Supplementary Information for
Halide Perovskite Dynamics at Work:
Large 2D cations at 2D-on-3D Interfaces are mobile
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Other supplementary materials for this manuscript include the following:
Movies (Movie 1-3)
**T1. Preparation of 2D/3D HaPs**

The 2D/3D films were prepared on highly (p-) doped Si (100) wafers. Preparation on the ultra-flat Si substrates was essential for avoiding beam damage during preparation of lamellae in the scanning electron microscope/focused ion beam (SEM/FIB) microscope due to sample charging or heating. Prior to deposition of the perovskite layer, the substrates were cleaned thoroughly by sequential ultrasonication in deionized (DI) water, acetone, and isopropanol. The cleaned Si substrates were then dried under nitrogen (N₂) flow and UV-ozone treated to prepare the surfaces prior to perovskite deposition. A 1.4 M MAPbI₃ solution was prepared by dissolving the precursors Methyl-Ammonium Iodide (CH₃NH₃I, MAI) and Lead di-iodide (PbI₂) in ~1:1 ratio in a mixed solvent (7:3 vol. ratio) of γ-butyrolactone (γ-GBL) and Dimethyl sulfoxide (DMSO). The solution was stirred for 2 h at 60 °C. Then, 70 μl of this solution was spin-coated onto the cleaned Si substrates via a two-step spin coating routine, i.e., 1000 rpm for 10 s and 4000 rpm for 30 s, in a N₂ glovebox. Toluene antisolvent (0.8 ml) was dropped onto spinning substrates 5 s before the end of the spin-coating routine. The substrates were then annealed on a hot plate, initially at 60 °C for 1 min and then at 100 °C for 5 min.

For the growth of a 2D layer on the 3D film, the MAPbI₃/Si samples were quickly transferred from the glove box to a home-designed and -built, controlled-atmosphere chamber where the samples were exposed to controlled amounts of organ-amine vapors (PEA or F-PEA) under a continuous N₂ flow. After the 2D growth, the samples were returned to the glovebox and annealed at 100 °C for 1 min. The samples were then sealed in the glovebox and transferred to the FIB for TEM sample preparation, without exposure to ambient.
**Fig. S1**  (a) Lower magnification SEM images of 3D and 2D/3D bilayer films. The boundaries between the 3D grains can be clearly discerned, also after the process of 2D growth on top of 3D HaP.  (b) UV-Vis absorbance spectra of pristine 3D MAPbI$_3$ thin films (“w/o 2D”) and those with thin and thicker vapor phase surface cation exchange-grown 2D PEA$_2$PbI$_4$ on the 3D surface (“w 2D (thin ~20-30 nm)” and “w 2D (thick ~80-100 nm)”).*
**Fig. S2** C 1s, F 1s, Pb 4f, and N 1s XPS spectra of bare films of 2D FPEA\textsubscript{2}PbI\textsubscript{4} on 3D MAPbI\textsubscript{3} ("w FPEA\textsubscript{2}PbI\textsubscript{4}") and pristine MAPbI\textsubscript{3} ("w/o FPEA\textsubscript{2}PbI\textsubscript{4}") without any protective C-coat.
**Fig. S3**- Illustrating the NanoBeam Scanning Electron Diffraction experiment on a 2D/3D, PEA$_2$PbI$_4$/MAPbI$_3$ sample on FTO. The grid in the virtual bright field image (a) shows the probing regions in a 45 x 25-pixel raster scan. (b) and (c) show example electron diffraction patterns, obtained from the regions marked as red (b) and yellow (c) dots in the grid. Animation showing all diffraction patterns in the raster scan, starting from the upper left, row by row is provided in the additional supplementary material (Movie 1). The exemplary data for this figure and Movie 1 were taken on a FEI F20 Twin instrument on a Gatan Orius CCD camera using DigiScan. Raster scan and synchronized camera recording were accomplished by a custom-written DigitalMicrograph script.
Fig. S4 - Degradation of iodide perovskite into PbI$_2$ and evidence for PEA$_2$PbI$_4$ formation/migration in the bulk 3D MAPbI$_3$.

(a) Virtual bright field image of a region of a PEA$_2$PbI$_4$/MAPbI$_3$/FTO-glass substrate. The dark-needle features are of the PbI$_2$ phase, formed as degradation product of the 2D/3D perovskite phases.

(b) Angular correlation map for the (001) basal plane reflections (1.43 nm$^{-1}$) of PbI$_2$ in $P3m_1$ crystallographic phase. The bright regions in the map shows the regions of presence of PbI$_2$ domains in particular orientation wrt. to the e-beam.

(c) An example EDP from the region, marked as yellow box in (b). The EDP matches well the simulated EDP (shown below in Fig. S6) for the PbI$_2$ phase with <110> viewing axis.

(d) Angular correlation map for 2D PEA$_2$PbI$_4$ (n=1) basal plane reflections (0.6 nm$^{-1}$). The bright domains in the correlation map are seen also in the regions within the bulk, i.e., the supposedly 3D MAPbI$_3$ regions, with some very close to the FTO interface. In this case, though the evidences for ion/e-beam damage here (i.e., appearance of PbI$_2$ domains) prevents drawing conclusions about 2D diffusion into the bulk.
**Fig. S5** - The 2D domain inside the 3D matrix, shown in Fig. 4 (b) lies around a grain boundary: (a) RGB-map of the scanning NBED angular correlation map of Fig. 4 b. The regions with characteristic lattice spacings of 2D material are shown in red. Angular correlation maps for lattice spacings of the 3D perovskite are shown in green and blue. The 2D perovskite is located at the grain boundary between two 3D grains (b) STEM bright-field image taken after the scanning NBED data, shown in Fig. 4 and 5 to avoid any possible pre-damage of the area of interest in the scanning NBED experiment. White arrow marker points to the location of the relevant grain boundary.
**Figure S6** - Evidence for quasi 2D phase formation from PL measurements on samples exposed/stored at different conditions *ex-situ*, seen in the time evolution of PEA-based 2D/3D MAPbI$_3$ films under annealing at 80°C in (a) inert atmosphere, (b) in 50-60% RH in the dark, and (c) 50-60% RH under white light illumination. PL peaks marked as n=2, n=3 correspond to higher n quasi-2D perovskites that form under different exposure/storage conditions. The time evolution of FPEA-based 2D/3D MAPbI$_3$ films is shown in (d) under annealing at 80°C in inert atmosphere, (e) in 50-60% RH in the dark, and (f) 50-60% RH with annealing 80°C. PL peaks, marked as n=2 refer to the n=2 quasi-2D perovskite, formed under different exposure/storage conditions. **Insets** shows the magnified region of interest in the spectrum, relevant to n=1 and n=2,3 PL emissions.
Figure S7- Simulated real space crystal structure for PbI$_2$ (P3m1) and EDP (viewing direction <uvw>=[110]).
Figure S8- (a) Region (marked in red) of the sample lamella from which a time series of electron diffraction patterns for the 3D MAPbI$_3$ perovskite is shown in the additional supplementary material (Movie 2). For the time series, 1000 electron diffraction frames per second were recorded. In the movie every 10$^{th}$ frame is shown. In the first 50 ms the beam is unblanked and settles on the target position marked within the red enclosure. (b)-(d) Few frames of time series diffraction patterns from the 3D perovskite region.
Figure S9- Simulated EDP for MAPbI$_3$ with viewing direction $uvw = <111>$
Figure S10- (a) Region (marked in red) of the sample lamella from which time series of electron diffraction is shown for the 2D FPEA$_2$PbI$_4$ perovskite, as a movie in the additional supplementary material (Movie 3). For the time series 1000 electron diffraction frames per second were recorded (as noted earlier for the 3D perovskite). In the movie every 10$^{th}$ frame is shown. In the first 40 ms the beam is unblanked and settles on the target position marked with in red enclosure. (b)-(d) Few frames of time series diffraction patterns from the 2D perovskite region.
T2. Additional Discussion on the FIB Procedure and the Role of ex-situ Carbon coat

Using the conventional procedure, we observed significant Ga and Pt presence in the electron beam-evaporated carbon layer and into the perovskite film (see black arrow marker in Fig. S12). With the improved procedure using an additional evaporated carbon layer (~80 nm), prior to FIB procedure, the spectra from the region of interest display a minor peak only for the Ga K transition (black arrow marker). The associated Ga concentration of 1.5 % is a lower bound for the Ga content, which is determined by sputter redeposition onto the surfaces of the thin lamella during the FIB cutting and polishing procedure. The profiles of Si and Pt are nearly identical with the Ga profile in this area and represent the baseline of contamination of FIB lamella surfaces by redeposition. The C map in the lower panel does not show evidence for significant C in-diffusion into the 2D perovskite layer. Rather, there is an abrupt change in the C concentration at the interface between the 2D perovskite and the capping layer, when considering the corrugated surface morphology.
Figure S12- HAADF image (upper left corners of each panel) and EDS elemental maps and profiles, demonstrating the absence of Ga and Pt implantation into the perovskite films after the optimized FIB sample preparation. **Upper panel:** Results from standard FIB preparation using a protection layer of electron-beam deposited carbon, followed by ion-beam deposition of Pt. **Lower panel:** Results with improved capping layer, consisting of an *ex-situ* thermally deposited carbon layer and a carbon/platinum layer prepared under the electron/ion beam in the FIB. Both panels show the area of the hyper-spectral map in a dark green rectangle in the HAADF image in the upper left corner. Selected elemental maps for C, I, and Ga display their atomic percentage, relative to the sum of Pb, I, C and Ga. All false color maps have been scaled to a 0-100 at. % range from The line profiles display the variation of the atomic concentration from the substrate into the perovskite film and the protection layer (green arrow markers in the HAADF images; the green rectangle marks the averaging width, orthogonal to the line). Spectra
were extracted for representative regions of interest in the 3D perovskite layer and the 2D perovskite capping layer (yellow rectangle markers in the HAADF images).

**T3. Specimen Orientation and Drift in the NBED Experiments**

Specimen grain orientations were taken as given because we cannot afford to expose the sample to the beam, before taking the diffraction data, because such pre-exposure is much too likely to degrade the sample before capturing the inherent crystallographic information, embedded therein. Hence there is no dose budget for an attempt to tilt certain grains into a zone axis. The textured growth of 3D and 2D grains (see XRD measurements, shown in Figs. 1 d and e) in the polycrystalline film, aligning with a preferred orientation along the substrate normal, leads to a high probability for the observation of the characteristic 2D layer spacings in the capping layer, despite the random selection. Phases were identified from the symmetry and spacings in the diffraction patterns, unaffected by possible dynamical diffraction effects on reflection intensities. The combined beam/sample drift rate of the set-up is about 1 nm for a typical exposure time of 1 minute, negligible in relation to the scan field of view on the order of a micrometer.

**T4. Discussion on Electron Fluence estimation**

The probe current was measured as the current on the fluorescence screen for propagation of the beam in vacuum. The current on the fluorescence screen was calibrated against that measured with a Faraday cup. The fluence was calculated by division of the beam current by the probe area containing 95% of the electrons for an exposure time of 1 ms. At oversampling conditions, the total fluence is given by the product of the number of electrons per dwell point times the total number of scan pixels divided by the frame size. The fluence rate peaks when the probe traverses a scan position; it was approximated by dividing the electron fluence by the diameter of the probe that contains 67% of the electrons and the scan dwell time of 1 ms.

**T5. Cumulative Fluence Calculation for a 500 nm × 500 nm scan**

Consider a 500 nm × 500 nm \((A = 2.5 \cdot 10^7 \text{Å}^2)\) frame that is raster scanned in 128 × 28 pixels with a primary beam current of 1 pA \((I)\) for 1 ms \((t)\) per pixel.

Total number of electrons that reach a pixel in 1 ms scan time \((n)\):
\[
n = \frac{I \times t}{1.6 \times 10^{-19} \cdot C} = 6250 \text{ electrons}
\]
Total no. of electrons used for 128 × 128 pixels:

\[ N = 6250 \times 128 \times 128 = 1.024 \times 10^8 \]

Cumulative Fluence \((F)\):

\[ F = \frac{N}{A} = \sim 4 e/\text{Å}^2 \]

**T6. NBED Probe Size Calibration**

A diffraction-limited STEM probe was formed in the microprobe setup, with a convergence angle of 0.19 mrad when focused. Probe sizes were calibrated quantitatively from direct images taken on a Gatan OneView CMOS camera (Fig. S13). To avoid high concentration of electron flux, a setting with an under-focused electron beam was used. The under-focus was between -4 μm and -10 μm. Typical probe sizes are in the range of a few 10 nm under these conditions. We note that the shape of the diffraction-limited probe changes upon defocus, so that it is the area that contains a certain fraction of electrons that has to be taken for reference, rather than e.g., the FWHM. In addition, an uncertainty of a few nm in probe diameter originates from a lack of precision of focusing when the depth of field is several μm.

**Figure S13** - Experimental images of the diffraction limited nanobeam and quantitative probe sizes. (a) Image of the focused and defocused probe with a semi-convergence angle of 0.19 mrad. The choice of the under-focus in the experiment avoids a central intense spot (as shown in left side above). (b) Probe sizes as a function of the defocus, measured from the focus of minimum confusion. The probe shape changes with defocus; hence, the probe diameter is given as the diameter \(d_x\) of the illuminated area that contains \(x=50\%\), \(x=67\%\) or \(x=95\%\) of the electrons. Experimental data were taken at under-focus, typically between -4 μm and -10 μm. The related probe diameters are in the range of a few 10s of nm.

**Movie Captions**

**Movie 1** - Exemplary movie showing the diffraction patterns obtained from scanning nanobeam electron diffraction (NBED) experiment performed 2D/3D HaP sample

**Movie 2** - Time series NBED from 3D perovskite region of 2D/3D HaP sample
Movie 3- Time series NBED from 2D perovskite region of 2D/3D HaP sample