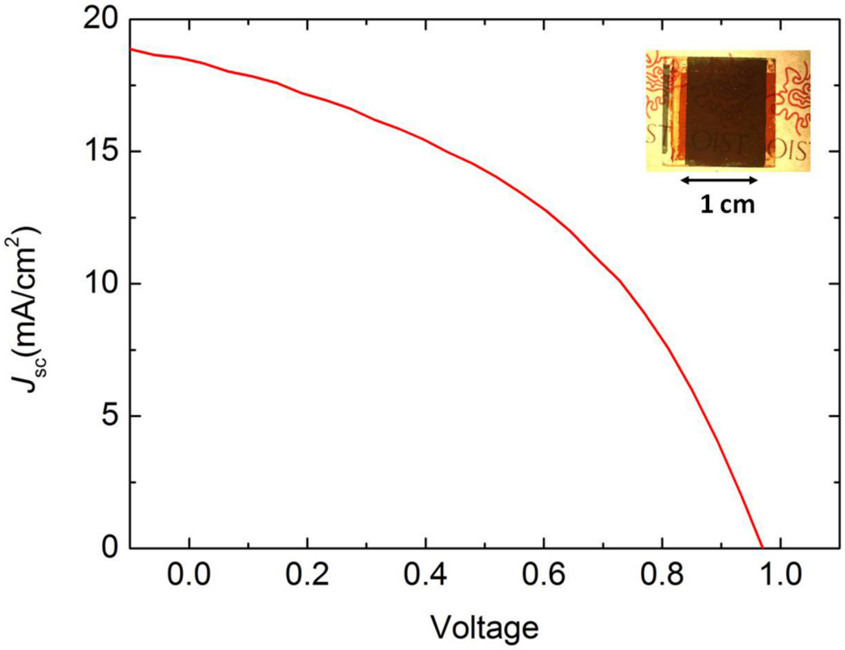

Fig. S5 Best performing large solar cell (1 cm^2) made using a reversible CVD process. The insert shows that the cell is semitransparent. The cell was measured to have V_{oc} of 0.97 V, J_{sc} of 18.4 mAcm^{-2}, fill factor of 43, and efficiency of 7.7%.

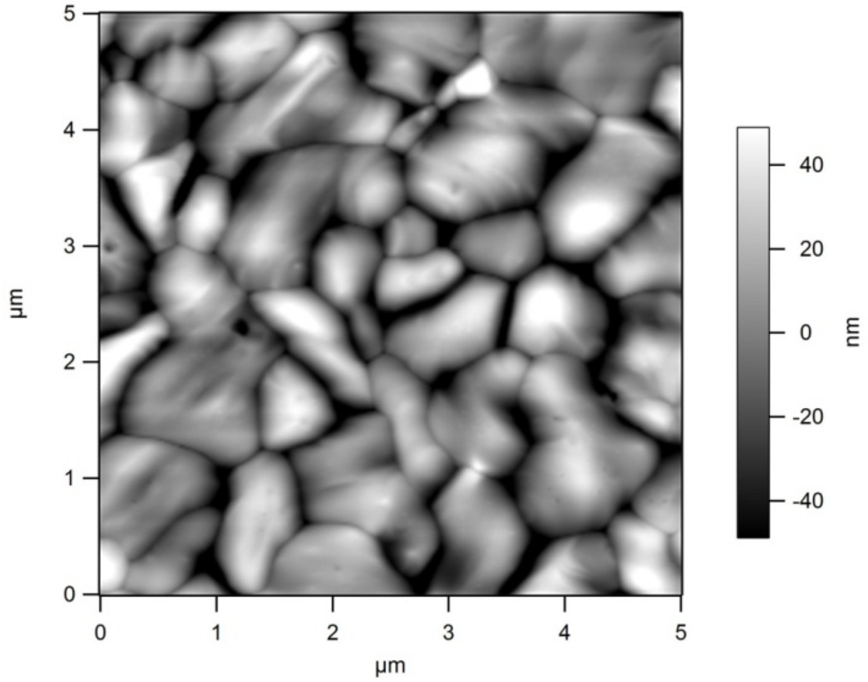

Fig. S6 Samples grown using PbI_2 can have large grains but low efficiency. The figure shows an atomic force microscope image of saturated perovskite growth using a 100 nm layer of PbI_2. Surface roughness was 23 nm. Grain size is comparable to those of samples created with “saturated” $PbCl_2$ growth, but devices made from this batch had lower efficiency.

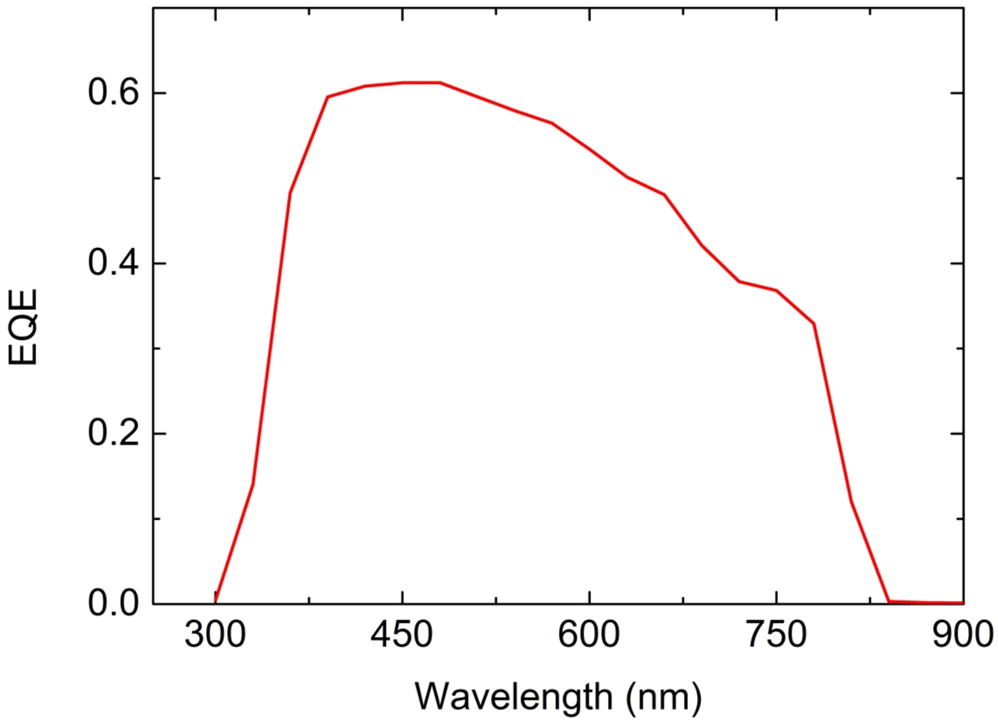

Fig. S7 External quantum efficiency measurement results. This measurement was performed with 60 sec of 1 sun pre-illumination, and within a few minutes mounted in the EQE setup and measured under low light intensity. The integrated J_{sc} for this EQE was around 13.6 mA/cm^2 using the AM1.5G illumination. The shape of the curves reflects the absorption spectrum, and may change depending on light intensity. To better understand the effect of light pre-illumination we measured EQE on another sample at a single wavelength (450 nm). At this wavelength, this sample without pre-illumination had an EQE of 39%. Then we illuminated the sample with a fiber optic lamp with an intensity of ~30 mW/cm2 for 2 min. The lamp was shut off and the measurement started seconds later, which provided an EQE of 69%. Therefore, it is clear that the integrated current from the EQE sensitively depends on pre-illumination conditions..

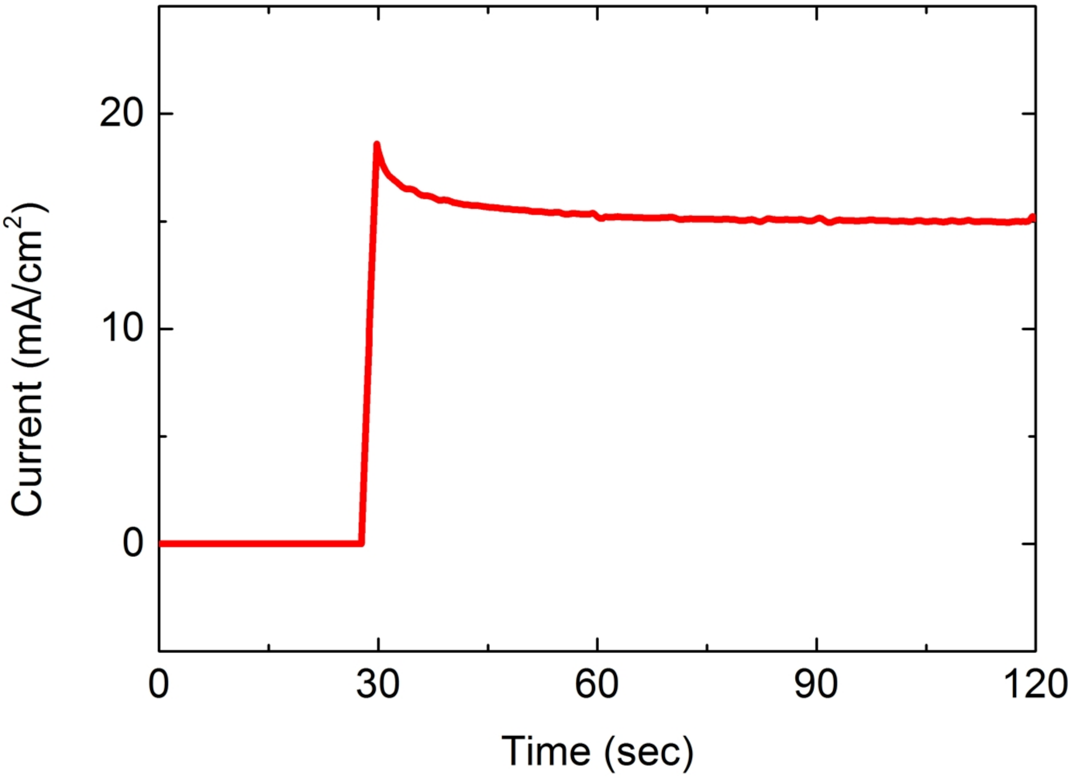

Fig. S8 Steady state current measurement. The cell was illuminated under 1 sun, and after 30 sec the circuit was closed and biased at 0.75 V. The steady state current is approximately 15 mA/cm^2. This gives a steady state power conversion efficiency of around 11.3%. This efficiency is comparable to the slow scan measurement presented in Figure S4.

Average chlorine gas concentration. The average chlorine concentration during growth was calculated based on the masses of $PbCl_2$ and FAI used in the CVD process. The mass of PbCl2 on the substrates can be found based on the film thickness and substrate area. The melting temperature of $PbCl_2$ is 501°C so it is assumed that no chlorine sublimates from the substrates unless it is replaced with iodine.

- Volume of 8 $PbCl_2$ cells,

  8 cells × ((1.5cm)^2 × 100 × 10^{-7}cm) × (5.85 g/cm^3)= 1 mg of $PbCl_2$

  PbCl2 is 278 gram/mol, 1 mg of $PbCl_2$ is 3.6 x10^{-6} mols or 7.2 ×10^{-6} mols Cl ions

- Growth consumed 30-50 mg FAI; therefore full conversion occurs at ~40 mg of sublimated FAI.

- The reaction completes in ~30 min, with 1 L/min of N_2 flow and consumes ~40 mg of FAI

  Average concentration of FAI is 40 mg / 30 L = 1.3 mg/L

  FAI is 172 g/mol so 1.3 mg/L/172 g = 7.7 × 10^{-6} mol/L at 1 atm

  Flow volume is measured at 1 atm, while pressure is 100 Pa, so the concentration in vacuum is ~8 × 10^{-9} mol/L

  We assume no FAI concentration gradient in the growth region at 160°C.

- We assume all chlorine is converted during the 30 min growth.

  7.2 × 10^{-6} mols Cl/ 30 L = 2.4E × 10^{-7} mol/L at 1 atm, or ~2E × 10^{-10} mol/L at 100 Pa

- The average concentration of chlorine to total halide is 3%.

$$2.4\text{E} \times 10^{-7} \text{ Cl mol/L} / (2.4\text{E} \times 10^{-7} + 7.7 \times 10^{-6} \text{ halide mol/L}) = 3\%$$

This 3% concentration is an average value over the entire growth process and the relative fraction of chloride ions is likely much higher during early stages of growth. However, the above calculation demonstrates that the concentration of chloride ions is not negligible and suggests that chlorine likely plays a role in perovskite formation.

Video. The video includes the 5 growths at different levels of saturation listed in table 1, and a clop of a 1×1 cm cell powering a fan. The videos of growth are played 240 times faster than real time.