Nanoscale Photoexcited Carrier Dynamics in Perovskites

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Abstract

The optoelectronic properties of lead-halide perovskite thing films can be tuned through compositional variations and strain, but the associated nanocrystalline structure makes it difficult to untangle the link between composition, processing conditions, and ultimately material properties and degradation. Here we study the effect of processing conditions and degradation on the local photoconductivity dynamics in $[(CsPbI_3)_{0.05}(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}]$ and $(FA_{0.7}Cs_{0.3}PbI_3)$ perovskite thin films using temporally- and spectrally-resolved microwave near-field microscopy with temporal resolution as high as 5 ns and spatial resolution better than 50 nm. For the latter FA-Cs formulation we find a clear effect of process annealing temperature on film morphology, stability, and spatial photoconductivity distribution. Under exposure to ambient conditions and illumination we find spectral evidence of halide segregationinduced degradation below the instrument resolution limit for the mixed halide formulation while for the FA-Cs formulation annealed at 180°C we find a clear spatially inhomogeneous increase in the carrier lifetime.

Graphical TOC Entry



Lead-halide-based perovskite materials have emerged as a superlative optoelectronic material for applications including light emitting diodes,^{1,2} single photon emitters,³ x-ray detection,^{4,5} and most prominently, photovoltaic (PV) absorber thin films.^{6–9} The perovskite lattice can accommodate a large range of coulombically-^{10,11} or structurally-induced¹² strain, which enables a broad range of chemical compositions to be used to tune and optimize desired properties such as the bandgap^{13,14} or film stability^{15,16} while maintaining long carrier lifetimes and high mobilities that readily enable photoexcited carrier diffusion to the electrodes for harvesting.¹⁷ However, despite their accommodating structure and robust optoelectronic properties, lattice substitution of constituent species nevertheless affects strain and the associated microcrystalline structure, which in turn influences optoelectronic properties and degradation mechanisms.

Current high-performance photovoltaic perovskite formulations emerged from efforts to address the poor stability of MAPbI₃^{18,19} while maintaining or even improving the high device performance metrics. Outright replacement of moisture-sensitive MA by FA has proven to be advantageous,¹⁴ though the larger size of the FA ion helps stabilize the undesirable "yellow" hexagonal δ_H -phase rather than the desired perovskite cubic α -phase.^{12,15} Blending the A-site cation with smaller species such as Cs can stabilize the α -phase by reducing the apparent size of this lattice site as described by the Goldschmidt tolerance factor.¹² Strain arising from the processing annealing temperature provides an additional parameter to control phase stability.²⁰ High-efficiency triple cation formulations also include MA in addition to FA and Cs^{16,21} and also frequently blend the halide composition to include bromine in addition to iodine.^{9,22,23}

Not only the overall optoelectronic properties, but the degradation mechanisms of these materials are directly linked to the microcrystalline structure that arises from the composition, processing, and associated strain. Understanding the mechanisms behind these degradation pathways is further complicated by the nanoscale chemical inhomogeneity^{13,24} and strain texture,^{25–27} where apparent structural grains are often polycrystalline and exhibit

twinning or other structural boundaries that are not readily discernible from film morphology or topography.²⁸ Although they are structurally hard to identify, these internal crystallographic discontinuities and associated traps and defects are strongly implicated in limiting device performance and accelerating degradation.^{29–31}

Understanding the structure-property relationship of perovskite thin films thus remains challenging in large part due to the very features that make this class of materials so unique. Although high-resolution techniques enable atomic-scale structural characterization,³² these often provide only indirect information on electronic structure and carrier dynamics. Conversely, functional device characterization and established spectroscopic techniques to measure carrier dynamics such as time-resolved photoluminescence (TRPL), absorption spectroscopy, or time-resolved microwave conductivity (TRMC) only indirectly capture the local effects of the micro- and nano-structure. Scanning probe techniques achieve nanometer spatial resolution but their temporal resolution is limited by cantilever resonance frequencies on the order of 100s of kHz.³³ In dedicated implementations temporal resolution as high as 10s of nanoseconds can be achieved in electrostatic force microscopy³⁴ and slower processes can readily be measured by related techniques.³⁵ Scanning probe-based near-field techniques achieve ultrafast temporal resolution using pump-probe methodologies,^{36,37} and measurements in the GHz range can readily achieve the nanosecond resolution desired for perovskite materials and are directly sensitive to the photoexcited free carrier concentration.³⁸⁻⁴⁰

In this work we study the nanoscale optoelectronic properties of perovskite thin films using photoconductive and time-domain near-field microwave impedance microscopy (MIM, also often called scanning microwave microscopy, SMM). We focus our efforts on two perovskite formulations: $[(CsPbI_3)_{0.05}(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}, mixed-composition (MC) per$ $ovskite] and double-cation formamidinium-cesium lead halide (FA_{0.7}Cs_{0.3}PbI_3, FACs per$ ovskite). The MC perovskite is representative of current high-performance formulationswhile the FACs perovskite provides insight into MA-free formulations that benefit from improved stability but are strain-sensitive.



Figure 1: (a) Schematic of the spectrally tunable, pulsed, optical excitation source based on a supercontinuum laser. (b) Schematic of the MIM with through-sample illumination and high-bandwidth IQ mixer-based demodulation. (c) Contact mode AFM topography and (d) corresponding photoconductivity map of an ALD-encapsulated MC-perovskite film. (e) Time domain MIM trace of the MC film along with corresponding TRMC and TRPL measurements.

As shown in Fig. 1a, the optical excitation is based on a pulsed broadband supercontinuum laser that we operate at 1 MHz repetition rate unless otherwise noted. We use spectral amplitude shaping to produce spectrally narrow (FWHM ≈ 10 nm) pulses from the broadband ($\approx 450 - 970$ nm) spectrum using a folded-4F geometry with a razor blade slit mounted on a motorized translation stage and placed at the Fourier plane. The amplitude shaper output is then coupled into a multimode fiber and delivered to the sample through the transparent substrate from below, as illustrated in Fig. 1b. The output of the fiber is allowed to diverge through the substrate to produce a uniform excitation field at the sample with a radius of r > 100 μ m and time-averaged intensity of < 2 kW/m².

The MIM is based on a commercial atomic force microscope (AFM, Agilent / Keysight^{*}) that has been extensively modified for external analog signal demodulation as described previously^{39,41} and schematically shown in Fig. 1b. We operate at a single microwave frequency of ≈ 17.3 GHz that is sourced from a vector network analyzer and delivered to the tip via a coaxial resonator. The complex-valued signal \tilde{S} reflected from the tip is demodulated using an IQ mixer providing demodulation (intermediate frequency, IF) bandwidth of 5 GHz with adjustable reference phase that can be set to simultaneously yield the in-phase S_G and outof-phase S_C components, or the corresponding magnitude $S \equiv |S_G+iS_C|$ in a single channel. The MIM signal directly reflects the tip-sample admittance $\tilde{Y} = G + i\omega C \propto \tilde{S} = S_G + iS_C$, is directly sensitive to the local conductivity⁴¹⁻⁴⁴ $\sigma_i = n_i e \mu_i$, with the local carrier density n_i , elementary charge e, and carrier mobility μ_i ($i = h^+$, e^-),⁴¹ and thus directly responds to changes in the local carrier density. These samples are in the low-conductivity regime and as a result the admittance magnitude $|Y| \propto S$ can be approximated as linear with the carrier density (see SI).

Upon photoexcitation we direct both S_C and S_G , or S, to a lock-in amplifier referenced to the acousto-optic modulator (AOM)-controlled repetition rate of the laser source for lockin demodulation to yield the photoconductive signals, S_C^{γ} and S_G^{γ} , or $S^{\gamma} \equiv |S_G^{\gamma}+iS_C^{\gamma}|$ (note that we use the γ superscript to refer exclusively to the lock-in detected photoconductive signal, see SI for a comparison of these signals and a discussion of the linearity of S^{γ}). We further acquire averaged time-domain traces of the photoconductivity, $S_C(t)$, $S_G(t)$, and the signal-maximized single channel S(t), with temporal resolution ≈ 5 ns limited by the 210 MHz acquisition rate of the lock-in amplifier (see SI for an in-depth discussion showing the equivalence between these channels). All spatially resolved S^{γ} images shown are acquired with near-band edge excitation at $\lambda = 750$ nm. Unless explicitly noted, MIM time-domain traces shown are acquired during scanning in order to facilitate averaging, while action spectra are acquired with the tip held stationary over the sample. In all cases we ensure that these are representative of the sample region studied, and any discernible spatial variations in the material response are reported.

Perovskite films are fabricated as described previously using a self-seeding growth (SSG) method. Although our films were not measured, this method can produce devices with photon conversion efficiency >20% for MC formulations⁹ and $\approx 15\%$ for the FACs formulation.²⁰ Our films are thinner than typical PV films, where the average thickness of ≈ 260 nm was chosen to allow full penetration of the optical excitation and rapid subsequent diffusion of

photoexcited carriers throughout the film. For all samples we study bare films in order to examine the evolution during degradation due to illumination and exposure to ambient conditions with laboratory humidity ≈ 30 %, as well as samples encapsulated in ≈ 10 nm of Al₂O₃ grown via atomic layer deposition (ALD).⁴⁵

ALD-encapsulated MC samples show long-term stability and no significant degradation under typical measurement conditions. Shown in Fig. 1c is the contact-mode AFM topography of an ALD-encapsulated MC film with the typical granular structure of perovskite films with length scales on the order of 100s of nm. The corresponding MIM spatial photo conductivity map in Fig. 1d shows variations in the local photoconductivity response on similar length scales as the granular structure but we see no clear correlation with the physical structure (See SI for additional data showing the lack of topographic cross-talk into the photoconductive S_C^{γ} , S_G^{γ} , and S^{γ} channels). The local time-domain MIM signal shown in Fig. 1e (red squares) is taken from the same sample region shown in c and d during scanning. Although the time-dependent photoluminescence or photoconductivity decays after the end of the laser pulse excitation can be used to characterize free carrier decay mechanisms by various recombination and trapping processes using an appropriate kinetic model, this detail is beyond the scope of this study. Here, unless otherwise noted we employ a simple biexponential fit of the photoluminescence or photoconductivity decay transients, and calculate the average carrier lifetime according to: $\tau_{avg} = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$. The dashed line in Fig. 1e shows the fit the MIM data used to extract $\tau_{\rm MIM} = 320$ ns.

Also shown in Fig. 1e are time-resolved microwave conductivity $(\text{TRMC})^{46,47}$ and timeresolved photoluminescence $(\text{TRPL})^{48,49}$ traces taken from sibling samples (see SI for experimental details). The comparable lifetimes of TRMC and MIM are expected as both probe the microwave conductivity and are sensitive to a linear superposition of the electron and hole conductivities $\sigma_{\text{tot}} = \sigma_{h^+} + \sigma_{e^-}$, though they probe different regions of the sample. The cavity-confined microwave fields used in TRMC readily penetrate through the film, providing bulk-averaged properties, but the tip-confined evanescent fields decay rapidly away from the



Figure 2: Contact-mode AFM topography of a bare mixed-composition perovskite acquired (a) 10 minutes and (b) 160 minutes after initial illumination with the broadband source set to $\lambda = 750$ nm is turned on, along with the corresponding S^{γ} images (c) and (d), respectively. Although the time-domain response does not change over the period of measurement (e), the band-edge action spectra show a clear red-shift of the absorption edge as the film deteriorates (f).

tip and decay within a few 10s of nm of the film surface (see SI). By comparison, TRPL shows a shorter carrier lifetime that can be attributed to the fundamentally different mechanisms. Similar to TRMC, TRPL probes the film bulk, but the radiative recombination measured by TRPL is bimolecular and therefore the product of the hole and electron carrier densities $\propto (n_{p^+})(n_{e^-})$.⁵⁰ For these ALD-encapsulated films we observe lifetimes $\tau_{\text{TRPL}} \approx \tau_{\text{TRMC}}/2$, which suggest that the radiative decay measured in TRPL is the primary decay pathway as expected for films yielding high-efficiency devices.

In the absence of an ALD-encapsulation our films degrade via moisture- and photondriven pathways, and we study the spatial characteristics of the photoconductivity, spectral response, and carrier lifetime as our films undergo degradation. We use samples previously stored in a glove box and all times reported are measured from initial illumination. Shown in Fig. 2 are measurements taken from the same region of a MC sample as it undergoes degradation, with Fig. 2a and b showing AFM topographies taken 10 and 160 minutes after illumination is turned on, respectively. Little change in the film morphology is seen and the overall grain-like structure is maintained, although there does appear to be some visible degradation of the film, likely due to overall softening of the surface as previously observed for MAPbI₃ films.³¹ Shown in Fig. 2c and d are the corresponding S^{γ} images. Due to the lack of topographic cross-talk in the photoconductive images we attribute the observed features to physical changes in the film. First, the unencapsulated films show clear spatial variations with well-defined low-photoconductivity regions corresponding to grain-like structures in the topography. Our measurements indicate that these dark regions evolve rapidly after illumination, and since we do not see them in the ALD-encapsulated films (Fig. 1) they are likely not present in pristine films. As degradation proceeds, these dark regions appear to grow, and the photoconductivity appears to become more inhomogeneous and shows an overall decrease as well.

Despite notable changes in the MC film photoconductivity as degradation proceeds, the measured lifetimes remain unchanged. Shown in Fig. 2e are a set of time-domain traces showing an extracted carrier lifetime of $\tau = 470$ ns taken at various times during the degradation process. As can clearly be seen, the lifetime remains unchanged, and we found no spatial variations in these as well. However, the corresponding action spectra in Fig. 2f show a clear redshift of the absorption edge as degradation proceeds, which we attribute to halide segregation originating from the redshift of iodine-rich regions. We found no evidence of spatial variations in the action spectra in these films, suggesting that these iodine rich regions are smaller than our spatial resolution of better than 50 nm (see SI), which is consistent with previous estimates on the order of 10 nm.¹³ This does suggest that the dark regions observed are not due to halide segregation. Instead, the lack of chemical distinction manifesting itself in carrier lifetime or absorption onset variations indicates a localized surface modification, accumulation of local traps, or possibly an associated subsurface impediment to carrier diffusion such as grain boundaries.^{27,51}

We now turn to perovskite compositions based on FA-Cs blends, which provide welldefined tunability in terms of composition and processing conditions to influence film morphology and phase stability. We begin by examining the effect of processing conditions using



Figure 3: Contact-mode AFM topography of ALD-encapsulated FACs perovskite films annealed at (a) 100°C and (b) 180°C along with the S^{γ} images, (c and d, respectively). Note the different scale bars. Action spectra comparing the band edge response of these films is shown in (e) along with an ALD-encapsulated mixed-composition film. Spectra have been normalized to the near-band edge region. Shown in (f) are the time-domain traces of these FACs samples, along with a biexponential fit (black dashed line).

 $FA_{0.7}Cs_{0.3}PbI_3$ films fabricated simultaneously and differing only in the annealing temperature during processing. And although the composition ratios of these films are expected to be stable in the α phase, the higher annealing temperature should nevertheless favor this desired phase via strain-driven stabilization.^{12,20} For instance, we consistently observe that degradation of these films in a glove box proceeds on the order of months via transition to the δ_H phase and that the 10 °C-annealed films transition significantly faster, consistent with previous results.¹²

Shown in Fig. 3a and b are the AFM topography of films annealed at 100°C and 180°C and encapsulated with a ≈ 10 nm alumina ALD conformal overcoat. The different length scales in these images emphasize that these are morphologically distinct, with the higher annealing temperature consistently favoring larger and more clearly faceted apparent grains. Similar to the AFM images, the S^{γ} maps shown in Fig. 3c and d show clear differences, with significantly higher signal levels seen in the 100°C-annealed film and distinct spatial variations. We see that although the relative variations in photoconductive response are comparable, the 100°C-annealed film shows little variation between the interior of apparent grains and

overall increased contrast between these grain-like features, while the 180°C-annealed film shows overall more uniform contrast but with pronounced regions of reduced photoconductive response. These apparent dark regions are a characteristic feature of these films and are consistently observed in different film batches fabricated 6 months apart. Although previous photoconductive mapping indicated that grain boundaries in Cs-doped FAPbI₃ do not present a significant barrier to carrier diffusion,⁴⁰ the dramatically different results here for films differing only in annealing temperature caution that such observations may not be universally applicable. A close comparison of the AFM topography and S^{γ} images shows that these low-photoconductivity regions often correlate with grain-like structures. A likely explanation is the corralling of a subset of grains by boundaries that impede the flow of charge carriers as previously observed for neat FAPbI₃ films.⁵¹ As further discussed in the SI, these dark regions do not always show boundaries that correlate with topographic features, suggesting the more complicated subsurface grain structure expected for these materials. It is also possible that these dark regions are in the δ_H yellow phase whose formation reduces the overall film-average strain, though the absence of discernible structural boundaries in all cases suggests this is unlikely.

The annealing conditions used for FACs films do not only appear to affect the morphology and spatial photoconductivity distribution, but also the optical properties. Shown in Fig. 3e are action spectra acquired from each of these films along with a spectrum from the ALDencapsulated MC film for comparison, all of which have been normalized to the band edge to facilitate comparison. Both FACs films show a red-shifted absorption edge relative to the MC film and a comparable spectral roll-off corner for the absorption edge. However, the 100°C-annealed film shows a distinct long-wavelength shoulder not seen in the 180°Cannealed sample. This long-wavelength shoulder was seen in all sample batches studied and suggests distinct chemical differences associated with the annealing temperature. The absorption onset of this shoulder corresponds well to the FAPbI₃ onset at ≈ 830 nm.¹⁴ The spectroscopic signature of FAPbI₃ in this film produced from blended precursors has several implications. First, we see no evidence of spatially distinct phases nor of Cs-rich regions with blue-shifted absorption, which suggests that the film either exhibits nanoscale phase separation that we cannot resolve, or that the overall stoichiometric FA:Cs ratio is increased relative to the 70:30 precursor solution. A reduced Cs composition would also destabilize the α phase and could explain the rapid degradation via transition to the yellow phase.

The effects of annealing temperature are also evident in the measured carrier lifetimes as shown in Fig. 3f, where we see that the weighted carrier lifetimes extracted from the biexponential fits decrease from $\tau = 175$ ns to $\tau = 33$ ns as the processing temperature is increased. We note that the shorter-lived decay of the 180°C-annealed sample consists of two characteristic lifetimes. This suggests that the rapid trapping of one carrier type and a longer lifetime associated with the untrapped species plays a significant role here, possibly associated with the low-conductivity regions seen. On the other hand, the longer-lived decay of the 100°C-annealed sample suggests an overall reduction in trap density. This points to a broader trade-off between increased α -phase stability at higher annealing temperatures and an associated increase in trap density.

Examining the degradation of bare FACs films, we note that no significant degradation was observed in 100°C-annealed films after ambient exposure; they instead appeared to degrade via transition to the yellow δ_H phase over a period of several days to a few weeks. As such, we will focus on films annealed at 180°C here. Shown in Fig. 4a and b is the AFM topography of a region of a 180°C-annealed film, with the AFM topography acquired 15 minutes and 135 minutes after illumination is turned on, respectively. The 180°C-annealed samples show a distinct softening of the sample surface as degradation proceeds, resulting in changes in the sample topography due to the contact mode scanning. The S^{γ} signal (c and d) shows the characteristic dark regions seen in the 180°C-annealed samples, and the photoconductive signal and overall contrast increase over time.

Unlike other samples studied here, the bare 180°C-annealed samples show clear spatial variations in the time domain and photoconductive response. Shown in Fig. 4e are time-



Figure 4: Contact-mode AFM topography of a bare FACs perovskite annealed at 180° C acquired (a) 15 minutes and (b) 135 minutes after illumination is turned on, together with the corresponding S^{γ} images (c and d). spatial variations in the measured region are seen in the time-domain traces (e) – taken at locations i (violet) and ii (green) in a – along with variations in the absorption edge (f). The evolution of measured lifetimes are shown in (g) showing clear spatial variations in measured carrier dynamics across the region studied.

domain traces acquired from locations i (violet) and ii (green) in a, showing a difference in measured carrier lifetimes and their evolution during degradation. In particular, the carriers at location i are longer lived and their lifetime increases more rapidly than at location ii. Spatial variations in the spectral response are also seen, with small but reproducible and clearly resolved differences in the absorption edge shown in Fig. 4e. Unlike the time-domain response in these films and the spectral response in the MC films, we find no change in the local spectral characteristics during degradation. These spatial variations in the absorption edge are likely due to varying FA:Cs ratios resulting from strain variations throughout the polycrystalline film. Lastly, shown in Fig. 4g are the carrier lifetimes extracted from weighted biexponential fits to the time-domain data for the regions indicated in a. Remarkably, the temporal response at the dark region marked iii is comparable to ii, albeit at a lower overall intensity. This underscores the differences in carrier dynamics on micron length scales.

The origin of the spatial variations and evolution in the time-domain response likely arises from traps. Similar to the ALD-encapsulated films discussed in Fig. 3, in the early stages of degradation the temporal transient clearly exhibits two characteristic lifetimes, which evolves to being dominated by a single lifetime as degradation proceeds. At the same time, the surface softening is clear evidence of surface degradation. We therefore postulate that the increased carrier lifetimes result from the formation of compensating traps such that both carrier types are trapped at comparable rates, which results in similar and longer electron and hole lifetimes. We also note that although we see no direct evidence of the influence of phase transitions and associated strain-induced changes in the electronic structure, these cannot be ruled out either as the overall film strain texture is the result of long-range competing forces that can be influenced by features outside of our field of view.

Throughout our measurements here we often do not observe significant spatial variations in the time domain and spectral photoconductive response unless explicitly noted. Although this reflects observations in similar measurements,⁴⁰ it is nevertheless surprising that the otherwise significant variations in the magnitude of the photoconductive response do not appear to correlate with temporal and spectral variations. Similarly, other than amplitude variations that are consistent with the action spectra, we see little variations in the photoconductive response as a function of excitation wavelength. The photoconductive signal does not show the topographic correlation typical of the capacitive signal and retains high spatial resolution (see SI), indicative of strong sensitivity to local properties. The signal itself directly arises from the amplitude and its temporal profile via its Fourier component at the lock-in demodulated first harmonic of the laser repetition rate. However, given the rapid carrier equilibration throughout perovskite films following pulsed optical excitation on the order of ns, it seems likely that throughout the photoconductive decay the carrier distribution re-equilibrates throughout the film in response to nonuniform trapping and decay. This would result in a quasi-equilibrium distribution of free carriers – affected only by significant barriers to carrier diffusion as may be the case for the FACs films annealed at 180° C – in the film that gives rise to an apparent spatially uniform lifetime and spectral response.

As our photogenerated carrier densities are higher than the generally low carrier densities observed under dark conditions⁵⁰ contributions due to both p-type and n-type carriers are observed. As a consequence, unlike minority carrier decay where comparable lifetimes would be expected in TRPL and microwave techniques, dramatic differences are observed. Here, the removal of one carrier type via an extraction layer such as C60 (see SI) or traps results in a rapid decay in the PL transient whereas the remaining long-lived carrier species results in correspondingly long-lived microwave conductivity transients. The longer lifetimes observed from bare films and degraded FACs points to traps as the driving factor. This runs somewhat counter to common assumptions relating longer apparent lifetimes with improved photovoltaic performance.

The use of pulsed optical excitation sources can be used to readily access fast and ultrafast dynamic processes, but their high peak field strength and fluence can complicate direct comparison to steady-state measurements.⁴⁸ With our pulse duration on the order of 10s of ps and modest pulse intensities < 200 nJ/cm² we do not expect to drive significant nonlinear optical processes, though our estimated per-pulse photogenerated carrier density of $n_{p^+} = n_{e^-} \approx 3 \times 10^{16}$ cm⁻³ is higher than typical steady-state values under 1-sun illumination on the of 10^{15} .⁵² These carrier densities are significantly below the threshold for third-order Auger recombination⁴⁸ and contributions from second-order processes are expected to be limited.⁵² We emphasize that our careful control of pulse powers enables a direct comparison between time-domain methods to validate time-domain MIM and to provide complementary information understand the electron and hole dynamics. Although we did not measure conventional absorption spectra, our illumination spectrum was calibrated using a spectrum analyzer and the spectrally-resolved light-induced generation of photoexcited carriers provides a direct measure of the device-relevant photoconductive response.

Here we have studied mixed composition $(CsPbI_3)_{0.05}(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ and FA-Cs $(FA_{0.7}Cs_{0.3}PbI_3)$ perovskite thin films using a combination of optically excited microwave near-field microscopy together with complementary time-domain photoluminescence and transient microwave conductivity measurements. Representative of high-performance films, the MC films showed only limited spatial variations in photoconductivity and overall uniform spectral characteristics and carrier lifetimes. Ambient exposure of bare MC films leads to degradation of the photoconductive response at localized sites corresponding to apparent grains. This degradation is accompanied by a spatially uniform redshift of the absorption edge as measured via MIM action spectra, suggesting halide ion segregation on length scales less than the ≈ 50 nm spatial resolution.

For the FACs films we find a dramatic difference in film morphology, spatial photoconductivity response, and spectral response as the processing annealing temperature is changed from 100°C to 180°C. These variations are likely due to inhomogeneous strain and correlate with decreased long-term stability of the 100°C-annealed film and a spectral response suggesting a reduced cesium content relative to the precursor ratio. The 180°C-annealed films consist of large apparent grains with localized regions of significantly reduced photoconductivity that likely arise due to subsurface barriers to charge carrier diffusion. Under ambient exposure bare FACs films show a notable increase in carrier lifetime likely due to an increased trap density while the spatially weakly nonuniform spectral response shows no change. This suggests a clear trade-off between trap density and overall film properties and long-term stability.

Supporting Information: Experimental details of the TRMC and TRPL measurements, discussion of spatial resolution and field penetration into the material bulk, comparison of the MIM signal channels, the effect of C60 surface treatment on MC perovskites, and a high-resolution dataset on the "dark grains" observed in FACs films.

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