
Supplementary information

Strain engineering and epitaxial stabilization of halide perovskites

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Supplementary Information for:

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Supplementary Discussion 1: Current Methods to Strain Halide Perovskites

Strain engineering of halide perovskites is now receiving increasing attention in the field to improve the device performance by understanding device physics and improving materials quality. Different from the conventional semiconductors and perovskite oxides, the controllable strain engineering by heteroepitaxial growth of halide perovskites has not been achieved yet, to the authors' best knowledge, which is due to inappropriate growth methods and the absence of suitable lattice-mismatched substrates, therefore the lack of strong chemical bonds formed with the substrates.

Epitaxial growth of halide perovskites has been reported by many groups, but most of the works have been van der Waals epitaxy that is absent from strong interfacial chemical bonds¹⁻³. Despite the weak nature of van der Waals bonds, nontrivial effects from van der Waals interaction to the epitaxial halide perovskites have been demonstrated due to the soft nature of halide perovskites⁴. Besides van der Waals epitaxy, chemical epitaxy by forming interfacial ionic bonds has also been reported^{5,6}. However, due to the extremely high growth temperature (~500 °C), the interface was destroyed by the high diffusion rate of ions at such a high temperature and therefore, no interfacial strain could be detected. Other than epitaxial strain, thermally strained halide perovskites have also been studied. The thermal expansion coefficient difference between a patterned substrate and the halide perovskite was utilized to induce thermal strain to a perovskite microcrystal⁷. A thermally strained halide perovskite by introducing a phase transition of the substrate via increasing the temperature has also been demonstrated⁸. In this case, the thermal strain is highly dependent on the temperature and the magnitude of the strain cannot be well controlled.

Besides manipulating single crystalline halide perovskites, researchers are also creating strain in polycrystalline thin films by a variety of methods. One of the most popular methods is the ion substitution of a larger/smaller ion that can induce local tensile/compressive strain in the perovskite lattice^{9,10}. Local compressive strain by small ion substitution was found to improve the stability of halide perovskites¹⁰. It was demonstrated that the local compressive strain by ion substitution could suppress the vacancy formation in halide perovskites⁹. Additionally, the crystalline quality of halide perovskites could be controlled by local strain via ion substitution¹¹. Besides ion substitution, it was also reported the control of the local strain by light-induced lattice expansion¹². The local strain was found to affect the optoelectronic properties of halide perovskites by creating defect distribution heterogeneity¹³. Recently, residual strain in polycrystalline halide perovskite films induced by the thermal annealing process has been reported. The residual strain in the polycrystalline methylammonium lead iodide film was found to have an impact on the perovskite stability¹⁴. Also, residual strain in the polycrystalline mixed halide perovskite film was reported to affect the carrier dynamics¹⁵ and phase transition¹⁶. Hydrostatic pressurization was another commonly used method to apply strain to the halide perovskites. The crystal structure¹⁷ and electronic band structure including bandgap¹⁸ and carrier dynamics^{19,20} were found to be highly subjective to the applied pressure. Metallic properties of halide perovskites were also reported under applied pressure²¹.

While all of these efforts demonstrated interesting strain engineering of halide perovskites, a controllable and scalable method for strain engineering single crystal halide perovskites is still critically needed. The epitaxially strained halide perovskite demonstrated

in this study meets this need by realizing the precise control of the strain in terms of magnitude and uniformity. The chemical bonds formed at the interface, rather than the weak van der Waals interactions, not only provide strong epitaxial strain to effectively alter the material structure and properties but also endow stability against environmental fluctuations so that the strain can maintain under different temperatures and pressures, which are qualitatively different from the thermally strained and the pressurized perovskites. The magnitude of the strain can be precisely controlled by designing different lattice mismatch rather than the residual strain that shows uncertainty and uncontrollability. Enhanced optical and electrical properties have been shown in the strained halide perovskites. Therefore, this method represents a significant scientific advance compared with other reported studies to strain halide perovskites.

Supplementary Discussion 2: Characterizing MAPbCl_xBr_{3-x} Substrates and Strain-free α -Formamidinium Lead Iodide (α -FAPbI₃)

Supplementary Fig. 1a shows the X-ray Diffraction (XRD) θ - 2θ scan pattern of strain-free α -FAPbI₃ powder²². For the cubic crystal structure, the lattice parameter can be calculated by:

$$\lambda = 2d_{hkl}\sin\theta$$

where λ is the incident beam wavelength, θ is the angle of incidence, and d_{hkl} is the lattice d-spacing. For strain-free α -FAPbI₃, the (001) peak position is at 13.92° and the corresponding lattice parameter is calculated to be 6.35 Å. All other peaks in the XRD pattern

are labeled and the corresponding lattice parameters can be calculated similarly.

Supplementary Fig. 1b shows a collection of the (001) peak locations from mixed methylammonium lead chloride/bromide ($\text{MAPbCl}_x\text{Br}_{3-x}$) single crystal substrates, which, regardless of the Cl/Br ratio, are reported to have a cubic structure²³. The peak position shifts to a higher 2θ angle with increasing Cl ratio, indicating a decrease in the lattice parameter.

The $\text{MAPbCl}_x\text{Br}_{3-x}$ substrates are grown by solvent evaporation of different molar ratios of MAPbCl_3 and MAPbBr_3 solutions. With the lattice parameters derived from XRD measurements, the actual compositions of the substrates can be calculated by Vegard's Law²⁴:

$$a_{\text{MAPbCl}_{1-x}\text{Br}_x} = (1 - x)a_{\text{MAPbCl}_3} + xa_{\text{MAPbBr}_3}$$

where $a_{\text{MAPbCl}_{1-x}\text{Br}_x}$ is the lattice parameter of the mixed crystal, and a_{MAPbCl_3} and a_{MAPbBr_3} are the lattice parameters of $\text{MAPbCl}_{3.00}\text{Br}_{0.00}$ and $\text{MAPbCl}_{0.00}\text{Br}_{3.00}$ single crystals, respectively. The Cl/Br molar ratios of the precursors, the composition of the $\text{MAPbCl}_x\text{Br}_{3-x}$ crystal, and the calculated lattice parameters are summarized in Supplementary Table 1.

Supplementary Discussion 3: Strained Epitaxial Growth of α -FAPbI₃

Supplementary Table 2 summarizes the (001) XRD peak positions of the epitaxial α -FAPbI₃ on different substrates. All epitaxial samples have a shift of the (001) peak to a lower 2θ angle compared with the peak position of the strain-free crystal (13.92°), indicating an increase of the out-of-plane lattice parameter due to the in-plane compressive strain. The epitaxial α -FAPbI₃ on $\text{MAPbCl}_{0.00}\text{Br}_{3.00}$ substrate shows a minimum shift to 13.89°. When

more Cl is incorporated into the substrate, the lattice mismatch between α -FAPbI₃ and the substrate increases. The (001) XRD peak of the epitaxial α -FAPbI₃ will further shift to a lower 2θ angle, indicating a further increase of the out-of-plane lattice spacing and a stronger in-plane compressive strain. The strain values are calculated by comparing the in-plane lattice parameter of strain-free α -FAPbI₃ and epitaxial α -FAPbI₃, showing a tunable strain as high as -2.4%.

The epitaxial growth conditions are systematically studied (Supplementary Fig. 1c, d). FAPbI₃ solutions with different concentrations are deposited on the substrates at different temperatures for epitaxial growth. Since FAPbI₃ has an inverse solubility in the γ -Butyrolactone (GBL) solvent, high concentration and high temperature will accelerate the crystallization of α -FAPbI₃. In Supplementary Fig. 1c, the (001) peak position of the epitaxial α -FAPbI₃ is studied as a function of the growth temperature. The vertical orange line labels the peak position (13.92°) of the strain-free α -FAPbI₃. The results show that growth temperatures below 180°C always generate diffraction peaks larger than 13.92° , while growth temperatures above 180°C can generate peaks smaller than 13.92° . The diffraction peak position reveals the out-of-plane lattice parameter of the epitaxial thin film. When the growth temperature is too high, crystallization of α -FAPbI₃ is fast and many defects are incorporated, which would relax the strain in the α -FAPbI₃. When the growth temperature is too low, the crystallization is too slow and Cl⁻/Br⁻ ions may dissolve from the substrate and re-crystallize into the epitaxial α -FAPbI₃, forming mixed alloys at the interface, although MAPbCl_xBr_{3-x} has an extremely low solubility in GBL. Diffraction peaks larger than 13.92° provide evidence for uniform lattice contraction caused by the incorporation of smaller Br⁻

and Cl⁻ ions.

The epitaxial growths with different FAPbI₃ precursor concentrations are also investigated (Supplementary Fig. 1d). Similar to the effect of temperature, FAPbI₃ precursor concentrations that are too high will result in fast crystallization and a high defect concentration. Precursor concentrations that are too low will lead to slow α -FAPbI₃ crystallization, and thus the incorporation of Cl⁻/Br⁻ ions that form alloys at the interface.

Supplementary Discussion 4: Quality of the Epitaxial Films

The crystalline quality of the substrate is found to have a significant impact on the quality of the epitaxial thin film since defects in the substrates will propagate through the epitaxial layer and relax the strain. The substrate crystal quality prepared using the Inverse Temperature Crystallization (ITC)²⁵ (Extended Data Fig. 1a) and the Slow Solvent Evaporation (SSE) methods (Extended Data Fig. 1b to 1f) are systematically characterized. The Full Width at Half Maximum (FWHM) value in rocking curve measurements characterizes crystal mosaicity. Substrates grown by the SSE method show a much smaller FWHM value ($\sim 0.020^\circ$) compared with those by the ITC method ($\sim 0.084^\circ$) due to the extremely slow crystallization speed of SSE, indicating a higher crystal quality of substrates prepared by the SSE than those by the ITC.

Extended Data Fig. 1g shows (001) XRD patterns of epitaxial α -FAPbI₃ grown on substrates with high quality (red curve) and low quality (black curve). For α -FAPbI₃ grown on the high-quality substrate, the FWHM of the XRD peak is also smaller than α -FAPbI₃

grown on the low-quality substrate. Additionally, the epitaxial α -FAPbI₃ grown on the high-quality substrate maintains the strained status with a shifted diffraction peak while the epitaxial α -FAPbI₃ grown on the low-quality substrate has a (001) peak close to that of the strain-free sample at 13.92° (position of the dashed line).

Evidence for the strain relaxation and the growth model can also be found by studying the surface topography of the epitaxial crystal. Atomic force microscopy is used to characterize topographic features of a fully strained film and a fully relaxed film under the tapping mode. The topography of the fully strained film (Extended Data Fig. 2a) shows a smooth surface with small terrains. The stepwise height profile (Extended Data Fig. 2b) corresponds to the red line in Extended Data Fig. 2a. Each step has a height of ~0.64 nm, the same as the height of a strained α -FAPbI₃ unit cell. This reveals that the epitaxial growth of α -FAPbI₃ follows a layer-by-layer model²⁶. Besides, no obvious cracks or pits can be observed, indicating a coherent growth of the epitaxial layer on the mismatched substrate.

The areal elastic strain energy will increase with the epitaxial layer thickness, which leads to the formation of defects (e.g., dislocations) that relax the strain energy. Also, the dislocations will glide and propagate to form cracks and pits at the surface of the epitaxial layer. The rough surface of the fully relaxed film shows the existence of such dislocations (Extended Data Fig. 2c). The corresponding height profile shows a very rough surface morphology, which indicates strain relaxation (Extended Data Fig. 2d).

α -FAPbI₃ fails to epitaxially grow on substrates with a Cl ratio higher than 50% (i.e., higher Cl content than that in MAPbCl_{1.50}Br_{1.50}), because higher levels of lattice mismatch will dramatically increase the strain energy and make the epitaxial growth less

thermodynamically favorable. Supplementary Fig. 2b shows the optical image of growth results on a $\text{MAPbCl}_{2.00}\text{Br}_{1.00}$ substrate prepared using the same method as the other substrates. In this case, the α -FAPbI₃ randomly crystallizes on the substrate, without forming a uniform epilayer; most of the black α -FAPbI₃ crystals undergo a phase transition to yellow δ -FAPbI₃ due to the phase instability of α -FAPbI₃ at room temperature.

Supplementary Discussion 5: Mechanisms of XRD Diffraction Peak Broadening

For XRD diffraction peak broadening, common reasons include²⁷: 1) lattice strain, 2) crystalline dimension, 3) misorientation induced by defects, 4) thermal movement of the atoms around the equilibrium states, and 5) instrumental effects like focusing imperfection. The fourth and fifth reasons are irrelevant to this study.

We attribute the main contributions of the diffraction peak broadening in Fig. 1c to the increased lattice strain and the reduced crystalline dimension rather than the misorientation. Based on the Williamson-Hall equation²⁸, the diffraction peak FWHM is linearly related to the lattice strain and reversely related to the crystalline dimension²⁷. In fact, such diffraction peak broadening is commonly reported in thin film heteroepitaxial growth where the thin epitaxial films usually exhibit broader diffraction peaks due to the lattice strain and low thickness²⁹.

In general, dislocation-induced lattice distortion and misorientation can also lead to broadening of the XRD diffraction peaks. For the strain relaxation of the epitaxial film, however, the diffraction peak broadening due to the dislocations usually leads to a huge

broadening that is several times broader than that of the free-standing materials and the fully-strained materials³⁰. We investigate the FWHM of the diffraction peaks in the epitaxial α -FAPbI₃ thin film under different strains. Results show that the diffraction peak FWHM of the free-standing single crystals is $\sim 0.05^\circ$ while the diffraction peak FWHM of the epitaxial α -FAPbI₃ thin film is $\sim 0.07^\circ$, suggesting a small broadening rather than the large broadening by the strain relaxation (Supplementary Fig. 3a).

We study the diffraction peak FWHM of the strained and the strain-relaxed α -FAPbI₃ thin films in Extended Data Fig. 1g. Note that in this case, we exclude the influence of the thickness-induced diffraction broadening by using films with the same thickness. Strain is relaxed by adopting a substrate with a high density of dislocations for the epitaxial growth. The XRD diffraction patterns shown in Extended Data Fig. 1g indicate that the strained epitaxial α -FAPbI₃ thin film shows a shift to the lower diffraction angle due to the in-plane compressive strain compared with that of the strain-relaxed epitaxial α -FAPbI₃ thin film. A broadening effect due to the high dislocation density of the strain-relaxed epitaxial α -FAPbI₃ thin film is also shown. Statistical study of the diffraction peak FWHM (Supplementary Fig. 3b) shows that the diffraction peak of the strain-relaxed α -FAPbI₃ is much broader (FWHM $\sim 0.25^\circ$) than that of the strained α -FAPbI₃ (FWHM $\sim 0.07^\circ$). Therefore, we can conclude that the broadening in the XRD diffraction peak in Fig. 1c is not due to strain relaxation.

Supplementary Discussion 6: Raman Spectroscopy and Simulation

1. Discussion of the Raman spectroscopy measurement

Full Raman spectra of the strain-free (Supplementary Fig. 4a) and the -2.4% strained (Supplementary Fig. 4b) α -FAPbI₃ show that there is only one peak in the region between 0 cm⁻¹ and 1200 cm⁻¹, which can be attributed to the vibration of Pb-I bonds^{22,31}. Note that the broad shoulder peak at ~250 cm⁻¹ in the strain-free sample is attributed to the Pb-O bond from the oxidation of Pb-I bond induced by the incident laser³¹. During the fitting process, the spectra were fitted with both Pb-I and Pb-O peaks, while only the Pb-I peaks were shown in Fig. 1f.

Raman spectroscopy is also used to study the substrates (Supplementary Fig. 4e) using a 488-nm laser as the excitation source. No Raman signals can be detected from these substrates in the wavenumber range of interest. Therefore, all Raman signals in this study are originated from the epitaxial thin film.

Thickness-dependent Raman study is based on epitaxial α -FAPbI₃ thin films on substrates with the same composition. The results show that increasing the epitaxial thin film thickness will cause strain relaxation (Supplementary Fig. 4f). The trend is similar to the strain-dependent Raman spectra in Fig. 1e.

2. Raman spectra simulation and peak broadening

The peaks are fitted, and the peak broadening can be attributed to the emergence of a shoulder peak due to the strain-induced out-of-plane bond elongation. This phenomenon is also reported in other strain-dependent Raman studies³²⁻³⁴.

To further confirm that the peak broadening in the Raman spectra originates from the strain-induced lattice deformation, we simulate the Raman spectra with first-principles calculations by the CASTEP in Materials Studios. The Raman spectra are simulated from 100 cm^{-1} to 400 cm^{-1} to compare with the experimental data.

Supplementary Fig. 4c shows the comparison between the experimental and simulated Raman spectra of the strain-free α -FAPbI₃ lattice. Simulated results show a Raman peak at 124 cm^{-1} , which can be assigned to the stretching of the Pb-I bond. This is correlated with the Raman peak at $\sim 136 \text{ cm}^{-1}$ in the experimental result. Underestimations of the simulated Raman peak wavenumbers are commonly reported³⁵⁻³⁷. Possible explanations may be that the anharmonicity of the bonds and the van der Waals interactions (between the inorganic cages and organic cations) can affect the simulated results³⁶. Besides, the assignment of the Pb-I stretching peak also agrees with the reported studies^{38,39}. Meanwhile, we also identify a weak peak at 377 cm^{-1} from the simulated Raman spectrum, which can be assigned to the bending of the FA⁺ cation. However, this peak vanishes in the experimental spectrum, probably because the organic cations in halide perovskites are highly dynamic in the inorganic framework⁴⁰⁻⁴². The reorientation of the cation will lead to the weakening of the peak under room temperature⁴³. This is also the reason why low-temperature Raman, which can freeze the orientation of the organic cation, can resolve the signal from the organic cations in halide perovskites^{36,43}. Note that the weak Raman band at $\sim 250 \text{ cm}^{-1}$ from the experimental Raman spectrum is assigned to the Pb-O bond induced by the laser oxidation³⁸.

We then apply -2.4% strain to the α -FAPbI₃ lattice and comparison between the experimental and simulated Raman spectra of the strained α -FAPbI₃ lattice is shown in

Supplementary Fig. 4d. An obvious peak splitting due to the in-plane Pb-I bond compression and the out-of-plane Pb-I bond stretching can be observed from the simulated Raman spectrum. This agrees with the experimental Raman peak, which shows obvious broadening due to the peak splitting. In fact, the strain-induced Raman peak splitting is also reported in other materials³²⁻³⁴. We also notice the increase of the peak intensity, which is due to the breakage of the Raman-inactive cubic symmetry⁴⁴.

Therefore, we demonstrate that the Raman peak broadening originates from the strain-induced peak splitting. Strain leads to the in-plane compression and out-of-plane stretching of the Pb-I bonds in the α -FAPbI₃ lattice, splitting the Pb-I stretching peak, and broadening the peak FWHM.

Supplementary Discussion 7: First-Principles Calculations of the Strained α -FAPbI₃

First-principles calculations allow a better understanding of the structural deformation and prediction of any emerging new properties. Cubic α -FAPbI₃ unit cells are calculated with the N-N axis of the FA⁺ cation along (001), (101), and (111), respectively (left panel of Extended Data Fig. 3a). These three low Miller index directions represent FA's typical orientations, and their calculated total energies could reveal potential orientation preferences. As the first step, we optimized the cubic lattice parameter a for each orientation to obtain the lowest total energy. Our calculations show $a = 6.35$ Å for the FA along (001), $a = 6.40$ Å for the FA along (101), and $a = 6.37$ Å for the FA along (111). The optimized structure with the FA along (101) has the lowest total energy of -52.73 eV, and the optimized structure with the

FA along (001) shows the highest total energy of -52.68 eV. The total energy difference between these two structures is within 50 meV, and thus the structural model with FA along (101) direction was used in our calculations.

Then we applied bi-axial strains in the *ab*-plane of the optimized structure for each orientation. The range is from 3% tensile strain to -3% compressive strain. The strained cells keep their original FA orientation after optimization along the *z*-direction. For bandgap calculations, spin-orbit coupling (SOC) was incorporated due to the heavy element Pb, and hybrid functionals within Heyd–Scuseria–Ernzerhof (HSE) formalism with 25% Hartree–Fock (HF) exchange were employed. The calculated bandgap energy (lower right of Extended Data Fig. 3a) and cell volume (upper right of Extended Data Fig. 3a) are displayed as a function of the bi-axial strain. The cell volume decreases as the strain changes from tensile to compressive for each FA orientation. This is a result of the decreased *a* and *b* and slightly increased *c*. The bandgap decreases as well when the strain changes from tensile to compressive for each FA orientation.

Extended Data Fig. 3c shows the out-of-plane lattice deformation with different in-plane strain levels. A Poisson's ratio of around 0.3 can be calculated, consistent with the experimental value by reciprocal space mapping. Meanwhile, C-N and C=N bond lengths in FA⁺ cation with different strain levels (Extended Data Fig. 3d) show no obvious changes with the strain, indicating a weak interaction between the FA⁺ cation and the inorganic Pb-I framework.

Supplementary Discussion 8: Bandgap Reduction of the Strained α -FAPbI₃

Fig. 2a shows photoluminescence (PL) spectra of the epitaxial α -FAPbI₃ thin films at different strain levels. With increasing the in-plane compressive strain, a clear redshift can be seen from ~ 1.523 eV to ~ 1.488 eV. To confirm whether the redshift of PL peaks is caused by the in-plane compressive strain, several possible mechanisms are discussed.

It has been reported that as the perovskite thickness decreases, surface charges will induce depletion micro-electric field near the perovskite surface and increase the bandgap, which causes the PL to blueshift^{45,46}, opposite to this case here. Thus, this surface field effect can be ruled out. We also rule out the possibility of reabsorption of short-wavelength photons by the material itself, which may cause PL redshift. This effect is only observed in bulk crystals and thick films (>1 μm in thickness) and can be neglected for <100 nm films in Fig. 2a⁴⁷. Additionally, the possible incorporation of Br or Cl element is excluded since those foreign atoms will lead to PL blueshift⁴⁸. Hence, we can conclude that the PL redshift is due to the compressive strain generated by the lattice mismatch.

The absorption spectrum is also studied to validate the bandgap measured by PL. Note that improper measurement methods can lead to inaccurate results in both absorption and PL. For example, the absorption spectrum of thick materials obtained by the transmission mode cannot distinguish the light being absorbed or being scattered due to the large thickness of the sample⁴⁹. Meanwhile, PL emission peaks show dependence on the illumination intensity⁵⁰ as well as material dimensions⁴⁵. Therefore, absorption and PL measurements can be used to validate each other.

Due to the large thickness (1 to 2 mm) and the high absorption coefficients ($\sim 10^5 \text{ cm}^{-1}$) of the substrates, light transmittance cannot be detected⁵¹. Therefore, we adopt the reflection mode of UV-VIS to detect the absorption onset of the samples. The collected absorption results (Extended Data Fig. 3b) also demonstrate a red-shift when the strain goes up, which is consistent with the PL measurements.

Meanwhile, we notice that there is a quantitative discrepancy between the calculated bandgap reduction ($\sim 120 \text{ meV}$) and the experimental bandgap reduction ($\sim 35 \text{ meV}$) under -2.4% compressive strain. Note that the first-principle calculations of the strain-dependent bandgap serve as a general prediction. The main purpose is to predict the trend of the change instead of showing quantitative agreement with experimental results. Due to the approximation in the exchange-correlation functionals, deviation in the order of 10^2 meV in calculated bandgap energy from experiments is within a reasonable and tolerable range. Additionally, the geometry approximation of the strained lattice model doesn't reveal the actual deformation of the strained lattice. For example, the lattice parameters a and b are set to be different values to mimic different in-plane biaxial strain levels in the simulation, which changes the bond length between atoms. In real lattice deformation, however, the bond angle will also change to accommodate the in-plane biaxial strain (e.g., by octahedral rotation). Therefore, the calculated values can be different from the experimental values.

Supplementary Discussion 9: Emission Peaks Broadening of the Strained α -FAPbI₃

PL FWHM of the epitaxially strained α -FAPbI₃ thin film is shown to increase with the

strain (Supplementary Fig. 5). There are multiple possibilities origins of the PL broadening. We can first rule out the influence of the domain size because the sample is a single domain thin film⁵². For semiconductors, emission linewidth broadening is governed by charged carrier-phonon coupling, including crystalline quality, acoustic phonon scattering, optical phonon scattering, and impurity⁵³. In semiconductors with heterojunctions, charged carrier transfer can also take place with specific band structure at the interfaces. Such charged carrier transfer usually leads to carrier quenching without direct recombination⁵⁴⁻⁵⁶, and emission peak shifting due to the energy change⁵⁷, while very few reported PL broadening due to the carrier relaxation⁵⁸. Here, we discuss the possible emission peak broadening mechanism in the epitaxially strained α -FAPbI₃ thin films.

1. Charge transfer

The α -FAPbI₃ grown on MAPbBr₃ is analyzed as an example. α -FAPbI₃ has a very different band structure compared with MAPbBr₃ in terms of bandgap, valance band maximum (VBM), and conduction band minimum (CBM) as shown in Supplementary Fig. 6. The heterojunction shows a straddling band alignment where the charged carrier transfer is only allowed from the larger bandgap side to the smaller bandgap side when the larger bandgap side is excited. During the PL measurement in this study, a 633-nm laser (corresponding to 1.95 eV) was used for exciting the epitaxial layer (bandgap 1.50 eV) without exciting the substrates (bandgap 2.30 eV). Upon absorption, electrons in the α -FAPbI₃ will be excited to the conduction band while the MAPbBr₃ remains unexcited.

Here, the large barrier between α -FAPbI₃ and MAPbBr₃ blocks the carrier transfer from the α -FAPbI₃ to the MAPbBr₃ across the interface (Supplementary Fig. 6).

This analysis also applies to other substrates MAPbCl_xBr_{3-x} in this study with different compositions from MAPbBr₃. When incorporating more Cl into the MAPbBr₃ substrate, the bandgap will further increase by lifting up the CBM and pushing down the VBM, and the energy barrier between the α -FAPbI₃ and the substrates will be even larger⁵⁹. Thus, interfacial charge transport will be even less favorable.

Additionally, we also consider the carrier transfer from the MAPbBr₃ to the α -FAPbI₃. Since the MAPbBr₃ remains unexcited due to the large bandgap, the intrinsic electrons are extremely minor compared with the excited carrier in α -FAPbI₃. Therefore, we exclude the possibility of carrier transfer from the MAPbBr₃ to the α -FAPbI₃.

Considering that the laser for the PL measurement doesn't excite the carriers in the substrate, as well as the large energy barrier that blocks the interfacial carrier transfer between the epitaxial layer and the substrate, we draw the conclusion that the charged carrier transfer between the epitaxial layer and the substrates will not take place in the PL measurements and, therefore, will not contribute to the PL broadening.

2. Emission broadening by charged carrier-phonon coupling

For inorganic semiconductors, emission linewidth is associated with different mechanisms of scattering between charged carriers and phonons or impurities, which can be expressed as⁶⁰:

$$\Gamma(T) = \Gamma_{\text{imp}} + \Gamma_{\text{ac}} + \Gamma_{\text{LO}} + \Gamma_0$$

where $\Gamma(T)$ is the temperature-dependent emission linewidth, Γ_{imp} is the broadening terms of scattering with impurities, Γ_{ac} and Γ_{LO} are the broadening terms of the scattering from the acoustic phonons and the optical phonons, and Γ_0 is a temperature-independent broadening term associating with the scattering due to the structural disorder, respectively.

2.1 Impurity

Experimentally speaking, as mentioned above, impurity during epitaxial growth can be controlled by adopting the same growth solutions and epitaxial growth protocol. Therefore, the impurity in the epitaxial films will have a similar concentration. The influence on the PL FWHM from impurity variation will be very minimal.

Additionally, theoretical studies have identified that impurity scattering should be an inhomogeneous broadening term for PL FWHM in halide perovskites^{53,61} and other semiconductors⁶², which should show a weak temperature dependence. This is because impurities can lead to local electric field heterogeneity, and the existence and scattering of impurities are independent on the temperature. The PL FWHM will not change much with the temperature. However, experiments have shown a homogeneous broadening behavior of the PL FWHM of halide perovskites, with a strong temperature dependency^{53,61}. Therefore, the contribution of impurity-induced emission broadening of the PL FWHM is considered to be minor in halide perovskites.

2.2 Acoustic phonon scattering

As we mentioned above, the temperature-dependent PL FWHM of halide perovskites shows a homogeneous behavior, which can be attributed to optical phonon and acoustic phonon scattering^{53,61}. This is due to the fact that acoustic and optical phonons are strongly temperature-dependent. However, the contribution of the acoustic scattering Γ_{ac} in the emission broadening is also demonstrated to be minor in halide perovskites⁶¹. According to the expression equation of the acoustic scattering, Γ_{ac} is linearly proportional to the temperature⁶¹. However, the experimental temperature-dependent PL FWHM of halide perovskites, especially FAPbI₃, behave nonlinearly with temperature⁶¹. This is due to the fact that the polar Pb-I bond mainly generates optical phonons. Therefore, the contribution of the acoustic phonon scattering to the emission linewidth broadening is considered to be minor, and the optical phonon scattering is the dominating factor.

2.3 Temperature-dependent PL FWHM study

As demonstrated by extensive prior works^{53,61,63,64}, the above equation can be expressed in the following form, with the consideration that the acoustic phonon scattering and the impurity scattering contribute little to the emission linewidth in halide perovskites:

$$\Gamma(T) = \Gamma_{LO} + \Gamma_0 = \frac{\gamma_{LO}}{e^{\frac{E_{LO}}{k_b T}} - 1} + \Gamma_0$$

where γ_{LO} is the charged carrier-optical phonon coupling constant, E_{LO} is the energy of the optical phonon, and k_b is the Boltzmann constant. Based on this equation, we studied the relationship between PL FWHM and the temperature for the strained and the strain-free α -FAPbI₃ (Extended Data Fig. 4a, b). A clear redshift can be observed while the intensity of

the emission peak increases with reducing the temperature due to the reduced scattering between the phonon and carriers at low temperatures. To better reveal the change in bandgap and FWHM as a function of the temperature, we normalize each of the PL peak intensity (Extended Data Fig. 4c, d). With decreasing the temperature, both strained and strain-free α -FAPbI₃ showed a bandgap narrowing, which is attributed to the contraction of the lattice. Meanwhile, the PL FWHM exhibits a uniform narrowing with decreasing the temperature. Extended Data Fig. 4e, f show the PL FWHM as a function of the temperature for a -2.4% strained and a strain-free sample, respectively.

Data were fitted with the equation introduced above. Fitted results indicate the main increment of Γ_0 in the strained sample can be attributed to the increased scattering by the crystalline quality reduction. Meanwhile, the increment of both γ_{LO} and E_{LO} suggests an enhanced charged carrier-optical phonon coupling and higher phonon energy in the strained lattice, which can be attributed to the strain-induced lattice deformation⁶⁵. Therefore, we can conclude that the PL FWHM difference of the strained and the strain-free sample mainly comes from the increased scattering by the strain-induced crystalline quality reduction.

To sum up, we discussed several possible mechanisms that might have led to the PL peak broadening and focused on the crystalline quality and charged carrier-optical phonon coupling. By analyzing the temperature-dependent PL FWHM of both strained and strain-free α -FAPbI₃, the calculation results demonstrate that the PL broadening with strain is caused by the strain-induced crystalline quality reduction (major) and enhanced optical phonon scattering (minor).

Supplementary Discussion 10: Strain Relaxation of the Epitaxial α -FAPbI₃

Confocal PL spectroscopy is used to study the PL emission with different focal points inside a 3 μm thick -2.4% strained epitaxial α -FAPbI₃ (Fig. 2b). Results show a PL redshift from ~ 1.523 eV to ~ 1.479 eV with the focal point moving from the film surface to the film/substrate interface. The large discrepancy indicates the strain is relaxed in the thick α -FAPbI₃ film. Here, we study the possible elastic strain relaxation due to the soft nature of halide perovskite and the plastic strain relaxation from the strain-induced dislocation.

1. Elastic strain relaxation

We study the elastic relaxation of the epitaxial α -FAPbI₃ thin film using finite element analysis (FEA) simulations. The simulation results are shown in Supplementary Fig. 8 where an α -FAPbI₃ thin film with a $30\ \mu\text{m} \times 30\ \mu\text{m} \times 3\ \mu\text{m}$ dimension in $l \times w \times t$. Elastic constants C_{11} , C_{12} , and C_{44} of α -FAPbI₃ come from the reported literature⁶⁶. Different biaxial compressive strains (-1.2% and -2.4%) are applied at the bottom of the α -FAPbI₃ to simulate the interfacial strain. Plastic relaxation from the dislocations is ignored in the simulation to focus on the influence of the elastic relaxation only. Supplementary Fig. 8a, b show the planar stress distribution from the bottom view of the -1.2% and -2.4% strained α -FAPbI₃, respectively. Supplementary Fig. 8c, d show the vertical stress distribution from the cross-sectional view of the -1.2% and -2.4% strained α -FAPbI₃, respectively.

Simulated results indicate a uniform strain distribution throughout the entire epitaxial α -FAPbI₃ thin film. We further study the thickness-dependent stress distribution along the

vertical direction (Supplementary Fig. 8e, f), as labeled by the blue line and the red line in the Supplementary Fig. 8c, d, respectively. From the results, the strain maintains almost the same along with the thickness. For a sample thickness of 3 μm , the elastic relaxation is calculated to be 0.096% and 0.093% for -1.2% and -2.4% strained $\alpha\text{-FAPbI}_3$, respectively. The small discrepancy between the elastic relaxation under the two strain magnitudes is due to the numerical dispersive error because the FEA simulation uses a dispersive model for approximation⁶⁷. Therefore, the elastic relaxation in the epitaxially strained $\alpha\text{-FAPbI}_3$ is not as prominent as we expected, due to the small thickness (in the range of hundreds of nanometers to a few micrometers) used in this study. Halide perovskites are in fact still brittle solids even though they are softer in nature than other conventional semiconductors⁶⁸.

2. Plastic strain relaxation

In heteroepitaxial growth, strain usually relaxes plastically rather than elastically. The calculations of the critical thickness where the dislocations form and relax the strain have been determined theoretically and experimentally. There are two models that have been widely used for the critical thickness calculations: the Matthews and Blakeslee (MB) model⁶⁹ and the People and Bean (PB) model⁷⁰.

The MB model is a mechanical equilibrium model that stems from the force balance of dislocations. In this model, the critical thickness is defined as the thickness when the strain force is equal to the dislocation tension force and can be expressed as:

$$h_c = \frac{b(1 - \nu \cos^2 \alpha)}{8\pi f(1 + \nu) \cos \lambda} \left[1 + \ln\left(\frac{h_c}{b}\right) \right]$$

where h_c is the critical thickness, b is the length of the Burger's vector, ν is the Poisson's

ratio, α is the angle between the Burger's vector and the line vector for the dislocation, f is the misfit strain, and λ is the angle between the Burger's vector and the line in the interface plane that is perpendicular to the intersection of the glide plane with the interface.

The PB model is an alternative prediction method based on the energy equilibrium that is widely studied and experimentally proved. In this model, the critical thickness is defined as the thickness where the strain energy is equal to the dislocation formation energy and can be expressed as:

$$h_c = \frac{(1 - \nu)b^2}{(1 + \nu)(16\sqrt{2}\pi a f^2)} \ln\left(\frac{h_c}{b}\right)$$

where a is the lattice constant of the material.

Many studies show large discrepancy with the MB model. Even the epilayer is thicker than the MB limit, the dislocations are still absent⁷¹. Therefore, the MB model underestimates the critical thickness. The MB model may not give a quantitatively matched result. Besides, α and λ in PB need to be determined for different dislocations. However, the PB model gives a closer estimation of the critical thickness⁷¹, and will therefore be used in this study.

We first study the thickness-dependent strain relaxation of the epitaxial α -FAPbI₃ thin films with different strains by in-plane XRD. In-plane XRD measures the in-plane lattice constant of the crystalline materials, which can be directly used to calculate the strain and contains information about the plastic strain relaxation in heteroepitaxy. Extended Data Fig. 5a, b show the thickness-dependent in-plane XRD patterns of two representative epitaxially strained α -FAPbI₃ thin films with -1.2% and -2.4% strain, respectively. The -1.2% strained epitaxial α -FAPbI₃ thin film with a thickness of 200 nm shows obvious plastic strain relaxation (Extended Data Fig. 5a), as evidenced by the peak shifting (to a lower angle, the

vertical line labels the fully strained peak position) and broadening. For the -2.4% strained epitaxial α -FAPbI₃ thin films, plastic relaxation can be measured in films above 50 nm with obvious peak shifting and broadening (Extended Data Fig. 5b). The vertical line labels the fully strained peak position. Besides, we can also obtain the thickness-dependent in-plane lattice constants, based on which we can calculate the in-plane strain by comparing with the in-plane lattice constant. The degree of plastic strain relaxation can be quantified by comparing the local in-plane strain with the highest measured in-plane strain.

Quantification of the degree of plastic strain relaxation is done by calculating the relaxation constant R :

$$R = \frac{a_{measured} - a_{strained}}{a_{\alpha-FAPbI_3} - a_{strained}}$$

where $a_{measured}$ is the measured in-plane lattice constant at different thicknesses, $a_{strained}$ is the in-plane lattice constant with maximum strain, and $a_{\alpha-FAPbI_3}$ is the lattice constant of the strain-free α -FAPbI₃. For the epitaxial film with the same substrate but different thicknesses, R ($0 \leq R \leq 1$) reveals the relationship between the film thickness and the degree of plastic strain relaxation. For R equals to one, the epitaxial film is considered as fully-relaxed. Otherwise, the film is considered as partially-relaxed. At relatively low thickness, R remains at zero without any relaxation. With increasing thickness, R will gradually increase due to the formation of dislocations, which plastically relax their surrounding strain.

The thickness-dependent relaxation constants of each epitaxial α -FAPbI₃ with different substrates (i.e., different strains) are calculated and shown in Extended Data Fig. 5c. The error bars label the range of calculated R of the films with the same substrate and thickness.

Results show that the film with a -2.4% strain quickly relaxes at the thickness of ~ 50 nm while the film with -0.8% start to relax at ~ 200 nm. Note that the thinnest film we can obtain is ~ 50 nm and we assume that the thin layer α -FAPbI₃ will be fully strained without relaxation. Critical thicknesses are extracted from Extended Data Fig. 5c where R is larger than 0 and fitted with both the MB and PB models (Extended Data Fig. 5d). Results show that the critical thickness decreases with increasing the strain. Our experimental results agree more with the predicted PB model, indicating that the plastic strain relaxation due to the dislocations generated during the epitaxial growth is the dominating relaxation mechanism.

Confocal PL spectroscopy is used to study the PL emission with different focal points inside a 3 μ m thick -2.4% strained epitaxial α -FAPbI₃ (Fig. 2b). Results show a PL redshift from ~ 1.523 eV to ~ 1.479 eV with the focal point moving from the film surface to the film/substrate interface. Besides, we also measured a strain-free bulk α -FAPbI₃ crystal sample and a 3 μ m thick mixed sample (Supplementary Fig. 7). Note that the mixed sample came from the mixed epitaxial growth with low temperature and low concentration in Supplementary Fig. 1. By using a low growth temperature and low concentration solution, the crystallization speed of the epitaxial film will be significantly retarded. The long-time contact of the substrate and solution will lead to a slow ion exchange between them and, therefore, form an epitaxial film containing mixed Cl and Br. In the case of Fig. 2a, we adopt an optimal growth condition with high temperature (180 $^{\circ}$ C) and high concentration (1.2 mol L⁻¹) to achieve a fast crystallization speed, so that the α -FAPbI₃ crystals will nucleate on the substrate, even before the Cl and Br ions dissolve and get mixed in the solution. The obtained interface will be clear and the epitaxial α -FAPbI₃ sample will be highly strained. The

strain-free sample shows a much less obvious PL peak redshift from ~ 1.523 eV to ~ 1.516 eV (Supplementary Fig. 7a), which can be attributed to reabsorption as discussed above. For the mixed sample grown under low temperature and low concentration (Supplementary Fig. 7b), the PL peak at the sample surface is at ~ 1.542 eV, indicating incorporation of Cl and Br elements from the substrate. With increasing focal depth to the film/substrate interface, the PL peak blueshifts to below 1.550 eV, which indicates a higher degree of mixing.

Film thickness-dependent PL measurements are based on samples at -2.4% strain with different epitaxial film thicknesses (Supplementary Fig. 9). A 633-nm laser with the standard mode is used as the excitation source to study the overall emission behavior of the film at all depths. The PL peak position shows a strong film thickness dependency. When the α -FAPbI₃ film thickness increases, the PL emission peak shifted from ~ 1.479 eV back to 1.523 eV, the same as that of the strain-free α -FAPbI₃, which indicates the strain has been fully relaxed.

Supplementary Discussion 11: Temperature-Dependent Bandgap of the Strained α -FAPbI₃

Due to the soft nature, external stimuli (i.e., temperature, pressure) can effectively alter the lattice structure of halide perovskites, and, therefore, change the electronic band structures^{18,20,72}. Under such considerations, temperature-dependent PL was studied on both epitaxial α -FAPbI₃ and free-standing α -FAPbI₃. Epitaxially grown thin films are subjected to the lattice deformation of the substrates due to the strong chemical bonds at the interface and the much bulkier size of the substrate. In this case, the epitaxial film will adopt a similar

thermal expansion coefficient α_t to that of the substrate⁷³. A reported study has shown that the α_t of halide perovskites are subjected to the molecular radius of halides. Therefore, the I-based perovskite epitaxial layer will have a larger α_t due to the large radius of I^- than the Br^- and Cl^- based halide perovskite substrate⁷⁴. The epitaxial α -FAPbI₃ on a Br^- and Cl^- based substrate exhibited a reduced temperature dependency compared with the freestanding α -FAPbI₃. Additionally, if the substrate has a larger α_t than that of the strained layer, we should expect to see the strained sample has a stronger temperature dependence than that of the free-standing sample.

Supplementary Discussion 12: Band Structure of the Strained α -FAPbI₃

UPS measurements are carried out on epitaxial α -FAPbI₃ films with different strain levels. Extended Data Fig. 6a shows the cutoff energy region and Extended Data Fig. 6b shows the valence band region of the α -FAPbI₃. Take the UPS spectrum of the strain-free α -FAPbI₃ as an example, the position of the electron affinity (Fermi level) *versus* vacuum is the difference between the high binding energy cutoff and the radiation energy of He I (21.22 eV):

$$16.09 \text{ eV} - 21.22 \text{ eV} = -5.13 \text{ eV}$$

The low binding energy cutoff (0.62 eV) determines the position of Valence Band Maximum (VBM). Therefore, the position of the VBM relative to the vacuum level is:

$$-5.13 \text{ eV} - 0.62 \text{ eV} = -5.75 \text{ eV}$$

Considering the measured optical bandgap of ~ 1.51 eV (Fig. 2a), the Conduction Band

Minimum (CBM) is determined to be -4.24 eV. This also suggests that the Fermi level is closer to the VBM than to the CBM, and therefore the strain-free α -FAPbI₃ is p-type. Similarly, all other strained epitaxial thin films show a p-type character.

Additionally, the results show that the valence band is pushed up by 50 meV while the CBM is only pushed up by 15 meV when strain increases from 0% to -2.4%. The reason why VBM is pushed up more than the CBM by the biaxial in-plane compressive strain is because the compressed PbI₆ octahedron contributes more to the VBM than the CBM. The VBM is composed of the coupled Pb 6s and I 5p orbitals that form the PbI₆ octahedral, while the CBM is mostly nonbonding localized states of Pb p orbitals⁷⁵.

Supplementary Discussion 13: Effective Mass Calculations and Carrier Mobility Characterizations of the Strained α -FAPbI₃

1. Effective mass calculations

To investigate the effect of strain on carrier dynamics in α -FAPbI₃, we analyzed the variation of charged carrier mobility via predicting effective masses of charged carriers from first-principles calculations. In the calculations, the mean free time of carriers was assumed to be a constant, and the reversely proportional relationship between the effective mass and charged carrier mobility was used. Carrier effective masses are determined by the curvature of the highest energy at the VBM for holes and lowest energy at the CBM for electrons in the k space. Figure 3a shows the calculated electron and hole effective masses of α -FAPbI₃ under different strain levels. Electronic band structures of α -FAPbI₃ under 3%, 0%, and -3% are

also shown in the lower panels of Fig. 3a. Results indicate that the hole effective mass m_h^* decreases when strain goes from tensile to compressive, while the electron effective mass m_e^* barely changes with the strain. The trend of m_h^* can be revealed from the curvature of the highest energy point of the VBM, which gets less dispersive with increasing compressive strain. This is due to the fact that the VBM that determines m_h^* mainly consists of Pb 6s and I 5p orbitals. Under tensile strain, the distance between Pb and I atoms increase and therefore the Pb-I bond interaction is weakened, thus leading to the increase of effective mass. In contrast, the hole mobility will increase under compressive strain due to the enhanced Pb-I bond interaction and the decreased effective mass. However, the CBM that determines the electron effective mass mainly consist of Pb p orbitals is less sensitive to the deformation of Pb-I bonds, which is why m_e^* barely changes with applied strain¹⁵.

2. Interfacial carrier transfer and Hall effect measurements

Hall effect is used to measure the strain-dependent carrier mobility of the epitaxial α -FAPbI₃ thin films. Before the measurement, we study the possible carrier collection from the substrates since the substrates are halide perovskites with high carrier mobility as well. We first analyze the device structure with the FEA simulation. The schematic device structure is shown in Supplementary Fig. 10a where four Au electrodes are deposited with a layer of Parylene-C beneath. The Parylene-C serves as the insulating layer to prevent the carrier collection from the substrate to the electrodes. To better understand the carrier transfer between the epitaxial layer and the substrate, we also study the band alignment between them (Supplementary Fig. 10b). Herein, α -FAPbI₃ and MAPbBr₃ are analyzed as an example.

α -FAPbI₃ has a very different band structure compared with MAPbBr₃ in terms of bandgap, valance band maximum (VBM) as well as conduction band minimum (CBM). For α -FAPbI₃, VBM and CBM are determined to be -5.75 eV and -4.25 eV by the ultraviolet photoelectron spectroscopy, respectively. For MAPbBr₃, VBM and CBM are determined to be -6.20 eV and -3.90 eV from the literature⁷⁶. For the Hall measurement, the injected carriers are subject to the Lorentz force applied by the vertical magnetic field and are accumulated at the diagonal electrodes to build up the Hall voltage. However, the large energy barrier at the heterojunction interface blocks the carrier injection from the α -FAPbI₃ to the MAPbBr₃. Therefore, there is a very low concentration of free carriers in the substrate that can hardly generate a significant Hall voltage during the measurement. This analysis also applies to other substrates MAPbCl_xBr_{3-x} in this study with different compositions from MAPbBr₃. When incorporating more Cl into the MAPbBr₃ substrate, the bandgap will further increase by lifting up the CBM and pushing down the VBM, and the energy barrier between the α -FAPbI₃ and the substrates will be even larger⁵⁹. Thus, interfacial charge transport will be even less favorable. Additionally, we also exclude the free carrier transfer from the MAPbBr₃ to the α -FAPbI₃.

We then simulate the current distribution within the device by FEA. We also intend to quantify the current density in both the epitaxial layer and the substrate to study the contribution of the substrate to the Hall measurement. With the combined energy diagram and the electric field distribution, we simulate the current distribution in the device (Supplementary Fig. 10c upper panel). The simulation results show that the current distribution is completely different from the electric field distribution. Current density in the

epitaxial layer (9.8 A m^{-2}) is much higher than that of the substrate (0.4 A m^{-2}), which means that the large energy barrier between the epitaxial layer and the substrate, as well as the minimal vertical electric field distribution and the insulation of the Parylene-C, minimizes the carrier injection to the substrate. A closer look at the area that is close to the electrode suggests that the carrier injection to the substrate is indeed prohibited (Supplementary Fig. 10c lower panel, red arrows indicate the direction of the current flow). To quantify the ratio of the current in the substrate to that in the epitaxial layer, we study the current density along the vertical orange line where the current flows horizontally (at a steady state). Supplementary Fig. 10d shows the vertical current density distribution along the vertical orange line where the heterostructural interface locates at 500 nm from the bottom (0 nm). The ratio of current density across the interface is shown to $\sim 24.5:1$ where the epitaxial layer is 9.8 A m^{-2} and the substrate is 0.4 A m^{-2} . By integrating the area below the current distribution curve, we obtain the ratio of the current density in the substrate to the total current density along the vertical line to be 0.8%. Therefore, we conclude that the carrier in the substrate is negligible compared with that in the epitaxial layer, and we attribute this result to the large energy barrier between the epitaxial layer and the substrate, as well as the minimal vertical electrical field distribution and the insulation of the Parylene-C layer.

Without the concern of possible carrier collection from the substrates, we perform Hall effect measurement to the epitaxial $\alpha\text{-FAPbI}_3$ thin films under different strains. Measurement results also show p-type character, which is consistent with the UPS results. The hole mobility as a function of strain is plotted in Fig. 3b, which doesn't show a linear tendency with increasing strain. Devices with -0.8%, -1.2%, and -1.4% strain show enhanced hole

mobility compared with that of the strain-free α -FAPbI₃ bulk crystal. A -1.2% strained device gives the highest mobility of $\sim 72 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Further increasing the strain results in a drastic drop in the hole mobility, because higher strain levels will relax at a lower thickness and induce high concentrations of dislocations that deteriorate the device performance.

3. Time-of-flight (ToF) measurements

To validate the results from the Hall effect measurement, we study the carrier mobility of the epitaxial α -FAPbI₃ thin films under different strains by ToF measurements. The schematic device structure is shown in the inset of Fig. 3d. A layer of Parylene-C was deposited between the Au electrode and the substrate to block the carrier extracted from the substrate as demonstrated above. Besides, we adopted a 685-nm laser as the excitation source so that the photon can only be absorbed by the epitaxial layer rather than the substrate that has a larger bandgap than the excitation laser energy. In this case, we guaranteed the measured photovoltages coming from the epitaxial layer absorption were the same. Similarly, the excited electrons that occupy the CBM of the α -FAPbI₃ are less likely to be extracted to the CBM of the substrate due to the large energy barrier, as shown in Supplementary Fig. 10.

ToF measurements were carried out with the designed structure where the distance between the two electrodes is controlled to be 100 μm in lateral directions. Meanwhile, the thickness of the epitaxial layer is controlled to be the same and all the devices are biased with 1 V. The measured transient photocurrents are shown in Fig. 3c where the carrier transit time can be extracted as the inflection point of the photocurrent curve. The carrier mobility can be calculated by:

$$\mu = \frac{d^2}{Vt}$$

where μ is the calculated carrier mobility, d is the thickness of the target region, V is the applied voltage, and t is the measured carrier transit time. The measured carrier mobilities are plotted in Fig. 3d. Our measured ToF mobility of the epitaxial α -FAPbI₃ with different strains showed a similar trend compared with the measured Hall mobility. -1.2% strained α -FAPbI₃ exhibits the highest carrier mobility while further increasing the strain can lead to faster relaxation, and the accumulation of dislocations will reduce the carrier mobility.

Besides, bias and laser power dependence of the ToF measurement are also discussed. ToF mobility is calculated by $\mu = \frac{d^2}{vt}$. The applied bias will only change the carrier transient time rather than the carrier mobility. This is because the carrier mobility is an intrinsic property of the semiconductor materials and is independent of the magnitude of the applied bias. This rule has been demonstrated by many ToF measurements of halide perovskites, in which the carrier mobility is independent of the applied bias but the measured carrier transient time is inversely proportional to the applied bias^{77,78}. In the measurements, as described in the manuscript, all experiments are tested under 1 V DC bias with other experimental parameters well-controlled. Therefore, the transient photocurrents of the epitaxial films under different strain magnitudes appropriately reveal the carrier mobility of the epitaxial thin films. For the ToF measurement, it has been reported that the photogenerated carrier density shows laser power dependency and a high carrier density can generate the space charge effect which affects carrier extraction^{79,80}. However, the space charge effect will be significant only in systems where the ratio between the electron mobility and the hole mobility exceeds two orders of magnitude⁸¹. According to the reported carrier

mobility of halide perovskites, the electron and hole mobilities are usually on the same order of magnitude when they are from the same literature⁸². Therefore, the space charge effect can be safely ignored and the laser power dependence of ToF measurements is less significant in this study. In the measurements, the laser intensity is kept at constant (10 mW cm^{-2}) throughout the entire measurement so that the only variation is the strain magnitude of the epitaxial thin film.

The possible influence of the current–voltage (I – V) hysteresis on the ToF measurement is also discussed here. During the ToF measurement, the devices are biased under a constant voltage, e.g., 1 V, to collect photogenerated carriers in the epitaxial thin films. In this case, the baseline current due to ion migration and mobile electron and hole carriers under a fixed electric field is considered to be in a steady state. Adding on top of the baseline current, a pulsed laser is used as the excitation source to generate carriers in the epitaxial thin film. The corresponding photocurrent-time characteristics are recorded by an oscilloscope. The timescale of the excited transient current, i.e., ToF, is measured to be $\sim 10^{-6} \text{ s}$ (as seen in Fig. 3 in the main text). I – V hysteresis is reported to originate from ion migration, device capacitive charging, and perovskite ferroelectric polarization^{83,84}. For the ion migration, the timescale is reported to be in the range of seconds to minutes in halide perovskites⁸⁵, which is much longer than that of the ToF. For the device capacitive charging, whose timescale is reported to be in the range of milliseconds to seconds⁸³, which is also much longer than that of the ToF. Also, the timescale of ferroelectric dipole switching is reported to be faster than 10^{-8} s ⁸⁶, which is much shorter than that of the ToF. Besides, since the devices are biased under 1 V DC voltage during the measurement, the capacitive charge and the ferroelectric

dipoles are almost kept constant in the devices. Therefore, it is safe to exclude the possible influence of the I - V hysteresis on the ToF measurement.

4. Analysis of the influence of ion migrations to the carrier mobility measurements

Ion migrations of halide perovskites have been studied in the literature and are believed to be the origin of the reported current-voltage hysteresis in halide perovskites. Reported studies showed that the mobility of the vacancies and the ions in polycrystalline perovskites were determined to be $\sim 1.6 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\sim 5 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively^{87,88}. However, these values are much smaller than that of the measured hole mobilities ($\sim 50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in this study. Additionally, the carrier transit time in the ToF measurement of this study was in the range of μs , which was too short for the ions to move a substantial distance. Therefore, it is safe to exclude the contribution of ions and structural vacancies from the measured hole mobility in this study.

Besides, grain boundaries of the polycrystalline halide perovskites were reported to be a major pathway for ion migrations⁸⁹⁻⁹¹. In this study, the epitaxial growth of single-crystalline perovskites minimizes the formation of grain boundaries and, therefore, minimizes the influence of the ion migrations. In a reported study, the ion migration mobility in both polycrystalline and single crystalline methylammonium lead iodide (MAPbI_3) were measured⁹². Compared with the ion migration in polycrystalline MAPbI_3 whose ion migration mobility was $\sim 1 \times 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, the ion migration in single crystalline MAPbI_3 can hardly be detected⁹². Therefore, we can conclude that the influence of ionic movements in the halide perovskites can be excluded from this study.

5. Crystalline quality characterization

The space-charge limit current (SCLC) method is used to quantitatively evaluate the crystalline quality of the epitaxial thin film (Extended Data Fig. 7 and Supplementary Fig. 11). Devices adopt the same structure as the one used in ToF measurement. Devices with different strain levels (strain-free, -0.8%, -1.4%, and -2.4%) are fabricated and tested. Note that bulk α -FAPbI₃ single crystals were used as the substrates to fabricate strain-free devices.

We first study the I - V characteristic curves of the devices with forward and reverse scans from 0.01 V to 2 V (Extended Data Fig. 7a to 7d). Note that the devices adopt a planar structure to correlate with the devices used in the Hall effect measurements. A layer of Parylene-C (50 nm) and a layer of Au (50 nm) are sequentially deposited on the substrates while the lateral distance between two Parylene-C/Au electrodes is 100 μ m. Epitaxially strained α -FAPbI₃ thin films are then grown from the gaps between the electrodes and cover part of the electrodes for electrical contact.

In the forward scan, the log-log I - V characteristic curves show different regions of behavior. At low voltages, the I - V curves exhibit a typical ohmic conduction behavior, where the current is linearly related to the applied voltage ($n \sim 1$, blue line). In this region, the quantity of the thermally generated free carriers exceeds that of the externally injected carriers⁹³. With increasing the applied voltage, the externally injected carriers gradually increase and start to fill the traps. Therefore, a trap-filling process is identified by the end of the linear ohmic region ($n > 3$, green). By further increasing the voltage, traps in the bandgap are completely filled by the externally injected carriers and the carriers move freely⁹⁴. In this

region, the current is squarely related to the applied voltage ($n \sim 2$, orange). V_{TFL} is extracted by finding the voltage where the ohmic region ends. The extracted V_{TFL} in samples with different strains is used to evaluate the trap density, which agrees with the results in the manuscript.

The forward scan is followed by a reverse scan where the I - V characteristic curves of the reverse scan show only a linear region. By fitting the I - V curves of the reverse scan, we find out that the current is squarely related to the applied voltage ($n \sim 2$, red). During the reverse scan, the filled traps will not undergo a de-trapping process because of the existence of the applied electric field as well as the continuously injected carriers. Therefore, the reverse scan cannot be used to study the trap-filling process, and the evaluation of the V_{TFL} can only be studied with the forward scan. Trap density of the epitaxial film n_t can be calculated by:

$$V_{TFL} = en_t d^2 / 2\epsilon\epsilon_0$$

where d is the layer thickness, ϵ (≈ 47) is the relative dielectric constant of α -FAPbI₃, and ϵ_0 is the vacuum permittivity.

We also statistically study the trap density in the epitaxial α -FAPbI₃ film with different strain magnitudes to evaluate the robustness of the measured trap density values. Here, five different devices of each strain value are tested. The trap density of the epitaxial α -FAPbI₃ film from different samples are calculated and displayed in Supplementary Fig. 11a. The average trap densities and the standard deviation are shown in Supplementary Fig. 11b. With increasing the strain, the average trap densities show an increasing trend, indicating that a higher strain level induces a higher defect density in the epitaxial α -FAPbI₃ film. This trend

correlates well with the data we showed in the manuscript. Meanwhile, the standard deviation of the trap density also increases with the strain, which reveals an increased disorder in the epitaxial α -FAPbI₃ film at higher strain values.

Besides, we also investigate I - V characteristic curves from the same device under different measurement conditions, e.g., different scan rates and scan directions. I - V curves of the halide perovskites are reported to be scan rate-dependent due to the fact that the scan rate can alter the charged carrier collection efficiency of the devices, which results in artificial I - V curves^{84,85,95}. However, this discrepancy can be effectively minimized by adopting a relatively slow scan rate⁸³ since a fast scan rate has been reported to go beyond the response speed of free carriers to the electric field⁹⁶. To prove that the 50 mV s⁻¹ scan rate we use in this work does not produce artificial I - V curves, we study I - V curves under four representative scan rates (Supplementary Fig. 11c). I - V curves with 10 mV s⁻¹, 50 mV s⁻¹, and 200 mV s⁻¹ scan rates show distinct trap filling behavior as we discussed above. The V_{TFL} extracted from the I - V curves with 10 mV s⁻¹ and 50 mV s⁻¹ scan rates are similar, indicating that 10 mV s⁻¹ and 50 mV s⁻¹ are sufficiently slow to avoid artificial I - V curves and V_{TFL} values. Meanwhile, increasing the scan rate to 200 mV s⁻¹ leads to a smaller V_{TFL} because of the limited response of free carriers to the rapid electric field change. No trap filling process can even be measured when further increasing the scan rate to 1000 mV s⁻¹, showing that the I - V curve under a very fast scan rate can skew the results. Therefore, we can conclude that the 50 mV s⁻¹ scan rate we use in the SCLC measurements helps produce reliable I - V curves and V_{TFL} . Besides, we study how the scan direction may possibly affect the SCLC measurement. Supplementary Fig. 11d shows I - V curves of the same device with different scan directions. The I - V curves from

positive and negative scan directions, with ~ 10 min in between the scans, are similar to each other, which is because the device adopts a symmetric Au/perovskite/Au structure. The initial direction of the forward scan along either direction should give the same result. Therefore, we can conclude that the SCLC measurements under different scan conditions, with a slow scan rate (50 mV s^{-1}), and a symmetric device structure can produce reliable results.

In this study, the goal is not to distinguish the origins or the densities of various traps but is to study the trap density increment in the epitaxial α -FAPbI₃ thin films when the strain magnitude is increased. For lattice-mismatched heteroepitaxial growth, the density of misfit dislocations will be increased with increasing the interfacial misfit magnitude and the epitaxial layer thickness, to partially release the strain⁹⁷. These misfit dislocations tend to degrade the properties of the epitaxial layers and, therefore, the performance of the devices by introducing below-gap trap states. For the impurity, the growth precursor was controlled to be the same, which will keep a similar impurity source for all α -FAPbI₃ films in this study. Without additional impurity source being introduced during epitaxial growth, the epitaxial film with different strain levels should share a similar impurity density. Therefore, we exclude the contribution of impurities to the measured trap density increment. For the other crystallographic defects (e.g., vacancies, interstitials, antisites, etc.), their contributions to the trap density increment are considered to be minor, because it is a convention that the generation of dislocations is the main reason for strain relaxation in heteroepitaxy^{97,98}. For the interfacial defects formed at the perovskite/electrode interface, all devices fabrication adopted the same protocol. Therefore, the interfacial traps caused by the interfacial defects are similar for different strain values and can be excluded from the possible reason for the trap density

increment in the epitaxial samples. In this case, the impurities and the interfacial defects will not lead to the significant trap density increment, up to ~1000% as observed in the studies with increasing the strain magnitude from 0% to -2.4%.

Based on the above discussions, we demonstrate that the trap density increments with increasing the interfacial misfit magnitude and film thickness can be attributed to the strain-induced dislocations. Even though there is currently a lack of an experimental characterization technique that would allow accurately quantifying the separate contribution of each defect due to the complexity of these defects⁹⁹, contributions from all other types of traps are minor and can be safely excluded in this study by adopting the unique variable principle throughout the experiment. Actually, the unique variable principle is commonly used to exclude irrelevant factors in trap density measurements, as evidenced by many examples in the literature. Vapor deposition of relatively thick perovskite film is reported to show reduced trap density due to the reduced crystallographic defects. The trap density increment in the relatively thinner sample excludes the contribution of impurities and the interfacial defects because they are considered to be similar to those of the thicker sample and will not lead to trap density reduction¹⁰⁰. Also, it is recently reported that the addition of CuBr into inorganic perovskite will reduce the trap density. The influence of the interfacial defects and the impurities are considered of minor influence to the trap density reduction in the control sample due to the same fabrication protocol¹⁰¹. Similarly, the addition of Eu^{3+} - Eu^{2+} ionic pair can reduce the crystallographic defects generated by the Pb^0 and I^0 . The trap density increment in the control sample rules out the contribution of interfacial defects and impurities because the samples share similar fabrication processes¹⁰². Additionally,

perovskite seeding growth is reported to improve the crystallinity and reduce the trap density. The interfacial defects and the impurities in the control sample are considered to be similar in the seeded grown sample and control sample¹⁰³. What's more, modifying the interface between the perovskite and the electron transporting layer is shown to reduce interfacial defects and trap density. The influence of the impurities and crystallographic defects can be excluded because they are considered to be similar in different devices¹⁰⁴. Finally, incorporating bilateral alkylamine additives is shown to reduce interfacial defects and trap density in the perovskite film. Contributions from impurities and crystallographic defects are ruled out due to the fact these two factors are similar in different devices¹⁰⁵.

We also investigate the literature to study the minimum trap density difference that can be measured by the SCLC method. Researchers demonstrated the reduced trap density by 15% due to the incorporation of Cl in the perovskite film¹⁰⁰. In two-dimensional perovskite nanowires with different layer numbers, a one-fold increment of trap density was also reported¹⁰⁶. Meanwhile, researchers demonstrated the decrease of trap density by ~20% with a modified tin doped indium oxide (ITO) surface¹⁰⁷. Similarly, a decrease of trap density by ~50% with a modified interface was also reported¹⁰⁸. Compared with the reported works, the results in this study demonstrate a difference from ~30% to up to ~1000%, which is sufficiently large to conclude that a higher strain can induce more defects.

Characterizing the trap density in halide perovskite thin films has been widely studied. Quantitative characterization of the trap density in halide perovskites are mostly done by the SCLC method (the dark I - V characteristic curve). It is believed to be the most facile, accurate, and direct technique for trap density characterization and has been extensively used^{77,78,109}.

Besides the SCLC method, tuning the excitation density of input photons in the transient photocurrent measurement is also reported to roughly estimate the trap density by generating different densities of free carriers and monitoring the decay rate^{110,111}. The measurement accuracy is relatively low. Additionally, capacitance-frequency ($C-\omega$) spectroscopy has been reported to study the trap density in organic materials^{112,113} and halide perovskites¹¹⁴⁻¹¹⁷. The low-frequency capacitance originates from the carrier trapping/detrapping of electronic traps while the high-frequency capacitance is attributed to the geometrical capacitance and the depletion capacitance^{114,116}.

In this study, we use the $C-\omega$ spectroscopy as an alternative probe for trap density of epitaxial α -FAPbI₃ thin films with different strain magnitudes. Devices for $C-\omega$ measurements have a lateral configuration with a 3 mm width. Au and ITO are used as the two electrodes with a 2×2 mm² area. During the measurement, a 0.5 V AC voltage is applied. The resulting electric field is 1.67×10^{-4} V μm^{-1} , which is insufficient for generating ion migration¹¹⁷. In this case, we exclude the contribution of charged ions to the measured capacitance. The capacitance of α -FAPbI₃ thin films with different strain magnitudes are measured in the frequency range of 1~10⁵ Hz in dark. To eliminate the influence of the parasitic capacitance from the substrate and air, we first measure the $C-\omega$ spectra of the bare substrate without the epitaxial layer. After measuring the $C-\omega$ spectra of the devices with the epitaxial layer, we subtract the spectra of the substrates from that of the devices to obtain the $C-\omega$ spectra of the epitaxial layer, which therefore exclude the capacitance contributions from the substrates and air. The results after subtraction are shown in Supplementary Fig. 12a. The measured capacitance gradually increases with increasing the strain magnitudes, indicating

the accumulation of electronic traps. We then calculate the trap density with the C - ω measurement results. The trap density can be calculated by

$$N_t(E_\omega) = -\frac{V_b}{qkAtT} \frac{dC(\omega)}{d \ln(\omega)}$$

where N_t is the trap density at a certain trap energy E_ω , V_b is the build-in potential and is estimated to be ~ 0.5 V from the work function difference between Au and ITO, q is the element charge, k is the Boltzmann constant, A is the device area, t is the thickness, and T is the temperature. Trap energy E_ω is calculated by

$$E_\omega = kT \ln\left(\frac{\omega_0}{\omega}\right)$$

where ω_0 is the attempt-to-escape frequency, which is reported to be $\sim 2 \times 10^{11} \text{ s}^{-1}$ for halide perovskites¹¹⁸. The calculated trap density of the epitaxial α -FAPbI₃ thin films with different strain magnitudes are shown in Supplementary Fig. 12b and an obvious trap density increment can be seen with increasing strain magnitudes.

To quantitatively evaluate the trap density in the epitaxial thin films, we fit the calculated trap density distribution with the following Gaussian distribution equation:

$$N_t(E_\omega) = \frac{n_t}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E_0 - E_\omega)^2}{2\sigma^2}\right]$$

where n_t is the trap density, σ is the disorder parameter, and E_0 is the mean energy of the traps. The fitted trap density (n_t) for 0%, -0.8%, -1.4%, and -2.4% strained epitaxial thin films are $2.6 \times 10^{11} \text{ cm}^{-3}$, $3.2 \times 10^{11} \text{ cm}^{-3}$, $7.2 \times 10^{11} \text{ cm}^{-3}$, and $2.4 \times 10^{12} \text{ cm}^{-3}$, respectively. The trap density increment with increasing the strain magnitude indicates an accumulation of dislocations under a higher strain magnitude⁹⁷. The trend also agrees with that measured by the SCLC method (Extended Data Fig. 7 and Supplementary Fig. 11). Note that the C - ω method measures the sum of electron and hole traps¹¹² while the SCLC methods can

distinguish electron and hole traps with selected electrodes⁷⁸. In the SCLC measurements, we adopt an Au/perovskite/Au structure that only reveals the hole traps due to the energy alignment of the Au electrode for hole injection⁷⁸. This may be the main reason that leads to the small discrepancy in the results measured by the $C-\omega$ and the SCLC methods.

Supplementary Discussion 14: Different Methods for Stabilizing α -FAPbI₃

1. Current methods

The high-temperature α -FAPbI₃ phase suffers from a spontaneous and quick phase transition to the low-temperature, photoinactive δ -FAPbI₃ phase at room temperature. The most popular stabilization method for α -FAPbI₃ is accomplished by mixing/doping small ions¹¹⁹⁻¹²¹. Several reported works discussed the possible stabilization mechanisms behind. Researchers explained the stabilization effect of mixing small ions by studying the entropy where the formation energy of the mixed δ phase was too large for the phase transition to take place¹¹⁹. Meanwhile, the internal strain of α -FAPbI₃ lattice was reported as the driving force of the phase transition and compensation of the strain by incorporating small ions could prevent the phase transition¹⁰. Despite the success and reliability of this method, it should be pointed out that the incorporation of the small ions usually leads to an enlarged bandgap¹¹⁹. As a result, light absorption at the long-wavelength region will be inhibited and the short-circuit current of the fabricated solar cells will decrease¹²². Recently, researchers reported several mixing strategies that stabilized the phase without the bandgap increment^{122,123}. However, such incorporation showed short-term stability of no more than

several weeks. Meanwhile, the incorporation of external ions that were not well-miscible with the α -FAPbI₃ matrix would eventually lead to disorders and heterogeneity in the lattice, and these heterogeneities would serve as non-radiative recombination centers that deteriorated the device performance⁵¹.

Other stabilization methods of α -FAPbI₃ were also reported. Surface functionalization and dimension reduction are popular due to the recent emergence of low-dimensional halide perovskites. The reduction of surface energy was accomplished by large-sized/nonconductive organic molecules¹²⁴. However, such functionalization with organic molecules would prohibit the transport of charged carriers and, therefore, led to relatively low performance. Recently, a new confinement strategy of α -FAPbI₃ stabilization was reported. α -FAPbI₃ was found to obtain phase stability within patterned nanochannels¹²⁵. Long-term stability was achieved by limiting the expansion of α -FAPbI₃ during phase transition to δ -FAPbI₃ with the confinement of the surrounding nanochannels. However, this method lacked compatibility with conventional fabrication protocols and could hardly be applied to device integration. Additionally, encapsulating the α -FAPbI₃ with mesoporous TiO₂ scaffolds was found to enhance the phase stability of α -FAPbI₃¹²⁶. However, the stability didn't last long.

2. Differences between the epitaxial stabilization and the current methods.

Besides the conventional stabilization by forming mixed perovskite alloys, the dimensional reduction, as well as the encapsulation effects, are also reported^{124,125,127,128}. Herein, we discuss the differences between these methods with the epitaxial stabilization in

this study and demonstrate that the epitaxial stabilization is from neither the dimensional reduction nor the encapsulation effect.

The dimensional reduction of the α -FAPbI₃ is usually accomplished by forming two-dimensional α -FAPbI₃ with several atomic layers or zero-dimensional quantum dot with a limited number of lattices¹²⁴. This low-dimensional α -FAPbI₃ is usually capped with surfactants/capping agents to reduce the surface energy so that the metastable α phase can be stabilized. In the case of the epitaxially stabilized α -FAPbI₃, however, the thin film is far beyond several atomic layers and, therefore, will not be considered as the effect of the dimensional reduction.

The encapsulation effect is also reported to stabilize the α -FAPbI₃. Embedding the α -FAPbI₃ into the mesoporous TiO₂ scaffolds was reported to retard the phase transition due to the partial encapsulation by the mesoporous TiO₂¹²⁶. Meanwhile, the stabilization of α -FAPbI₃ within nanochannel was also reported^{125,128}. The encapsulation of the α -FAPbI₃ with the nanochannels prohibits the phase transition by constraining the volume expansion of α -FAPbI₃ to δ -FAPbI₃ in the nanochannels. However, in both cases, an epitaxial relationship between the mesoporous TiO₂/nanochannel and the constrained α -FAPbI₃ is not necessary. In the case of the epitaxial stabilization, the α -FAPbI₃ is grown on the substrate with only the bottom surface chemically bonded to the substrate. The α -FAPbI₃ lattice is constrained to the substrate, which is the essential difference from the encapsulation method.

By comparing these two methods with the epitaxial growth, we can conclude that both the dimensional reduction and the encapsulation effect require the entire capping/encapsulation of the α -FAPbI₃ by either the capping agents or space-confinement

objects. In the epitaxial stabilization, the epitaxial α -FAPbI₃ grows on the substrate and leaves the top surface and the side surfaces uncapped. The stabilization effect comes from the coherent growth of the α -FAPbI₃ with the substrates. During nucleation, the crystallized FAPbI₃ will adopt the most conformal atom sequence to accommodate the existing substrate crystal structure. Once crystallized, the formed epitaxial lattice will be constrained to the substrate due to the strong chemical bonds between them. Therefore, the epitaxial growth is also used to stabilize the polymorphs that are unstable under ambient condition¹²⁹⁻¹³¹. The origin of the epitaxial stabilization actually comes from the coherent interface rather than the reduced dimension or the encapsulation effect. The epitaxial α -FAPbI₃ thin film strongly bonds to the substrate, leaving other surfaces uncapped. Not to mention the passivation effect of the surfactant. Therefore, we can exclude the possibility of dimensional reduction and encapsulation effects regarding the phase stabilization of α -FAPbI₃.

Besides, a recent study shows that the residual strain produced from the thermal expansion coefficients difference during the thermal annealing can be used to temporarily stabilize the polycrystalline α -CsPbI₃ film¹⁶. However, the mechanism is different from the internal lattice strain neutralization. The isotropic (to the randomly orientated polycrystalline perovskite lattices) residual strain originates from the thermal expansion coefficients difference between the glass slide and the polycrystalline perovskites. During cooling down, the constraint from the glass will prevent the phase transition of the α -CsPbI₃ film. The weak constraint by van der Waals contact between the glass slides and the perovskite will be unstable against the environmental fluctuations and can gradually lose the stabilization effect. In the case of chemically epitaxially strained α -FAPbI₃, we suggest that strong constraint

from the ionic bond at the epitaxial interface restrict the phase transition, and neutralization of the lattice internal tensile strain can also be an important reason for stabilization. The strain we applied by epitaxial growth is an anisotropic lattice strain (to the aligned single crystal lattices), which is different from the isotropic residual strain from the reported work¹⁶.

Supplementary Discussion 15: Composition of the Strained α -FAPbI₃

To study the composition of the stabilized epitaxial α -FAPbI₃ thin film, X-ray photoelectron spectroscopy (XPS) is used to examine the targeted key elements (I, Pb, Br, and Cl), as shown in Extended Data Fig. 8a to 8d. The results indicate a pristine surface of the epitaxy α -FAPbI₃ thin film without any contamination from the Br and Cl elements, which excludes the possibility of any stabilization effects by Br and Cl incorporation⁴⁸.

Supplementary Discussion 16: First-Principles Calculations of Epitaxial Stabilization

First-principles calculations were performed to investigate epitaxial stabilization of α -FAPbI₃ with respect to δ -FAPbI₃ on MAPbBr₃ substrates. A typical model of epitaxial stabilization calculations compares the total energy changes of nucleating the two phases on the substrate¹³². Equation (1) shows an expression of this model for this specific system:

$$\Delta E^{\alpha-\delta} = (\Delta E_f^{\alpha} - \Delta E_f^{\delta})d + (\Delta E_s^{\alpha} - \Delta E_s^{\delta})d + (\sigma^{\alpha||S} - \sigma^{\delta||S}) \quad (1)$$

where the terms on the right-hand side for phase i ($i = \alpha, \delta$) are bulk formation energy (ΔE_f^i), strain energy (ΔE_s^i), and interfacial energy ($\sigma^{i||S}$, S means substrate) terms. Here, we use

area-specific bulk energy terms (ΔE_f^i and ΔE_s^i) by setting the film thickness to $d = 1$ nm. The sum of the three energy-difference terms is the total energy difference between strained α -FAPbI₃ and δ -FAPbI₃ ($\Delta E^{\alpha-\delta}$). A negative $\Delta E^{\alpha-\delta}$ indicates that growth of α -FAPbI₃ is energetically more favorable than δ -FAPbI₃ on the MAPbBr₃ substrate, and thus the metastable α -FAPbI₃ is epitaxially stabilized. Calculation details and results for each energy term are discussed below.

The bulk formation energy (ΔE_f^i) is the energy difference between bulk i -FAPbI₃ and its elemental components, as shown in Equation (2):

$$\Delta E_f^i = E_i - E_{FA} - E_{Pb} - 3E_I \quad (2)$$

Because we are dealing with polymorphs with the same composition, the elemental components for both α and δ phases are the same. The total energy of the FA⁺ cation is calculated based on an isolated molecule. Total energies of Pb and I are calculated using their most stable crystal structures, with a space group of $Fm3m$ and $Cmce$, respectively. By setting the film thickness to 1 nm, we get area-specific bulk formation energies $\Delta E_f^\alpha = -2.279 \times 10^{-1} \frac{eV}{\text{\AA}^2}$ and $\Delta E_f^\delta = -2.31 \times 10^{-1} \frac{eV}{\text{\AA}^2}$. The results indicate that δ -FAPbI₃ is more stable, which agrees with the experimental findings that δ -FAPbI₃ is more stable than α -FAPbI₃ at room temperature⁴⁰.

The strain energy of i -FAPbI₃ (ΔE_s^i) is induced by constraints from the substrate due to epitaxial nucleation and lattice mismatch. It equals to the energy difference between the films with and without the strain (Equation (3)).

$$\Delta E_s^i = E_i^{strained} - E_i \quad (3)$$

In the case of α -FAPbI₃, we have confirmed in the experiments that both MAPbBr₃ substrate

and α -FAPbI₃ film are (001) oriented. Our calculations also show that lattice constants of α -FAPbI₃ and MAPbBr₃ have a relatively large mismatch of 6%. Therefore, we can explicitly obtain $E_{\alpha}^{strained}$ in Equation (3) by calculating α -FAPbI₃ with 6% bi-axial compressive strain along ab -axes. The area-specific ΔE_s^{α} is calculated to be $1.2 \times 10^{-2} \frac{eV}{\text{\AA}^2}$.

In the case of δ -FAPbI₃, the possible growth model is not straightforward. Therefore, we perform a search for the lattice plane of minimal lattice mismatch with MAPbBr₃ (001). The hexagonal (001) close-packed plane of δ -FAPbI₃ has dimensions of $a = b = 8.62 \text{ \AA}$ and $\gamma = 120^\circ$. Based on this plane, the termination we found that is most compatible with MAPbBr₃ (001) substrate has a large vector strain of 13.2% and 3.43° , and an area strain of 18.3%. This obviously exceeds the strain threshold for a coherent interface, which is usually below 10%¹³². We thus consider δ -FAPbI₃ forms incoherent interface with MAPbBr₃ (001). A film with the incoherent interface is not constrained by the substrate and the strain energy ΔE_s^{δ} is therefore 0.

To calculate the interfacial energy for α -FAPbI₃ (001)/MAPbBr₃ (001) ($\sigma^{\alpha||S}$), we build heterostructural models consisting of m layers of substrate and n layers of film. The two heterostructural models are shown in Supplementary Fig. 13a. They represent two different terminations, namely FAI/PbBr₂ ($m = 5, n = 9$) and PbI₂/MABr ($m = 5, n = 11$). Note that only nine layers of film material are shown in each structure for clarity.

The other two possible terminations for the α -FAPbI₃ (001)/MAPbBr₃ (001) interfaces are FAI/MABr and PbI₂/PbBr₂ (not shown here). Through initial analysis of bonding characteristics, we find that these terminations cannot form ionic bonds between the film and the substrate like the Pb-I or Pb-Br bonds in FAI/MABr (PbI₂/PbBr₂). ‘Physical contacts’ like

FAI/MABr and $\text{PbI}_2/\text{PbBr}_2$ ¹³³ at the interface are less stable than ‘chemical contacts’ like FAI/ PbBr_2 and PbI_2/MABr . Therefore, we only focus on FAI/ PbBr_2 and PbI_2/MABr in this investigation.

After the heterostructural models are confirmed, the interfacial energy can be calculated by subtracting the bulk energy of all components in the heterostructural model. Specifically, interfacial energy equations for these two heterostructural models are shown as Equations (4) and (5).

$$\sigma_{\text{TERM1}}^{\alpha||S} = \frac{1}{2A} (E_{\text{HS1}} - 2 \times E_{\text{MAPbBr}_3} - 4 \times E_{\text{FAPbI}_3}^{\text{strain}} - \mu_{\text{Pb}}^{\text{MAPbBr}_3} - 2 \times \mu_{\text{Br}}^{\text{MAPbBr}_3} - \mu_{\text{FA}}^{\text{FAPbI}_3} - \mu_{\text{I}}^{\text{FAPbI}_3}) \quad (4)$$

$$\sigma_{\text{TERM2}}^{\alpha||S} = \frac{1}{2A} (E_{\text{HS2}} - 2 \times E_{\text{MAPbBr}_3} - 5 \times E_{\text{FAPbI}_3}^{\text{strain}} - \mu_{\text{MA}}^{\text{MAPbBr}_3} - \mu_{\text{Br}}^{\text{MAPbBr}_3} - \mu_{\text{Pb}}^{\text{FAPbI}_3} - 2 \times \mu_{\text{I}}^{\text{FAPbI}_3}) \quad (5)$$

where E_{HS} is the total energy of the heterostructural model, E_{MAPbBr_3} is the total energy of the strain-free MAPbBr_3 lattice, $E_{\text{FAPbI}_3}^{\text{strain}}$ is the total energy of the strained $\alpha\text{-FAPbI}_3$ lattice, and μ represents the chemical potentials of the corresponding atoms/molecules. Each of the heterostructural models contains two identical interfaces, and A is the interfacial area.

On the right-hand side, the trailing terms represent the bulk energy of each component in the heterostructure. For example, there are nine layers of $\alpha\text{-FAPbI}_3$ in FAI/ PbBr_2 , which equals to four intact $\alpha\text{-FAPbI}_3$ unit cells (each has two layers) plus one extra layer of FAI. The extra or un-stoichiometric components require the determination of their chemical potentials in the corresponding film or substrate material. Here we show in detail how we obtained chemical potentials of un-stoichiometric $\alpha\text{-FAPbI}_3$ components.

$$\Delta\mu_{\text{FA}} + \Delta\mu_{\text{Pb}} + 3\Delta\mu_{\text{I}} = \Delta H(\text{FAPbI}_3) = -5.78 \text{ eV} \quad (6)$$

$$\Delta\mu_{Pb} + 2\Delta\mu_I < \Delta H(PbI_2) = -2.02 \text{ eV} \quad (7)$$

$$\Delta\mu_{FA} + \Delta\mu_I < \Delta H(FAI) = -3.74 \text{ eV} \quad (8)$$

According to thermodynamic stability limits expressed in Equations (6) - (8), we plot the phase diagram for α -FAPbI₃ against the chemical potential change $\Delta\mu_I$ and $\Delta\mu_{Pb}$. Supplementary Fig. 13b shows the phase diagram, and the long, narrow green region indicates the thermodynamic stability region for the synthesis of α -FAPbI₃. We select three representative points throughout the whole region for the following calculations: A ($\Delta\mu_I = -1.02 \text{ eV}$, $\Delta\mu_{Pb} = 0 \text{ eV}$), B ($\Delta\mu_I = -0.50 \text{ eV}$, $\Delta\mu_{Pb} = -1.03 \text{ eV}$), and C ($\Delta\mu_I = 0 \text{ eV}$, $\Delta\mu_{Pb} = -2.04 \text{ eV}$).

Similarly, we obtain the phase diagram for MAPbBr₃ substrate (not shown) and select one representative point P ($\Delta\mu_{Br} = -0.70 \text{ eV}$, $\Delta\mu_{Pb} = -1.47 \text{ eV}$) in the middle of the thermodynamically stable range. The values of point P are used as constants in Equations (4) and (5) for the un-stoichiometric MAPbBr₃ components.

We also added the stability limit for FAI/MABr and PbI₂/PbBr₂ in the phase diagram (Supplementary Fig. 13b). As the red dashed line shows, FAI/MABr is more stable in the region below this limit, and it covers the whole stability range of α -FAPbI₃. Therefore, we only need to calculate the interfacial energy for FAI/MABr, and the results are $2.86 \times 10^{-4} \text{ eV } \text{\AA}^{-2}$, $4.29 \times 10^{-4} \text{ eV } \text{\AA}^{-2}$, and $2.86 \times 10^{-4} \text{ eV } \text{\AA}^{-2}$ at A, B, and C points, respectively. Interestingly, the composition of interfacial terminations and their preferred chemical potential conditions agree with each other. For the δ -FAPbI₃/MAPbBr₃ (001) interface, the interfacial energy $\sigma^{\delta||S}$ is given as $6.242 \times 10^{-2} \text{ eV } \text{\AA}^{-2}$ (i.e., 1 J m^{-2}), a typical value for incoherent interfaces¹³².

Results for all energy terms in Equation (1) are summarized in Supplementary Table 3.

The calculated total energy change of nucleating α -FAPbI₃ is around -2.155×10^{-1} eV Å⁻² (regardless of chemical potential conditions), while the value for δ -FAPbI₃ is -1.6858×10^{-1} eV Å⁻². Apparently, $\Delta E^{\alpha-\delta}$ has a negative value of around -4.7×10^{-2} eV Å⁻² (i.e., -0.75 J m⁻²), which indicates epitaxial stabilization of α -FAPbI₃ with respect to δ -FAPbI₃ on MAPbBr₃ substrates. This result is comparable to prior successful prediction of epitaxial stabilization.

From Supplementary Table 3, we can see that the bulk formation energy is the largest term but yields a small difference (3.1×10^{-3} eV Å⁻²) between α -FAPbI₃ and δ -FAPbI₃. The strain energy term is in favor of δ -FAPbI₃ by a large value of 1.2×10^{-2} eV Å⁻². The main contribution to $\Delta E^{\alpha-\delta}$ is from interfacial energy, which is above 6×10^{-2} eV Å⁻² and decides the overall energy preference. Notably, to accurately determine energetics using DFT calculations, we apply a large interfacial mismatch (strain = -6%) to calculate the strain energy term for α -FAPbI₃. However, the calculations represent an upper limit of strain's influence and guarantee a negative $\Delta E^{\alpha-\delta}$ in lower-strain circumstances. Strains below 6% would definitely yield a ΔE_s^α less than 1.2×10^{-2} eV Å⁻² and a more negative $\Delta E^{\alpha-\delta}$, which better ensures epitaxial stabilization of α -FAPbI₃. Another experimental variable is the substrate composition. We use MAPbBr₃ as the substrate in the heterostructural model to calculate the interfacial energies, but in experiments we also use mixed-halide substrates with Cl composition up to MAPbCl_{1.50}Br_{1.50}. This will not change the conclusion of the discussions here because the substrate energy is excluded in the calculation of the interfacial energy, as shown in Equations (4) and (5).

Besides, the consideration of the stabilization mechanism is based on the system with

both the α -FAPbI₃ and substrate lattices rather than just focusing on the α -FAPbI₃ lattice alone. Two different heterostructures (i.e., the α -FAPbI₃/substrate and the δ -FAPbI₃/substrate) are used to study the interfacial energy of nucleus crystallization during the epitaxial growth. The structure with lower interfacial energy will be more favorable during nucleus crystallization and, thus, more favorable to form. Calculation results show that the interfacial energy of the α -FAPbI₃/substrate (0.0286×10^{-2} eV Å⁻²) is much lower than that of the δ -FAPbI₃/substrate (6.242×10^{-2} eV Å⁻²). Therefore, the total energy of the α -FAPbI₃/substrate system is much smaller than that of the δ -FAPbI₃/substrate system because of the interfacial energy benefit, which stabilizes the epitaxial α -FAPbI₃ on the substrate. Additionally, the phase transition depends on not only the energy landscapes of both phases (phases before/after phase transition), but also the energy barrier between the two phases. This is where the epitaxial constraint from the substrate comes into play. In order to make the phase transition to happen, the α -FAPbI₃ need to break the ionic bonds with the substrate, which represents a very high energy barrier. Therefore, due to the synergistic effects of strain and epitaxial constraint, the α -FAPbI₃ is stable for long term as observed in this study. In summary, our calculations show reliable and robust validation of the epitaxial stabilization of α -FAPbI₃.

Supplementary Discussion 17: Stability Investigation of the α -FAPbI₃ Removed from the Substrate

Due to the constraint of the substrate lattice, the epitaxial α -FAPbI₃ thin film shows long-term stability without phase transition. To experimentally demonstrate the phase stability originates from the substrate lattice constriction, we partially remove the epitaxial α -FAPbI₃ thin film from the substrate and investigate the phase stability of the removed α -FAPbI₃. Due to the limited thickness of the epitaxial α -FAPbI₃ thin film, it is difficult to remove the epitaxial thin film by a sharp razor blade or needle. Therefore, we remove the epitaxial α -FAPbI₃ by polishing a substrate covered with the epitaxial α -FAPbI₃ thin film with a sandpaper. As shown in Supplementary Fig. 14a, removed α -FAPbI₃ attached to the upper half of the sandpaper while the removed substrate (MAPbBr₃ in this case) attached to the lower half of the sandpaper due to over-polishing. Meanwhile, the right half of the substrate, which remains unpolished, is covered with epitaxial α -FAPbI₃ while the left half exposes the substrate due to the removal of epitaxial α -FAPbI₃. The removed α -FAPbI₃, which attaches to the sandpaper, remains in black α phase right after removal. After 24 hours, the removed α -FAPbI₃ changes to yellow δ phase while the epitaxial α -FAPbI₃ on the right half of the substrate remains black and stable (Supplementary Fig. 14b). This experiment shows that the epitaxial stabilization of the α -FAPbI₃ thin film originates from the constraint by the substrate lattice and relies on the existence of the substrate. The MAPbCl_xBr_{3-x} substrates are highly stable and therefore the epitaxial α -FAPbI₃ is expected to be highly stable as well.

Supplementary Discussion 18: Photodetectors Based on the Strained α -FAPbI₃

Based on the device structure and working principles, the halide perovskites photodetectors are divided into two main categories: the photodiode-type and the photoconductor-type. Here, we fabricate photodetectors with both structures and discuss them below.

1. Photodetector with a photoconductor structure

Photodetectors with a vertical photoconductor structure based on the strained α -FAPbI₃ thin films are fabricated with a structure shown in Supplementary Fig. 15. Compared with the photodiode-type one, the photoconductor-type photodetectors will have a much higher responsivity and the EQE will be larger than 100% due to the injected carriers¹³⁴⁻¹³⁶. All devices we tested have a thickness of around 1 μ m. A transparent ITO electrode is deposited as the top electrode with an area of 1×1 mm². I - V characteristics are measured under -1 V bias with a 685-nm laser as the excitation source. The responsivity of the photodetectors is calculated by:

$$R = (J_{light} - J_{dark})/P,$$

where J_{light} and J_{dark} are the current densities under illumination and dark conditions, respectively, and P is the input light power density. Extended Data Fig. 9a shows the responsivity of photodetectors at different strain levels under 0.015 W cm⁻² illumination. Compared with the strain-free device, devices at -0.8%, -1.2%, and -1.4% strain levels show enhanced responsivity. Further increasing the compressive strain level will lead to a deterioration of the responsivity due to the accumulation of defects. Supplementary Table 4 summarizes the highest responsivity measured on α -FAPbI₃ in the literature. The

responsivity of the device is comparable with the highest responsivity of a strain-free system with a similar device structure but at a much weaker illumination and higher bias voltage.

Besides, the detectivity, which characterizes how weak light can be detected, and the gain, which describes the number of charges flowing through an external circuit per incident photon, are calculated by:

$$D = R / \sqrt{2qJ_d} \text{ and } G = 1240R / 685$$

where D is the detectivity, R is the responsivity, q is element charge, J_d is the dark current density, and G is the gain. They are also plotted as a function of illumination power level for both -1.2% strained and strain-free devices (Extended Data Fig. 9b, c). Results demonstrate that the strained device has better performance than the strain-free device.

Normalized external quantum efficiency (EQE) spectra are shown in Extended Data Fig. 9d to highlight the extended absorption range of the strained device compared with the strain-free device.

2. Photodetectors with a photodiode structure

With electrons/holes blocking layers, the photodiode-type photodetectors exhibit a minimized dark current by blocking the external current injection. In this study, we aim at fabricating a detector with high responsivity. Therefore, we fabricate and test the photodetector with the photodiode structure for comparison. We fabricated a photodiode-type photodetector by inserting poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as the hole transporting layer and tin oxide (SnO_2) as the electron transporting layer. The structure of the photodiode type photodetector is

Au/PEDOT:PSS/FAPbI₃/SnO₂/ITO, which is shown in Supplementary Fig. 16a. From the band diagram, the carrier injection under reverse bias is blocked due to the large energy barrier. The characterization of the photodetector was carried out with a 685-nm red laser, which is selected based on the highest EQE wavelength, under different input power levels. Supplementary Fig. 16b shows the I - V curves of the photodetector under the dark condition as well as under 1 μ W illumination. The I - V curves show a typical diode-like behavior while the dark current under -0.5 V is measured to be $\sim 2 \times 10^{-8}$ A. This value is more than two orders of magnitude lower than that of the photoconductor type detector. However, under the same illumination power level, the photocurrent is much smaller than that of the photoconductor type detector (~ 600 times lower at a 10^{-6} W incident power), and therefore, leads to a lower responsivity (~ 500 times lower at a 10^{-6} W incident power). The responsivity and the photocurrent under different illumination power levels are also shown in Supplementary Fig. 16c. Under different illumination power levels, the responsivity of the photodetector is always lower than 1 A W^{-1} (in comparison with the responsivity of 200 A W^{-1} of the photoconductor type detector), indicating the block of external current injection with the presence of the different transporting layers.

Supplementary Discussion 19: Broader Impact of the Epitaxial System

The technique we developed enables the controllable strain engineering of halide perovskites with epitaxial growth, which has a fundamental difference from the previous works. The free-standing α -FAPbI₃ suffers from severe phase transition under room

temperature while the epitaxial strain can stabilize the α -FAPbI₃ without changing the perovskite composition. The pure phase α -FAPbI₃ with long-term stability is a property that is absent in the free-standing α -FAPbI₃.

Secondly, the epitaxial system we developed is a generalized approach that can presumably be applied to the entire halide perovskites family. We have already demonstrated the growth of epitaxial α -FAPbI₃ on various substrates, which means that we can grow various epitaxial halide perovskites on one or multiple halide perovskite substrates.

Additionally, the epitaxial strain can be applied to stabilize polymorphs of metastable perovskites. Perovskites with new compositions are recently predicted through computational designs¹³⁷. However, those predicted new perovskites with novel optical and electronic properties may have unstable crystal structures under room temperature or normal working conditions. In this case, epitaxial stabilization can potentially be applied to stabilize these unstable or metastable perovskites on suitable substrates. The reported approach can be generalized to other halide perovskites with different compositions and structures.

Supplementary Table 1. Summary of the substrate growth precursor ratios, the resulting substrate compositional Br ratios, and lattice parameters.

Cl/Br Solution Ratio	Compositional Br Ratio (%)	Formula	Lattice Parameter (Å)
Cl Only	0	MAPbCl _{3.00} Br _{0.00}	5.70
1/2	50.0	MAPbCl _{1.50} Br _{1.50}	5.83
1/2.5	58.0	MAPbCl _{1.25} Br _{1.75}	5.86
1/3	62.1	MAPbCl _{1.15} Br _{1.85}	5.87
1/4	64.3	MAPbCl _{1.05} Br _{1.95}	5.88
1/6	76.8	MAPbCl _{0.70} Br _{2.30}	5.89
1/8	80.6	MAPbCl _{0.60} Br _{2.40}	5.90
1/19	85.2	MAPbCl _{0.45} Br _{2.55}	5.92
Br Only	100	MAPbCl _{0.00} Br _{3.00}	5.95

Supplementary Table 2. Summary of epitaxial growth substrates and the corresponding strain measured in α -FAPbI₃.

Substrate Composition	α -FAPbI ₃ (001) Peak (degree)	Strain (%)
MAPbCl _{1.50} Br _{1.50}	13.82	-2.4
MAPbCl _{1.05} Br _{1.95}	13.84	-1.9
MAPbCl _{0.70} Br _{2.30}	13.86	-1.4
MAPbCl _{0.60} Br _{2.40}	13.87	-1.2
MAPbCl _{0.00} Br _{3.00}	13.89	-0.8

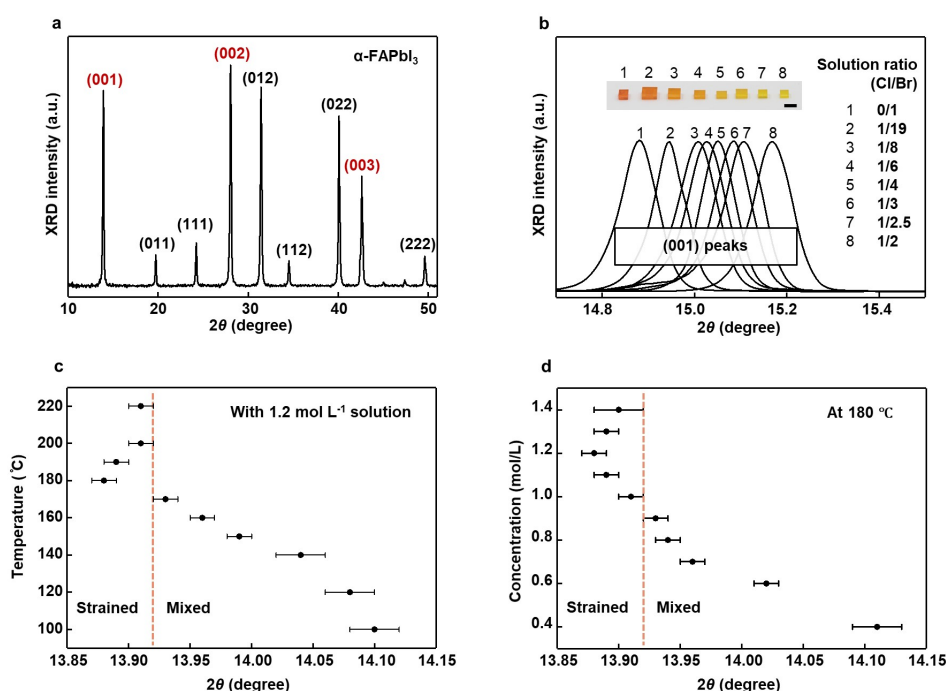
Supplementary Table 3. Thermodynamic terms relevant to epitaxial nucleation of α -FAPbI₃ and δ -FAPbI₃ on cubic MAPbBr₃ substrates.

	α -FAPbI ₃			δ -FAPbI ₃
	A	B	C	--
ΔE_f	-22.79×10^{-2}			-23.10×10^{-2}
ΔE_s	1.20×10^{-2}			0
σ	0.0286×10^{-2}	0.0429×10^{-2}	0.0286×10^{-2}	$6.242 \times 10^{-2*}$
ΔE	-21.5614×10^{-2}	-21.5471×10^{-2}	-21.5614×10^{-2}	-16.858×10^{-2}
$\Delta E (\alpha-\delta)$	-4.7034×10^{-2}	-4.6891×10^{-2}	-4.7034×10^{-2}	--

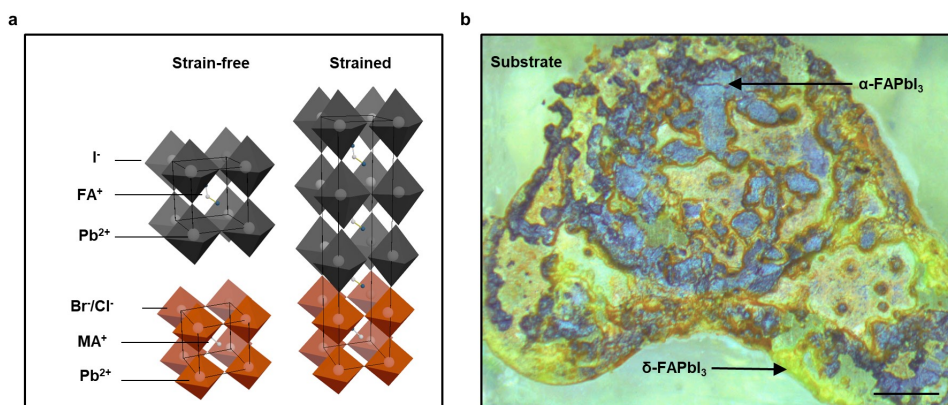
The bulk formation energy (ΔE_f), strain energy (ΔE_s), interfacial energy (σ), total energy change (ΔE), and the difference between of the two phases ($\Delta E (\alpha-\delta)$) are in eV Å⁻². The value marked with * indicates that the interface between the substrate and the δ -FAPbI₃ is considered incoherent, and the interfacial energy term is set at $1 \text{ J m}^{-2} = 6.242 \times 10^{-2} \text{ eV Å}^{-2}$.

Supplementary Table 4. Summary of representative halide perovskite photodetectors with high responsivities in the literature.

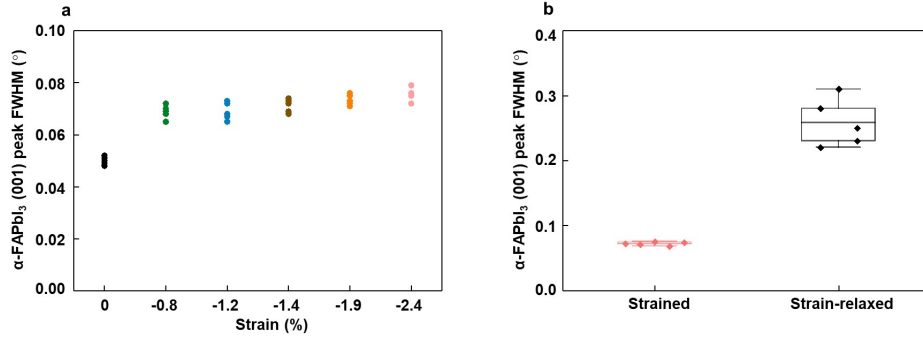
Device structure	Structure	Highest R	Light power	Bias	References
Au/MAPbBr ₃ /Au	Planar	~10 A W ⁻¹	0.01 mW cm ⁻²	-2 V	138
Cr/MAPbI ₃ /Cr	Planar	~20 A W ⁻¹	0.1 mW cm ⁻²	-1 V	139
Au/MAPbI ₃ /Au	Planar	~20.4 A W ⁻¹	2 μW cm ⁻²	-1.5 V	140
Au/MAPbBr ₃ /Au	Planar	40 A W ⁻¹	54 μW	-5 V	141
Au/ (BA) ₂ (MA) _{n-1} Pb _n I _{3n+1} NWs/Au	Planar	2×10 ⁴ A W ⁻¹	10 ⁻⁶ mW cm ⁻²	-2 V	106
Au/FAPbI ₃ /ITO	Vertical	1.3×10 ⁶ A W ⁻¹	1.1×10 ⁻⁷ W cm ⁻²	-1 V	This Work



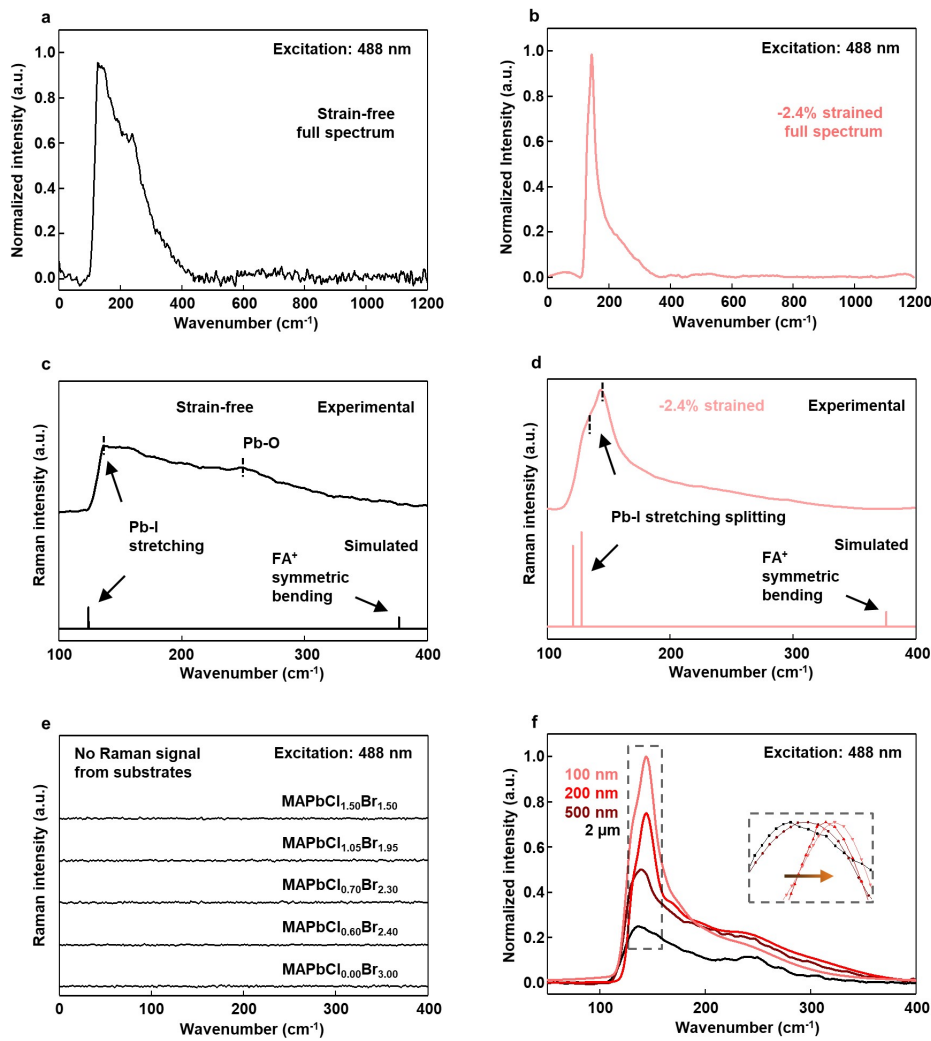
Supplementary Fig. 1 | Characterization of the lattice parameters and the study of growth condition. **a**, Powder XRD pattern of α -FAPbI₃, which is used as a reference of strain-free α -FAPbI₃. The lattice parameter of cubic α -FAPbI₃ is calculated to be 6.35 Å using the (001) diffraction peak at 13.92°. Peaks from {001} directions are labeled in red. **b**, Powder XRD patterns of substrates with different ratios of the composition. By tuning the Cl/Br molar ratio in the growth solution, we can change the Cl/Br ratio as well as the lattice parameter of the substrate crystal. We note that MAPbCl_{3.00}Br_{0.00}, MAPbCl_{0.00}Br_{3.00}, and their alloys all have cubic structures. Lattice parameters can be directly calculated by the 2 θ peak positions. The inset is an optical image of the corresponding substrates with different Cl/Br ratios. All powders are made by grinding the bulk single crystals. Scale bar: 5 mm. **c**, XRD (100) peak positions of α -FAPbI₃ at different growth temperatures. The temperature to grow α -FAPbI₃ with the highest strain is found to be ~180 °C. Further increasing the growth temperature results in a high growth rate and a thick epitaxial layer of α -FAPbI₃ and therefore low crystal quality that relaxes the strain. Decreasing the growth temperature below 180 °C can lead to slow crystallization and thus a mixed epitaxial alloy layer at the interface, which shifts the XRD peak position to higher angles. **d**, XRD (100) peak positions of α -FAPbI₃ at different growth solution concentrations. Concentrations above 1.2 mol L⁻¹ result in high defect concentration and therefore strain relaxation, due to the fast crystallization rate and the thick epitaxial layer. Concentrations below 1.0 mol L⁻¹ will slow down the crystallization process and lead to a mixed epitaxial alloy layer at the interface. The vertical dash lines in **c** and **d** show the peak position of a strain-free powder sample. (a.u., arbitrary units).



Supplementary Fig. 2 | Schematic crystal structures of epitaxial α -FAPbI₃ on MAPbCl_xBr_{3-x} and the optical image of α -FAPbI₃ on a Cl-rich substrate. **a**, Schematic crystal structures of α -FAPbI₃, MAPbCl_xBr_{3-x}, and the epitaxial heterostructure showing the crystallographic orientation of the epitaxial α -FAPbI₃ and the MAPbCl_xBr_{3-x} substrate, with distorted PbI₆ octahedron inorganic framework in the epitaxial layer under compressive interfacial strain. **b**, An optical image of FAPbI₃ grown on MAPbCl_{2.00}Br_{1.00} substrate using the same growth method as the other substrates. Due to the large lattice mismatch between the substrate and α -FAPbI₃, the α -FAPbI₃ crystallizes randomly rather than epitaxially on the substrate surface. The lack of epitaxial stabilization leads to quick phase transformation from metastable α -FAPbI₃ to δ -FAPbI₃ at room temperature. Scale bar: 200 μ m.

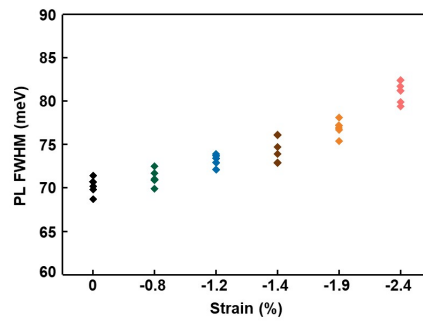


Supplementary Fig. 3 | XRD diffraction peak FWHM. **a**, Diffraction peak FWHM study of the epitaxial α -FAPbI₃ thin films under different strain magnitudes. Results show that the epitaxially strained α -FAPbI₃ thin films have a relatively higher diffraction peak FWHM than that of the strain-free α -FAPbI₃ crystal due to the lattice strain and the reduced dimension. **b**, statistical study of the α -FAPbI₃ (001) peak FWHM of the strained and the strain-relaxed samples. Results show that the diffraction peak FWHM of the strained epitaxial α -FAPbI₃ thin films ($\sim 0.07^\circ$) is ~ 3 times smaller than that of the strain-relaxed one ($\sim 0.25^\circ$). Note the strain-relaxed epitaxial α -FAPbI₃ thin films come from Extended Data Fig. 1g. Number of experiments $n = 5$ for each strain value.

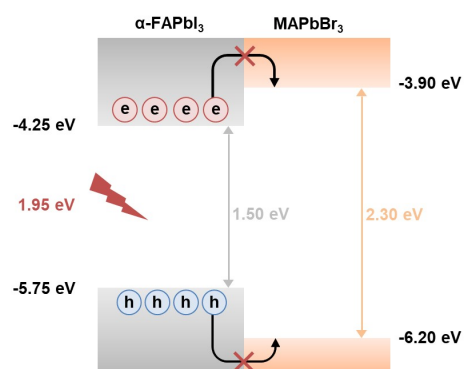


Supplementary Fig. 4 | Raman spectra of α -FAPbI₃ and the substrates. Raman full spectra of **a**, strain-free α -FAPbI₃ bulk crystal and **b**, -2.4% strained α -FAPbI₃ thin film showing the absence of other peaks outside the range of 100 to 400 cm⁻¹. The strain-free α -FAPbI₃ crystal is less Raman-active than the strained α -FAPbI₃ thin film, so the relative peak intensity of the strain-free crystal is much weaker. The comparison of the experimental and simulated Raman spectra of the **c**, strain-free, and **d**, -2.4% strained α -FAPbI₃ lattices. The discrepancy between experimental and simulated Pb-I stretching wavenumbers may be due to the anharmonicity of the bonds and the van der Waals interactions between the inorganic cages and organic cations. For the strained lattice, an obvious peak splitting takes place in both the experimental and the simulated spectra. The splitting of the Pb-I symmetric stretching peak originates from the in-plane compression and out-of-plane stretching, while the intensity enhancement comes from the breakage of the cubic symmetry. The weak FA⁺ cation bending peak at 377 cm⁻¹ fails to be detected, which is due to the dynamic FA⁺ cation rotation at room temperature. **e**, Raman spectra of MAPbCl_{0.00}Br_{3.00}, MAPbCl_{0.60}Br_{2.40}, MAPbCl_{0.70}Br_{2.30}, MAPbCl_{1.05}Br_{1.95}, and MAPbCl_{1.50}Br_{1.50} substrates with a 488-nm laser as the excitation source. No Raman signals can be detected in the wavenumber range of interest. Therefore, possible interference from the substrates can be excluded. **f**, Thickness-dependent Raman spectra of -2.4% strained α -FAPbI₃ samples. Strained α -FAPbI₃ thin film has a sharp

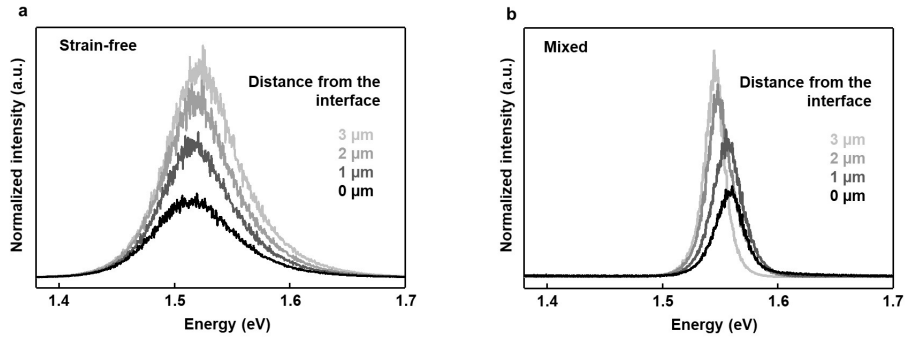
1370 and strong signal, which can be attributed to the increased tetragonality of the crystal
1371 structure. As the film thickness increases, the strain gets gradually relaxed and the lattice
1372 transforms back to less Raman-active cubic structure. The Raman peak position also shifts to
1373 lower wavenumbers because of the softer and longer Pb-I bonds (inset image).



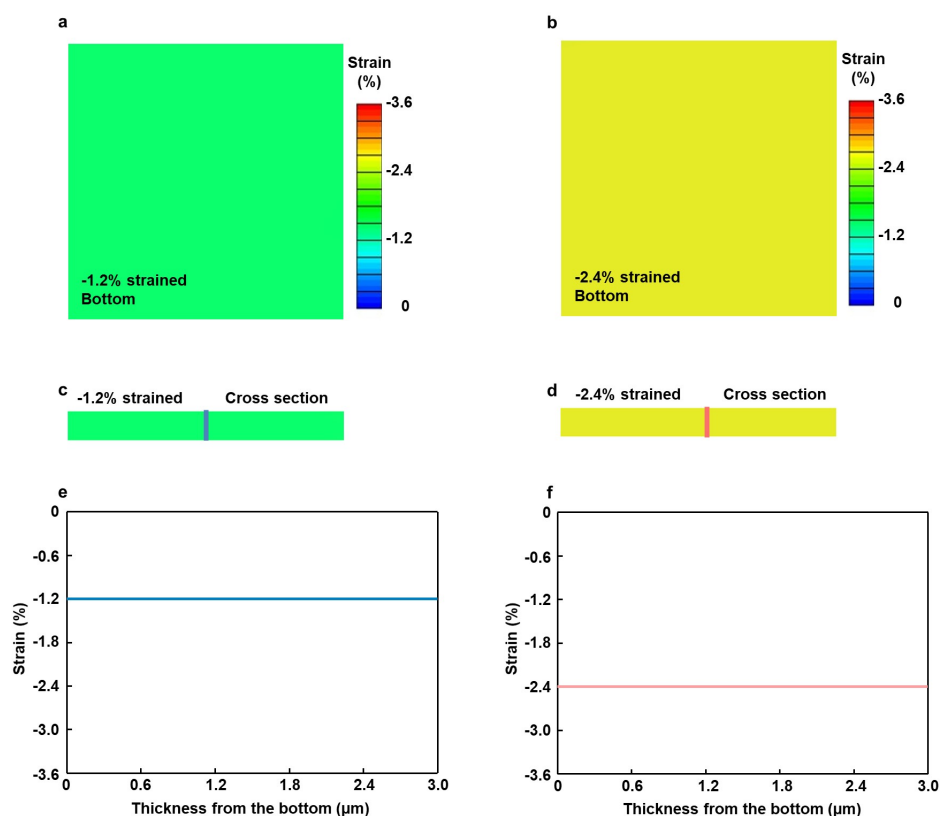
Supplementary Fig. 5 | FWHM of the PL peaks of epitaxial layers under different strains. The results show that the FWHM of the PL peak increases with the strain, due to the strain-induced dislocations that broaden the PL peak. A bulk α -FAPbI₃ single crystal is used as the strain-free reference. Note the number of experiments $n = 5$ for each strain value.



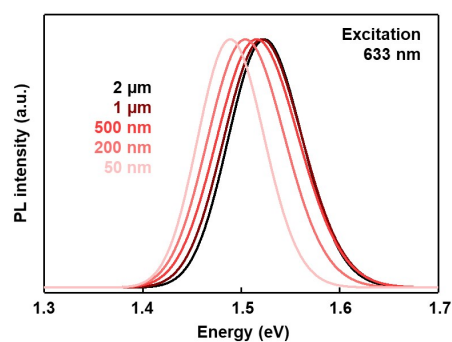
Supplementary Fig. 6 | Band diagram of the heterostructure and the interfacial charge transfer. Excited carriers in the α -FAPbI₃ will not transfer to the MAPbBr₃ due to the energy barrier. The analysis shows that the charged carrier transfer in the heterojunction can be excluded due to the straddling band alignment with a prohibited carrier transfer direction and a large energy barrier.



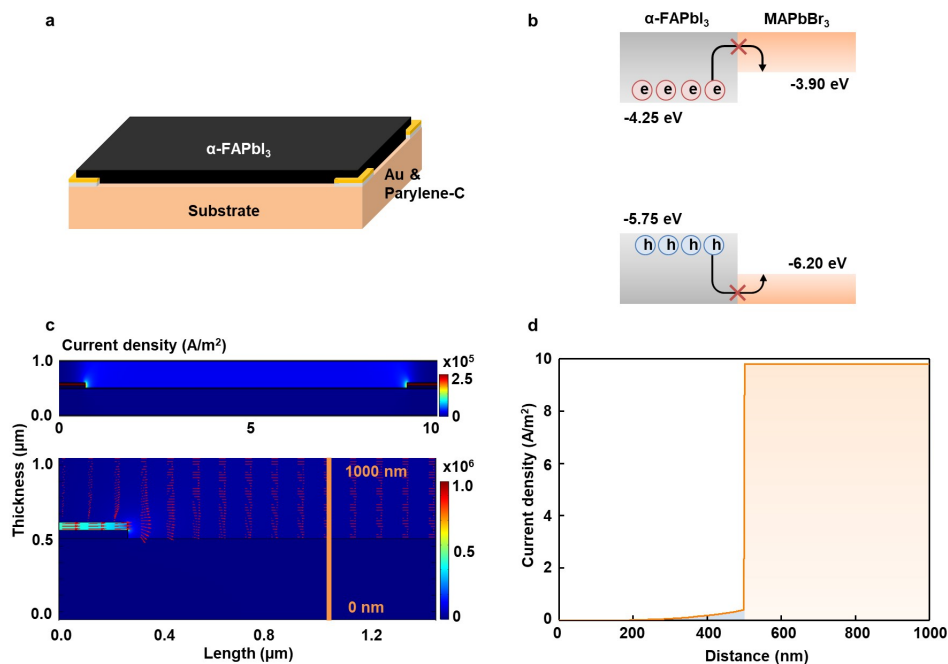
Supplementary Fig. 7 | Focal point dependent PL measurements of strain-free and mixed α -FAPbI₃. **a**, Focal-point-dependent confocal PL spectra of a strain-free α -FAPbI₃ bulk crystal. The redshift of the PL peak from ~ 1.523 eV to ~ 1.516 eV, less pronounced than the PL peak redshift of the strained sample in Fig. 2b, is due to reabsorption. **b**, Focal-point-dependent confocal PL spectra of a mixed epitaxial α -FAPbI₃ grown at a low temperature. Note the mixed sample came from the mixed epitaxial growth with low temperature and low concentration in Supplementary Fig. 1. The increase of focus depth causes the PL peak to blueshift, due to the increase of Br and Cl incorporation in the epitaxial layer.



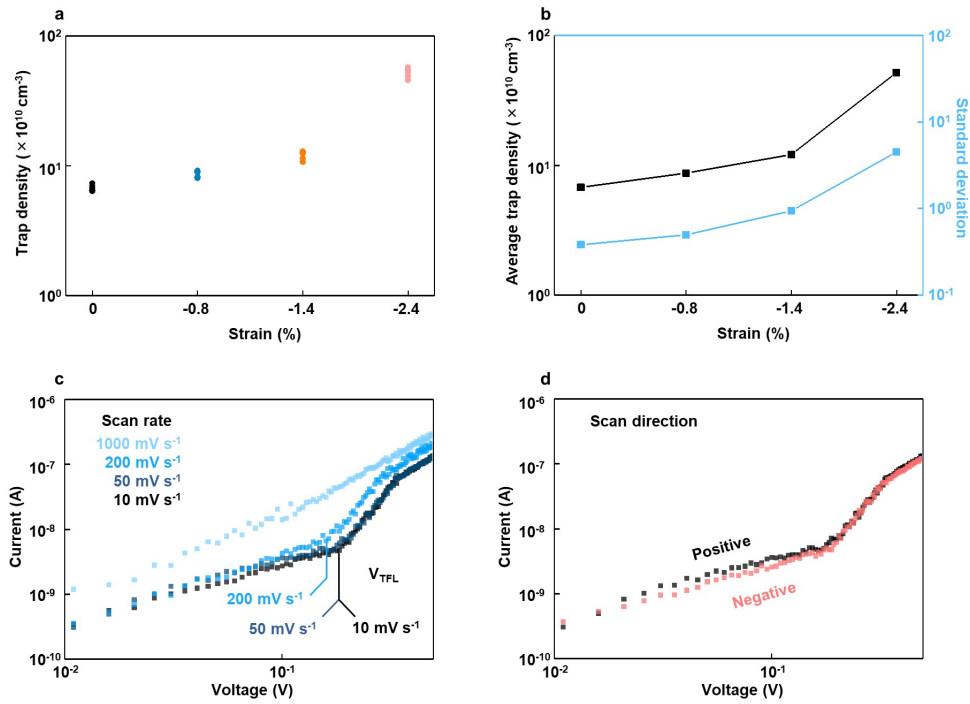
Supplementary Fig. 8 | Elastic strain relaxation study of the epitaxial α -FAPbI₃ thin films. Planar strain distribution of the α -FAPbI₃ with **a**, -1.2% and **b**, -2.4% strain. Vertical strain distribution of the α -FAPbI₃ with **c**, -1.2% and **d**, -2.4% strain. Results show uniform strain distribution in both α -FAPbI₃ thin films. Thickness-dependent strain distribution of the α -FAPbI₃ with **e**, -1.2% and **f**, -2.4% strain. Colors are correlated with the lines in **c** and **d**. Results indicate that the elastic strain relaxations in both α -FAPbI₃ thin film are 0.096% and 0.093%, respectively.



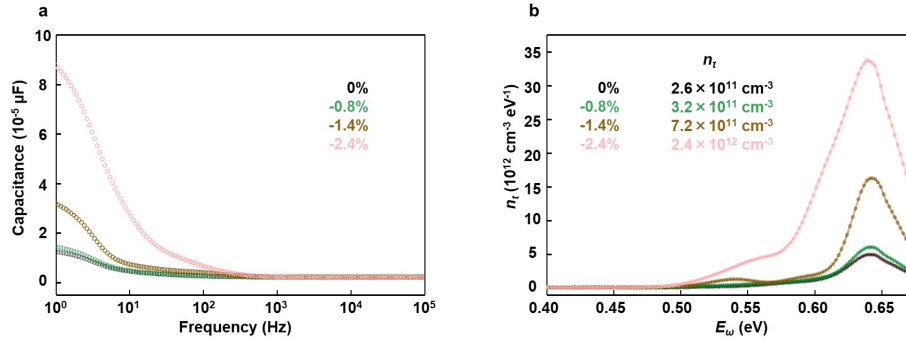
Supplementary Fig. 9 | Film-thickness-dependent PL measurements of epitaxial α -FAPbI₃ on MAPbCl_{1.50}Br_{1.50}. The PL properties of strained α -FAPbI₃ films show a strong thickness dependence. As the film thickness increases, the PL position gradually shifts back to the position of the free-standing bulk crystals. This can be attributed to the plastic strain relaxation as the film gets thicker.



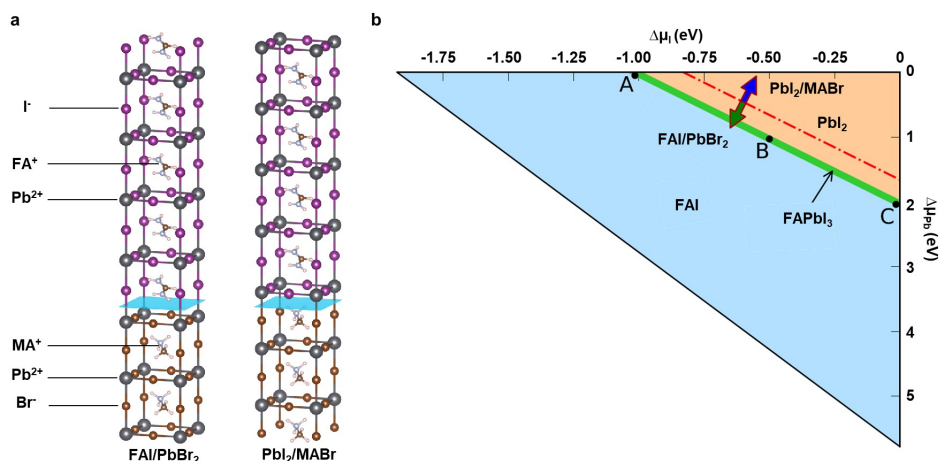
Supplementary Fig. 10 | Possible carrier collection by the interfacial carrier transfer during Hall effect measurements. **a**, The schematic structure of the device. Parylene-C (grey) is used as an insulating layer to prevent the injection of carriers from the Au electrode (yellow) to the substrate. **b**, The bandgap diagram of the heterostructure shows that the large energy barrier between the α -FAPbI₃ and the MAPbBr₃ blocks the carrier injection to the MAPbBr₃. **c**, Current density distribution by FEA simulation. The upper panel shows the current mapping where the current density in the epitaxial layer is much higher than that of the substrate. The lower panel shows the zoomed-in current distribution image around the electrode. Red arrows show the direction of current flow, which suggests a minimal carrier injection into the substrate due to the energy. **d**, Current density distribution along the vertical orange line in **c**, where the current in the substrate takes 0.8% of the total current.



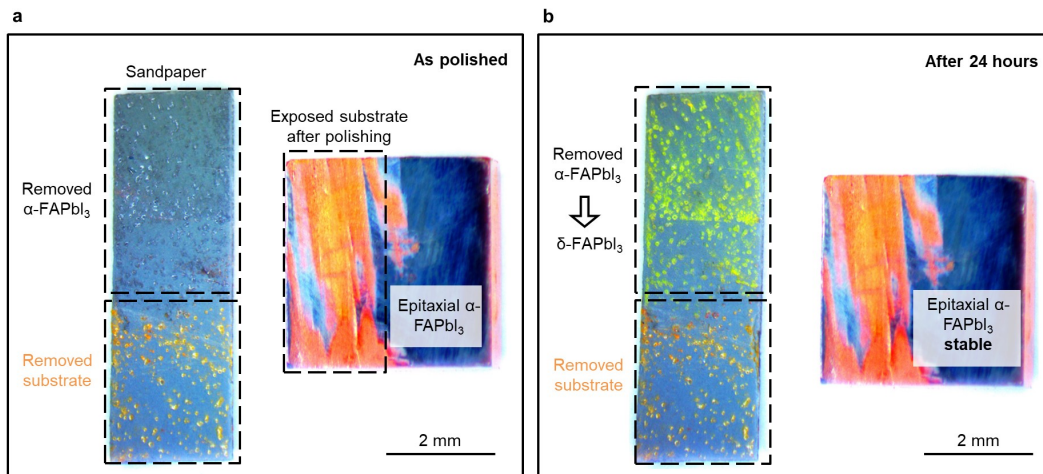
Supplementary Fig. 11 | SCLC measurements of the epitaxial α -FAPbI₃ with different strains. **a**, Strain-dependent trap density of the epitaxial α -FAPbI₃. Note the number of experiments $n = 5$ for each strain value. **b**, Statistics of the strain-dependent trap density. Results show that the average trap density will increase with increasing the strain, which can be attributed to the strain-induced defects. Meanwhile, the standard deviation of the trap density values also increases with the strain, indicating the increased disorder due to the higher defect density with the strain. **c**, Scan-rate-dependent I - V curves. I - V curves with 10 mV s^{-1} and 50 mV s^{-1} scan rates are similar, indicating that these scan rates are sufficiently slow to avoid artificial results. The I - V curve with 200 mV s^{-1} results in a smaller V_{TFL} because of the limited response of free carriers from the fast scan. Further increasing the scan rate to 1000 mV s^{-1} leads to the vanish of the trap-filling process. **d**, I - V curves with different scan directions of the same device. The high similarity of the two curves concludes that the scan direction will not affect the SCLC measurements due to the symmetric Au/Perovskite/Au device structure.



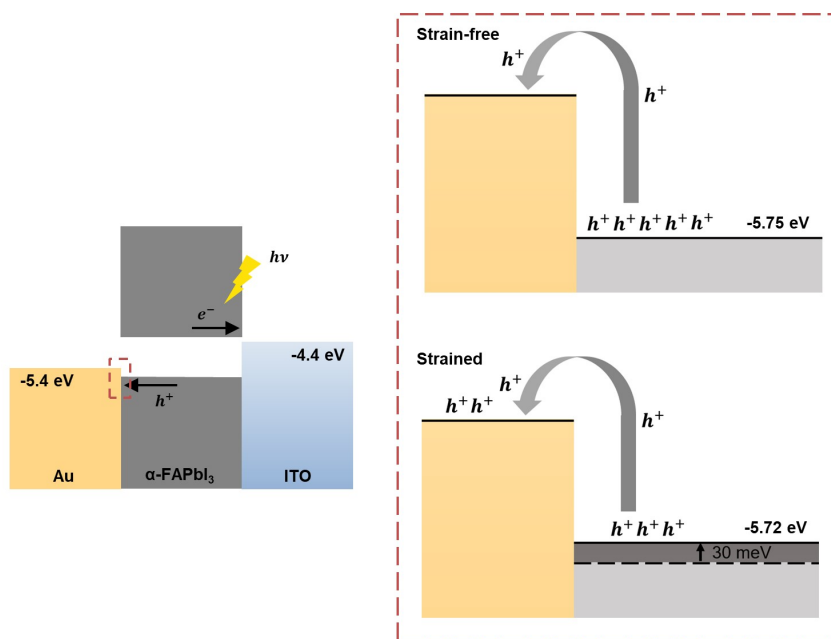
Supplementary Fig. 12 | C - ω measurements of the epitaxial α -FAPbI₃ to evaluate the trap density. **a**, C - ω spectra of the epitaxial α -FAPbI₃ thin films with different strain magnitudes. The low-frequency capacitance originates from the carrier trapping/detrapping processes. The larger capacitance at a higher strain magnitude suggests a higher density of traps. The high-frequency capacitance is attributed to the geometrical capacitance and the depletion capacitance. **b**, Trap density distribution extracted from the C - ω spectra. An obvious trap density increment is evident with increasing the strain magnitude. The fitted trap densities (n_t) by the Gaussian distribution equation indicate a higher trap density at a higher strain magnitude.



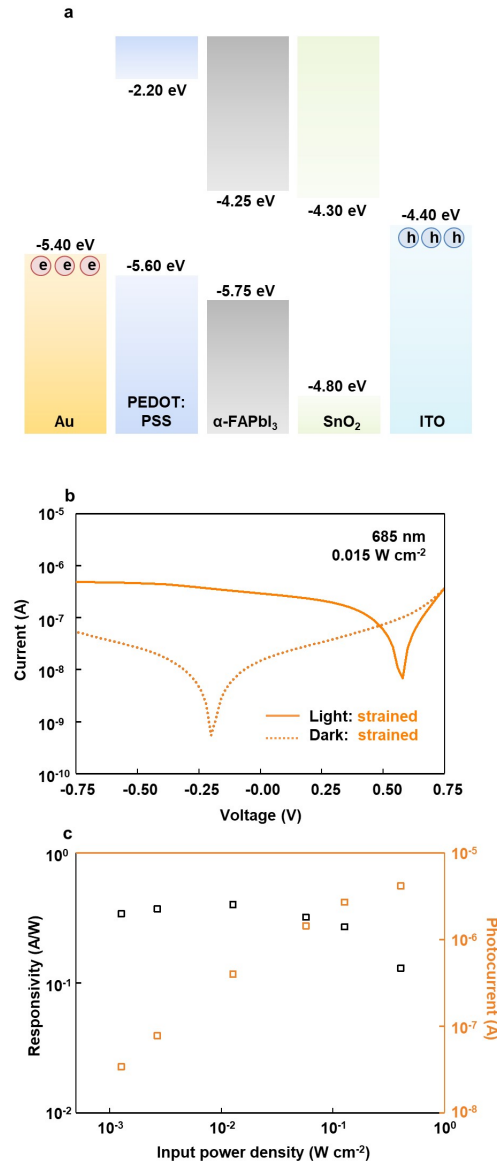
Supplementary Fig. 13 | First-principles calculations of epitaxial stabilization. **a**, Schematic heterostructural models used to calculate the epitaxial α -FAPbI₃ (001)/MAPbBr₃ (001) interface. The two interface terminations studied are FAI/PbBr₂ and PbI₂/MABr. In each model, the blue plane indicates the interface, the upper section indicates the FAPbI₃ film, and the lower section indicates the MAPbBr₃ substrate. **b**, Calculated phase diagram for α -FAPbI₃ and epitaxial α -FAPbI₃ (001)/MAPbBr₃ interface. The long, narrow region marked in green depicts the thermodynamically stable range for equilibrium growth of α -FAPbI₃ under different I and Pb chemical potentials. Outside this region, the compound decomposes into FAI or PbI₂. Three representative points A ($\Delta\mu_I = -1.02$ eV, $\Delta\mu_{Pb} = 0$ eV), B ($\Delta\mu_I = -0.50$ eV, $\Delta\mu_{Pb} = -1.03$ eV), and C ($\Delta\mu_I = 0$ eV, $\Delta\mu_{Pb} = -2.04$ eV) are selected for calculating the interfacial energy. The red dashed line separates the phase diagram into stability regions of the two different interfacial terminations in **a**. μ represents the chemical potentials of the corresponding atoms.



Supplementary Fig. 14 | Stability investigation of the epitaxial and the removed α -FAPbI₃. Images of the **a**, as-polished and the **b**, 24-hour aged epitaxial α -FAPbI₃ thin film. The left half of the epitaxial α -FAPbI₃ thin film is removed by a sandpaper while the right half of the epitaxial α -FAPbI₃ thin film remains on the substrate. Removed α -FAPbI₃ that is attached to the upper half of the sandpaper suffers from phase transition from black α phase to yellow δ phase after 24 hours. The epitaxial α -FAPbI₃ thin film remains on the substrate is stable without phase transition. Results show the epitaxial stabilization of the epitaxial α -FAPbI₃ thin film relies on the constraint from the substrate lattices.



Supplementary Fig. 15 | Schematic band diagrams of photodetectors. Left panel is the flat band diagram of the photodetector. Due to the compressive strain, the VBM of α -FAPbI₃ at the interface will be pushed up and align better with the Au Fermi level (-5.4 eV), which allows better hole transfer from α -FAPbI₃ to Au and therefore enhances the device performance.



Supplementary Fig. 16 | Photodiode-type photodetector characterizations. **a**, The band diagram of the photodetector. An Au/PEDOT:PSS/α-FAPbI₃/SnO₂/ITO structure is used to build a photodiode. In this structure, the injection of external carriers under reverse bias is efficiently blocked due to the large energy barrier. **b**, $I-V$ curves the photodetector. The dark current is reduced to $\sim 10^{-8}$ A due to the diode structure. **c**, Responsivity and photocurrent of the photodetector under different illumination power levels. Results show that the responsivity is lower than 1 with the diode structure.

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