Impact of trap filling on carrier diffusion in MAPbBr₃ single crystalsN. Ganesh,¹ Anaranya Ghorai,¹ Shrreya Krishnamurthy,² Suman Banerjee,¹ K. L. Narasimhan³,
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We present experimental evidence showing that the effective carrier diffusion length L_d and lifetime τ depend on the carrier density in MAPbBr₃ single crystals. Independent measurements reveal that both L_d and τ decrease with an increase in photocarrier density. Scanning photocurrent microscopy is used to extract the characteristic photocurrent I_{ph} decay-length parameter L_d , which is a measure of effective carrier diffusion. The L_d magnitudes for electrons and holes are determined to be ~ 13.3 and $\sim 13.8 \mu\text{m}$, respectively. A marginal increase in uniform light bias ($\leq 5 \times 10^{15}$ photons/cm²) increases the modulated photocurrent magnitude and reduces the L_d parameter by a factor of 2 and 3 for electrons and holes, respectively, indicating that the recombination is not monomolecular. The L_d variations are correlated to the features in photoluminescence lifetime studies. Analysis of lifetime variation shows intensity-dependent monomolecular and bimolecular recombination trends with recombination constants determined to be $\sim 9.3 \times 10^6 \text{ s}^{-1}$ and $\sim 1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively. Based on the trends of L_d and lifetime, it is inferred that the sub-band-gap trap recombination influences carrier transport in the low-intensity excitation regime, while bimolecular recombination and transport dominate at high intensity.

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I. INTRODUCTION

Hybrid organic-inorganic perovskites (HOIPs) have demonstrated unprecedented potential for device applications such as solar cells, photodetectors, light-emitting diodes (LEDs), and lasing [1–5]. Record high efficiencies, reaching 25% [1,6,7] in HOIP single-junction solar cells, can be explained due to properties such as a high absorption coefficient, long diffusion lengths, decent mobility, and long-lived carrier lifetimes τ [8–10]. The long diffusion length L_{diff} in HOIPs has been attributed to processes such as photon recycling, Rashba splitting, high bimolecular recombination rates, and defect tolerance [11–15]. Estimates of L_{diff} in the range from 100 nm to 3 mm, spanning across four orders of magnitude, have been reported [8,16,17]. This difference is partly due to different techniques such as transient photoluminescence (TRPL), transient photovoltage (TPV), transient absorption, impedance spectroscopy, and transient microwave conductivity (TRMC) to determine τ [8,9,18–20]. Additionally, techniques such as the space charge limited current, time of flight, Hall effect, TRMC, and terahertz conductivity are employed to determine carrier mobility μ [8,10,17,19,21]. Determination of the diffusion length L_{diff} , a parameter indicative of efficient carrier transport, relies on twin measurements of τ and μ . Long L_{diff} are characteristic of good quality films with large grain

size. Recombination at the grain boundary limits the L_{diff} to grain size length scales [22]. To overcome grain size effects on L_{diff} studies, sizable (2–3 mm) methylammonium lead bromide (MAPbBr₃) single crystals (MSCs) were utilized. Hybrid perovskite single crystals are evolving as suitable solar cell candidates due to low trap density, high L_{diff} , and high sub-band-gap absorption, reaching efficiencies of 21% [21,23,24]. Applications based on their emission and optoelectronic properties are also emerging [25].

In the first part of the paper, we present the direct spatial estimation of effective diffusion length L_d measurements on single crystals as a function of light bias intensity using scanning photocurrent microscopy (SPCM). We then report and analyze the emission characteristics using TRPL recombination lifetime techniques. These emission studies enable understanding of the processes and the role of DC light bias on the measured L_d .

II. SAMPLE DETAILS

In this study, large MSCs (on the order of a few millimeters) were prepared using the technique of inverse temperature crystallization (details in the Supplemental Material [26]) [19]. The sharp x-ray-diffraction (XRD) peaks in Fig. S1 in [26] are a measure of the crystal quality. Scanning photocurrent microscopy studies were carried out on MSC devices. For efficient collection of photogenerated carriers, selective contact layers were deposited: poly(*N*, *N'*-bis-4-butylphenyl-*N*, *N'*-bisphenyl)benzidine (Poly-TPD) and phenyl-C71-butyric

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FIG. 1. (a) Band alignment diagram depicting the MSC device used in the SPCM experiments. (b) Schematic of scanning photocurrent microscopy used for effective diffusion length measurement. The incident chopped probe-beam position is varied by translating the sample. The lock-in profile $I_{ph}(x)$ is utilized to estimate L_d . (c) Plot of $I_{ph}(x)$ showing the I_{ph} peak at the interface. The single-exponential fit to the I_{ph} decay profile corresponds to the L_d of the corresponding carrier. The inset shows the image of the bulk single crystal.

acid methyl ester (PC₇₁BM) with Au and Ag electrodes for hole and electron extraction, respectively, schematically shown in the band diagram in Fig. 1(a).

III. RESULTS

A. Scanning photocurrent microscopy

Figure 1(b) is a schematic of the setup used for SPCM (experimental details in the Supplemental Material [26]). In this experiment, an $\sim 3\text{-}\mu\text{m}$ spot size (Fig. S2 in [26]) intensity-modulated 405-nm ($\sim 27\text{-mW/cm}^2$) laser beam, which is incident normally on MSCs, is translated laterally between the two contacts. The modulated short-circuit photocurrent $I_{ph}(x)$ shown in Fig. 1(c) is measured using a lock-in amplifier at different positions of the incident beam between the two electrodes. The maxima in $I_{ph}(x)$ correspond to the electrode positions at either end. The contact resistance at the electrodes is estimated and verified to be negligible due to charge-selective interfacial layers, with the built-in voltage V_{bi} falling entirely along the interelectrode length. In the present case of undoped sizable MSCs [$d \sim 1 - 2\text{ mm}$, inset in Fig. 1(c)], the built-in electric field $E_{bi} = V_{bi}/d$ is negligible (less than 6 V/cm), resulting in a dominant diffusion contribution to the observed I_{ph} .

The determination of effective diffusion length L_d from the $I_{ph}(x)$ measurement can be arrived at by solving the drift-diffusion equation. In the simplified case of single-carrier one-dimensional (1D) transport, the minority excess carrier δn is given as [27]

$$\frac{\partial \delta n}{\partial t} = D \frac{\partial^2 \delta n}{\partial x^2} + \mu E \frac{\partial \delta n}{\partial x} + G - \frac{\delta n}{\tau}. \quad (1)$$

The generation rate G is given by the δ function $G = G_0 \delta(x - x_0)$, where $x = x_0$ is the position of illumination. Under conditions of steady-state illumination ($d\delta n/dt = 0$), negligible electric field, and $x \neq x_0$, the diffusion current can be expressed as (derivation in Sec. 11 of the Supplemental Material [26])

$$I_{ph}(x) = I_0 \exp\left(-\frac{x}{L_d}\right), \quad (2)$$

where the effective diffusion length L_d corresponds to the $I_{ph}(x)$ decay. It should be noted that the effective diffusion length L_d is different from the minority carrier diffusion

length L_{diff} . Here L_{diff} is the microscopic quantity related to the diffusion coefficient D and expressed as $(D\tau)^{1/2}$, where τ is the carrier lifetime. In disordered or amorphous systems, owing to the dispersive nature of transport, L_d and L_{diff} can differ appreciably [28,29]. However, L_d has been shown to be a representative of the long-lived carriers corresponding to states in the tail distribution, in organic and polymeric semiconductors [29,30]. The L_d parameter in the present case of HOIP single crystals is expected to be a closer representation of L_{diff} owing to dominant band transport [31]. In the present case of SPCM on MSC devices, it should be noted that the L_d parameter is obtained upon fitting over the entire decay range and accounts for additional factors such as finite beam spot, 3D carrier diffusion, and ambipolar transport away from the electrodes.

The $I_{ph}(x)$ response in Fig. 1(c) can be qualitatively described as follows. Photoexcitation results in a point spread of electrons and holes via 3D diffusion, a fraction of which diffuse towards the electrodes. When the excitation is at a distance equivalent to many diffusion lengths from the contacts, the diffusing photocarriers get (i) trapped in shallow states and (ii) recombine, resulting in a low current. When the excitation beam is within L_d from the electrode, the current increases exponentially with the probe distance [Eq. (2)], enabling one of the carriers to be extracted, leaving the other carrier in the perovskite to transit to the other electrode. The extraction of one carrier and the long lifetime associated with the displacement of the counter carrier render the extracted carrier a minority, with excitation close to ($x \leq L_d$) the extraction electrode. Transient I_{ph} measurements (Fig. S3 in [26]), indicating longer $\tau_{transit}$ for excitation near the electrodes compared to a distant region, confirm this viewpoint. Previous reports of SPCM have determined the minority carrier diffusion length using doped crystals and a charge-selective Schottky barrier [17,32]. In the present case of MSCs, L_d corresponds to the selectivity of the extraction layer in undoped single-crystal devices.

Using Eq. (2), L_d for electrons and holes was determined to be 13.3 ± 0.6 and $13.8 \pm 0.5\text{ }\mu\text{m}$, respectively. Intensity-dependent studies reveal that the carrier L_{diff} varies with excitation density similar to TPV studies, where $L_{diff} \sim 3\text{ mm}$, at low-intensity excitation [8,10]. These studies of L_{diff} determination relied on indirect estimation. To investigate the effect of intensity dependence on directly measured spatial

FIG. 2. (a) Plot of $I_{ph}(x)$ variation on both ends of the MSC device with a 405-nm probe beam and 390-nm light bias. (b) Normalized $I_{ph}(x)$ profiles indicating sharp decay at higher light bias. (c) Plot of L_d extracted with the exponential fitting of $I_{ph}(x)$ decay as a function of light bias.

L_d , intensity-dependent SPCM studies are carried out by (i) varying the intensity of the probe beam and (ii) superposing a uniform background illumination or light bias using a 390-nm LED with the probe beam. [The optical absorption depth (~ 125 nm) of the 390-nm light is similar to the 405-nm probe beam [33]].

Figure S4(a) in [26] shows $I_{ph}(x)$ upon probe-intensity variation in the SPCM measurement. The excess generated probe photocarriers δn_{probe} diffuse away from the point of generation and decay as $\delta n(x) = \delta n_{probe}(0) \exp(-\frac{x}{L_{diff}})$. The corresponding L_d values in Fig. S4(c) in [26] as a function of probe beam intensity shows that L_d is independent of probe beam intensity. The invariance of L_d can be understood since the photocarriers decay to background carrier concentration within $\sim 3L_{diff}$. The addition of light bias, on the other hand, maintains uniform charge generation across the transport length of the probe carrier. It was ensured that the effects of light-induced halide redistribution and phase segregation are minimal by maintaining the MSC device in the dark under short-circuit conditions after each measurement, under a positive pressure of the inert atmosphere [34,35]. Figure S5 in [26] provides evidence of the sample “self-recovering” as the ions equilibrate, confirmed by the increase in the magnitude of $I_{ph}(x)$. It should be noted that we have not performed any measurements under applied bias, where one expects a sizable ionic contribution.

Figure 2(a) depicts the $I_{ph}(x)$ profile at different DC light biases (additional plots and details in Fig. S6 in [26]). The I_{ph} magnitude increases with the light bias as indicated in the $I_{ph}(x)$ maxima at the electrodes. Figure 2(b) shows the normalized $I_{ph}(x)$ decay at either end of the MSC-electrode interface. The steep decay of I_{ph} away from the electrode is evident under high light bias conditions. The L_d parameter is extracted by fitting the decay profile to Eq. (2). The estimated L_d (values of L_d given in Table S1 in [26]) as a function of light bias photon flux, presented in Fig. 2(c), reveals the decrease of L_d with DC light bias intensity. The extracted L_d parameter decreases by a factor of 3 for holes and a factor of ~ 2 for electrons upon increasing the light bias from zero to $\sim 5 \times 10^{15}$ photons/ cm^2 . To investigate the effects of surface recombination, the probe λ_{ex} was changed to 532 nm in the presence of 532-nm light bias (corresponding to absorption depth ~ 10 μm) [33,36] as shown in Fig. S7 in [26]. Qualita-

tively similar results were observed for $\lambda_{probe} \approx 532$ nm. For the cases of both 405- and 532-nm excitation, beyond a certain high-intensity light bias, the I_{ph} magnitude reduces as shown in Figs. S6(c) and S7(d) in [26], respectively. This reduction is attributed to the effects of light soaking [37].

The decrease of the L_d at high DC light bias suggests that the recombination kinetics of the excess carriers is not monomolecular [36]. This was verified by photophysical studies using intensity- and time-dependent photoluminescence (PL) measurements.

B. PL measurements

MAPbBr₃ is characterized by absorption, largely in the UV-VIS spectral range (Fig. S8 in [26]). Photothermal deflection spectroscopy and light transmission experiments have shown the presence of sub-band-gap states extending to ~ 2.0 eV [33,38]. Figure 3(a) is the plot of PL spectra for 3-eV (405-nm) excitation in reflection and transmission geometry. In reflection mode, the PL spectra exhibit a peak at 2.27 eV (545 nm) with a shoulder at 2.15 eV (575 nm). In transmission mode, the 2.27-eV peak is masked due to self-absorption. The 2.27-eV peak is identified and attributed to the band-to-band transition (free carrier recombination). The 2.15-eV peak has been attributed to different mechanisms, viz., to radiative recombination from a defect level or to bound exciton recombination [38,39]. The 2.15-eV peak is observed exclusively in crystals and not in MAPbBr₃ thin films (Fig. S9 in [26]). Photoinduced absorption studies at different T of samples with different degrees of crystallinity can be used to attribute the 2.15-eV feature, in the present case, to long-range dipole-dipole interactions of defects in the bulk of single crystals [36,40]. Without loss of generality and for simplicity of modeling and analysis, we identify the 2.15-eV (575-nm) emission as trap-mediated radiative emission in the bulk of MSCs. This is shown schematically in Fig. 3(d).

Figure 3(b) shows the intensity dependence on external PL quantum efficiency (E-PLQE). The E-PLQE increases with an increase in the excitation intensity. Figure 3(c) (and also Fig. S10 in [26]) shows that the intensity dependence of emission on the excitation density for the 545- and 575-nm emission follows a power law $\langle I_{PL} \rangle = \langle I_{ex} \rangle^x$ and is in agreement with previous observations [38,41]. For the 545-nm

FIG. 3. (a) Plot of the PL data depicting 545- and 575-nm peaks corresponding to PL measured in the reflection and transmission geometries, respectively. (b) Plot showing the increase in E-PLQE at higher excitation fluence. (c) Emission intensity exhibits linear and quadratic dependence on excitation for 545 nm and linear variation for the 575-nm emission. (d) Schematic showing band-to-band recombination and trap emission.

peak (2.27 eV), $x \approx 1$ at low intensity (blue shaded region) and $x \approx 2$ at high intensity. In contrast, the 575-nm (2.15-eV) emission peak reveals a linear $x \approx 1$ response throughout. These results can be understood from a simple physical model where the effective excess carrier lifetime τ_{eff} is expressed as $\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{SRH}}} + \frac{1}{\tau_R}$, where τ_{SRH} is the Shockley-Read-Hall (SRH) trap-mediated nonradiative recombination lifetime and τ_R is the radiative recombination time. The Auger recombination component, which becomes prominent at high excitation flu-

ence (greater than 10^{17} photons/cm²), is neglected. Then $1/\tau_R$ can be expressed as

$$\frac{1}{\tau_R} = B(N_A + \delta n), \quad \frac{1}{\tau_{\text{SRH}}} = R_{\text{SRH}}N_T, \quad (3)$$

where δn is the excess carrier density, B the radiative constant, N_A the background doping concentration, R_{SRH} the nonradiative constant, and N_T the trap density. The radiative recombination rate is given as

$$\frac{\delta n}{\tau_R} = A_R \delta n + B(\delta n)^2, \quad (4)$$

where $A_R = BN_A$.

At low fluence, the radiative recombination rate increases linearly with the excitation and quadratically with fluence at a higher intensity. This explains the excitation dependence of the 545-nm peak. The 575-nm peak arises due to recombination from a shallow trap. If δn is smaller than the trap concentration, the emission rate is linearly dependent on the excitation intensity, in agreement with the observation in Fig. 3(b). This basic model satisfactorily accounts for the PL observations.

Figure 4(a) shows the time-resolved emission spectra upon pulsed 405-nm excitation (19 mW/cm²) on MSCs. From the decay trends of the two peaks [Fig. 4(b)], it can be observed that 545 nm is characterized by a faster decay lifetime in comparison to the trap emission at 575 nm.

The PL lifetimes were studied by varying the excitation intensity. Figures 5(a) and 5(b) show the luminescence decay for both 545 and 575 nm, respectively, as a function of excitation power. The lifetime of the 545-nm emission decreases with an increase in excitation power. The results are summarized in Fig. 5(c). The lifetime measured in the TRPL corresponds to τ_{eff} , which is given as

$$\frac{\delta n}{\tau_{\text{eff}}} = A \delta n + B(\delta n)^2, \quad (5)$$

where $A = BN_A + R_{\text{SRH}}N_T$.

FIG. 4. (a) Time-resolved emission spectra on MSC upon pulsed excitation with a 405-nm source. (b) TRPL at 545 and 575 nm shows a shorter band-recombination lifetime at 545 nm.

FIG. 5. (a) TRPL depicting the decrease in the PL lifetime at high fluence illumination (545 nm). (b) TRPL for 575 nm depicts the constancy of lifetime for the range of excitation intensities. (c) Compilation of intensity-dependent lifetimes for 545- and 575-nm emission. For 545-nm emission, the lifetime is constant at the lower intensity (less than 10^{15} photons/ cm^2) and is reduced at a higher intensity (greater than 10^{15} photons/ cm^2). For the 575-nm emission, the lifetime is uniform in the entire intensity regime.

The effective PL lifetime corresponding to 545-nm emission marginally varies up to a fluence of 10^{15} photons/ cm^2 and at higher fluence decreases as $\tau_R \propto 1/B\delta n$. In contrast, for trap emission at 575 nm, the observed τ_{eff} is independent of excitation intensity, implying monomolecular emission. Using Eq. (5) and the trends observed in Fig. 5(c), the coefficients A and B for 545-nm emission were determined to be $(9.3 \pm 0.2) \times 10^6 \text{ s}^{-1}$ and $(1.4 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively (details in Sec. 12 in the Supplemental Material [26]). These values are in good agreement with recombination rate constants for direct band-gap semiconductors [33,42]. Since the E-PLQE is on the order of τ_{eff}/τ_R , for a fluence greater than 10^{15} cm^{-2} , τ_R decreases with increasing fluence. The E-PLQE increases with increasing fluence as shown in Fig. 3(b).

IV. DISCUSSION

We now correlate L_d to the PL lifetime. In the absence of light bias, the tightly focused probe beam (405 nm, 5×10^{16} photons/ cm^2) in the SPCM studies generates a high concentration of electron-hole pairs and correspondingly the excess carrier lifetime observed from PL studies [Fig. 5(c)] is small (less than 28 ns). The excess carriers diffuse outside the illuminated zone and recombine gradually and the corresponding carrier lifetimes at these levels of concentration increase as observed in PL lifetime studies [545 nm, Fig. 5(c)]. As the modulated probe carriers diffuse to the electrodes, they are also trapped in deep trapping states, effectively reducing the photocurrent. When the probe beam is within a couple of diffusion lengths away from the electrode, an increasing number of carriers (for instance, electrons at the electron transport layer contact) are collected and the holes diffuse to the hole transport layer contact setting up a current in the external circuit. When the carrier concentration is sufficiently reduced, the excess carrier lifetime converges to ~ 125 ns, and L_{diff} assumes the low-intensity value. The addition of DC light bias in the SPCM studies results in two effects. (1) The DC light bias establishes a new DC equilibrium by populating the deep trapping states. This results in suppression of trapping along the pathway for the carriers generated by the modulated probe beam. The reduced trapping accounts for the I_{ph} increase with light bias, explaining features in Fig. 2(a) and Fig. S6(c) in [26]. (2) The magnitude of the DC light bias determines the lateral excess carrier concentration. The excess carrier lifetime decreases to a limit which is set by the DC light bias magnitude. This scenario explains the decrease of L_d with increasing light bias.

The light bias feature elicits the trap-assisted recombination processes [43]. The monomolecular recombination lifetime depends on radiative rate, Shockley-Read-Hall recombination rate, and trap density as shown in Eq. (5). An estimated trap density of $\sim 10^{15}$ traps/ cm^3 [33,36] significantly influences band recombination and lifetimes. Loss of charge carriers to traps is reduced in the presence of bias light, presumably since trap occupancy increases with bias light. Under light bias, a higher fraction of the probe carriers bimolecularly recombine, resulting in shorter τ and L_d .

To understand the microscopic carrier diffusion dynamics, simulation of SPCM using the finite-element method,

FIG. 6. (a) Schematic of the simulation of the SPCM experiment using the finite-element method. The probe excitation (at $x = 0$) is assumed to be a point source in addition to uniform dc light bias on the MSC sample. The blue line at $x = 0$ in all the plots indicates probe excitation. (b) Plot of spatial carrier decay profile considering 1D diffusion of probe carriers. The decay profile changes with different intensities of light bias. (c) Excess carrier lifetime at different dc light biases. The excess carrier lifetime depends on the background carrier density [shown in (b)]. Dashed lines indicate the lifetimes of the light bias generated carriers. As excess probe carriers diffuse in space and recombine, the excess carrier density decreases, resulting in an increased excess carrier lifetime. This results in a spatial dependence of the excess carrier lifetime. (d) Effective diffusion length decreasing with increasing light bias. Dashed lines indicate L_{diff} of light bias generated carriers. Since the lifetime increases as the excess carriers diffuse away from $x = 0$, the effective diffusion length also increases.

incorporating 1D carrier diffusion, was carried out, the results of which are presented in Fig. 6 (simulation details in Sec. 13 in the Supplemental Material [26]). A probe excitation is introduced at $x = 0$ in addition to uniform DC light bias on the MSC sample, as shown in Fig. 6(a). The excess carrier concentration at x is given as

$$n_{\text{tot}}(x) = \delta n_{\text{probe}}(0) \exp\left(\frac{-x}{L_{\text{diff}}}\right) + n_{\text{exc}}(\mathcal{L}). \quad (6)$$

The first term on the right-hand side of Eq. (6) represents the diffusion of probe carriers and the second term corresponds to excess carrier generation due to the light bias $\mathcal{L}$. The plot of $n_{\text{tot}}(x)$ for different light bias conditions is given in Fig. 6(b). The photogenerated carriers diffuse from $x = 0$ and also

simultaneously recombine with lifetime τ , which depends on excess carrier concentration [Fig. 5(c) and Fig. S12(b) in [26]]. As the excess probe carriers diffuse away from $x = 0$ the carrier density decreases, thus increasing τ . However, the effective τ decreases with increasing light bias as shown in Fig. 6(c). A similar trend is observed for the L_{diff} , as shown in Fig. 6(d). As the probe carriers diffuse from $x = 0$, the increase in lifetime [Fig. 5(c)] results in an increased value of L_{diff} . The effective L_{diff} decreases with increased light bias. The simulation results capture the observed trend of decreasing L_d [Fig. 2(c)].

The other parameter, apart from lifetime, that determines L_d is the diffusion coefficient. Ščajev *et al.* have shown that the balancing effects of phonon scattering at low intensity and carrier scattering at high intensity were observed to have a marginal effect on D [31]. Therefore, the intensity-dependent factor that influences diffusion dynamics is determined largely by τ . Photon recycling in perovskites is an additional factor that contributes to the transport length in perovskite-based systems and devices [12,44]. In Sec. 14 of the Supplemental Material [26] we have presented a discussion which shows the simulated excess carrier density accounting for photon recycling. Considering sizable reabsorbed carriers ($n_{\alpha} = 0.54$ [45]) and an upper limit on the photon propagation length ($L_{\alpha} = 1/\alpha \sim 10 \mu\text{m}$ for 545 nm), Fig. S13 in [26] shows that the changes in n_{tot} , τ , and L_{diff} are marginal upon inclusion of photon recycling.

V. CONCLUSION

An elegant consistency was observed from the measurements of $I_{\text{ph}}(x)$ and PL studies. In addition, L_d was observed to decrease as a function of light bias in HOIP single crystals. This observation was correlated with PL lifetime studies, which revealed the contribution of trap recombination dynamics in addition to free carrier dynamics. These results provide insight into the contribution of free carrier and trap emission dynamics to L_d . The sizable L_d in systems where carrier transport is trap mediated points to the defect-tolerant capability of HOIP-based device structures.

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