Accurate Determination of Semiconductor Diffusion Coefficient Using Optical Microscopy

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Energy carrier transport and recombination in emerging semiconductors can be directly monitored with optical microscopy, leading to the measurement of the diffusion coefficient (D), a critical property for design of efficient optoelectronic devices. D is often determined by fitting a time-resolved expanding carrier profile after optical excitation using a Mean Squared Displacement (MSD) Model, where \( D = \frac{\sigma_x^2(t)-\sigma_x^2(0)}{2t} \). Although this approach has gained widespread adoption, there is no clear consensus as to which material systems, and under what experimental conditions (i.e. laser fluence), it can be applied. Here, we simulate diffusive processes in both excitonic and free carrier semiconductors and present a tailorable MSD Model that can accurately predict D for various materials. For perovskites, it is most accurate when sample D values are > 1 cm² s⁻¹ and excitation densities are < 1x10¹⁶ cm⁻³. At higher carrier densities, non-linear recombination terms can dominate the expansion of the carrier profile and lead to fitting error. We find that differences in grain size and boundary behavior, present in most thin films, can lead to distinct profiles that are not captured by MSD Models. Finally, we present clear strategies to investigate and control energy transport in disordered materials for more effective design and optimization of electronic and optoelectronic devices.
1. Introduction

Energy carrier diffusion length and lifetime-mobility product are critical properties of semiconductor materials used for the design of photovoltaics, display technologies, transistors, optical sensors and sources.[1] Accurate determination of these values is essential in the fabrication and development of efficient optoelectronics. For example, the carrier diffusion length is important in determining the layer and electrode spacing in interdigitated back contact (IBC) device architectures,[2] the target active layer thickness to maximize absorption without sacrificing photogenerated charge collection efficiency,[3] and the bulk heterojunction donor/acceptor ratios for efficient excitonic dissociation at interfaces.[4] As an evaluative optoelectronic parameter, there are now several methods capable of determining diffusion length. Bulk methods for vertical and lateral diffusion include photoluminescence (PL) quenching,[5] terahertz or microwave conductivity,[6] Hall effect measurements,[7] and transient grating/diffractive optics experiments.[8]

More recently, the advent of microscopy has allowed for local determination of diffusion rates and lengths, where energetic disorder within the sample such as grain boundaries, and other morphological features can impact local energy transport.[9] The direct visualization of carrier diffusion using both optical and electron microscopies have yielded exciting breakthroughs in semiconductor research. Transient absorption, reflection, and fluorescence microscopies have revealed ballistic transport of hot carriers on short time scales in perovskite thin films.[10] Stimulated emission depletion (STED) microscopy has shown exciton migration on its native nanometer length scale in conjugated polymers.[11] Advanced setups such as four-dimensional electron microscopy, where an optical pulse can create femtosecond dynamics for an electron probe, has revealed super-diffusive behavior in doped silicon.[12] All of these methods can offer femtosecond temporal resolution and nanometer spatial resolution, with exciting scope for further
advancements. In particular, most optical measurements rely on imaging the expanded energy
carrier distributions under a focused (i.e. diffraction-limited) excitation spot and monitoring the
expansion over a series of time delays. A kinetic model is then used to fit the diffusion constant
and can take into account the diffusion tensor as well as the photoexcited carrier recombination
kinetics. This often requires setting up a three-dimensional partial differential equation and
numerically solving for the excited state density at various time steps through finite element
analysis. Due to the complexity of this approach, several approximations have been developed to
simplify the analysis and reduce the computational cost.

One approach that has gained widespread adoption fits the spread of the photoexcited carrier
spatial distribution to Gaussian functions to monitor the change in profile variance (here referred
to as the Mean Squared Displacement (MSD) Model).[13] This method has been applied to small
molecules,[13-14] silicon,[14] gallium arsenide (GaAs),[15] transition metal dichalcogenides
(TMDs),[16] and both single crystal and polycrystalline perovskite samples.[17] Despite the
apparent versatility of this model, there is no clear consensus as to when this approximation holds
and when it fails. It has previously been shown that, at high excitation densities, exciton-exciton
annihilation can lead to the non-diffusive broadening of the Gaussian profile due to faster
recombination at regions of higher exciton density.[18] A few recent studies have commented that
these higher-order recombination processes can lead to fitting errors in perovskite samples, which
could explain the wide range in reported diffusion coefficient values.[9, 19] In either case, a
systematic study exploring the limitations of the MSD Model and a general framework to study
carrier transport in emerging semiconductors has not been developed.

Here we apply a theoretical approach informed by perovskite experimental parameters to study
carrier broadening effects showing that higher-order processes should be considered across
commonly reported microscopic experimental conditions. We find that the utility of the MSD Model is not only heavily dependent on the experimental conditions, but on the material-specific photophysics and the sample morphology (i.e. grain size and boundary behavior). Even in what many consider the low fluence (i.e. < 5 µJ cm^{-2}) or low carrier density (< 1 \times 10^{17} \text{cm}^{-3}) regime, significant errors can still arise in the fitting of the diffusion coefficient. As more studies focus on imaging carrier diffusion over disordered energy landscapes, we expect that this work will enhance the understanding of how to model charge and energy transport mechanisms and accurately derive transport parameters, hence more effectively guiding the design of emerging semiconductors on the microscale.

2. Mean Squared Displacement (MSD) Model for First-Order Kinetics (i.e. PL \sim kN)

First, we consider conditions under which the MSD Model can be applied. We simulate a standard two-dimensional diffusion scenario for a semiconductor that exhibits only first-order kinetics (i.e. radiative and non-radiative excitonic recombination, such as in a molecular solid)

\[
\frac{\partial N(u,t)}{\partial t} = \nabla \cdot (D_{ij}(u,t)\nabla N(u, t)) - k_{\text{tot}} N(u, t) \tag{1}
\]

Here the spatial coordinates are represented by the vector \( u = (x, y) \), \( N(u, t) \) is the spatially and temporally dependent carrier density, \( D_{ij}(u, t) \) is the diffusion coefficient tensor, \( \nabla \) is the gradient operator, and \( k_{\text{tot}} \) is the sum of the radiative \( (k_R) \) and non-radiative \( (k_{\text{NR}}) \) recombination rate constants (i.e. \( k_{\text{tot}} = k_R + k_{\text{NR}} \)). Equation 1 can be numerically solved and the diffusion tensor iteratively fit, but this level of analysis may be excessive and computationally expensive for standard samples. Therefore, the diffusive processes are assumed to be time-independent, isotropic (i.e. \( D_{ij} = 0 \) when \( i \neq j \); \( D_{ij} = D \) when \( i = j \)), and the diffraction-limited laser spot used in confocal microscopy measurements, which resembles an Airy disk, is often approximated as a
Gaussian function. These simplifications allow (1) to be rearranged and written as (2) (see SI for more details)

\[ D = \frac{\sigma_x^2(t) - \sigma_x^2(0)}{2t} \]  

where the numerator is the change in the mean-squared displacement, \( \sigma_x(t) \) is the Gaussian standard deviation of the carrier density profile along the spatial dimension \( x \) as a function of time \( t \), and \( \sigma_x^2 \) is the variance. Advantages of Equation 2 are that it allows \( D \) to be extracted by simply fitting the slope \( (m) \) of the linear curve with respect to time where \( (D = m/2) \). It can also be used to quickly determine if transport behavior deviates from normal diffusive behavior and it removes any broadening contributions due to the point-spread-function (PSF) of the measurement setup. We note that an \( \alpha \) parameter, as an exponential modifier of time \( t \), is often used as a free variable in this equation to quantify energetic disorder or sub-diffusive transport, here we only consider normal diffusion where \( \alpha = 1 \), hence \( \alpha \) is not present in Equation 2.

**Figure 1** shows the result of this model when applied to simulated PL maps, where the PL \( \sim k_R N \) (for simplicity we assume \( k_R \gg k_{NR} \) and therefore \( k_{tot} \sim k_R \)). We first use Equation 1 to generate a 2-dimensional set of PL data with a commonly reported, diffusion coefficient of 0.05 cm²/s, and refer to it as \( D_{sim} \). We then plot the mean squared displacement \( (\sigma_x^2(t) - \sigma_x^2(0)) \) as a function of \( t \) and fit the data to Equation 2, which was separately derived, to extract the fitted diffusion coefficient \( (D_{fit}) \). In other words, we generated a realistic data set with physical parameters that have been reported in the literature, and have a-priori knowledge of the \( D \) value we seek to recover through our fit of Equation 2. Figure 1a-c show the PL maps over typical time intervals of 0, 10, and 20 ns with an initial integrated carrier density \( (N_0) \) of \( 1 \times 10^{16} \text{ cm}^{-3} \), where we observe the diffusion of carriers outside of the initial Gaussian excitation spot (which has full width at half maximum (FWHM) of 660 nm) and a decrease in emission intensity due to first-
order \((k_{\text{tot}})\) recombination (see Figure S1 for similar simulations assuming an Airy disk excitation
distribution). Figure 1d shows normalized PL intensity line profiles of the generated data along
the \(x\)-axis (red dashed line in Figure 1a) as a function of time, where the Gaussian standard
devation \((\sigma_x)\) is also shown. Figure 1e shows the fit to the mean squared displacement as a
function of time using Equation 2, where \(D_{\text{sim}} = D_{\text{fit}} = 0.05 \text{ cm}^2\text{s}^{-1}\). This result demonstrates that
Equation 2 can be used to accurately extract the \(D\) value input into the simulation and can be
applied to samples with isotropic diffusion where the PL \(\sim k_R N\). Although Equation 2 appears to
accurately yield \(D\) for materials which display simple first-order recombination kinetics (as
would be found in the excitonic solids, such as molecular films), it is unclear whether this same
framework can be used for photogenerated free carriers in a semiconductor, which recombine
with PL \(\sim kN^2\), and where higher-order recombination processes might be present.
Figure 1. a-c) Simulated photoluminescence (PL) diffusion maps following first-order ($k_{tot}N$) recombination kinetics (Domain size = 5 x 5 μm; $N_0 = 1 \times 10^{16}$ cm$^{-3}$; $k_{tot} = 1 \times 10^6$ s$^{-1}$; $D_{sim} = 0.05$ cm$^2$ s$^{-1}$; PL $\sim k_R N$, where $k_{tot} \sim k_R$). d) Temporal line profiles along the x-direction, indicated by the red dashed line shown in (a). e) Mean squared displacement (MSD) as function of time along with a fit using the MSD Model, where $D_{fit} = \frac{\sigma_x^2(t) - \sigma_x^2(0)}{2t}$. The fitted diffusion coefficient ($D_{fit} = 0.05$ cm$^2$ s$^{-1}$) matches the pre-defined $D_{sim}$ value used to generate the simulated PL diffusion data.

2.1. MSD Model for Higher-Order Recombination Kinetics (i.e. PL $\sim kN^2$)

Equation 2 has been applied to both excitonic and free carrier semiconductors.[9, 13, 17a, 17b, 21] In excitonic materials measured at low carrier densities, the PL primarily scales as $N$, until exciton-exciton annihilation effects begin to dominate.[18] In these systems, higher-order effects are often neglected due to the low non-linear recombination coefficients, but are expected to be important in free carrier semiconductors, such as metal halide perovskites, where the PL scales quadratically with $N$.[19b, 24] Equation 3 describes the spatiotemporal carrier density with the inclusion of higher-order recombination terms.

$$\frac{\partial N(u,t)}{\partial t} = \nabla \cdot (D_{ij}(u)\nabla N(u, t)) - k_1 N(u, t) - k_2^{int} N(u, t)^2 - k_3 N(u, t)^3$$ (3)

Where $k_1$ is the non-radiative, first-order (monomolecular) recombination constant; $k_2^{int}$ is the internal radiative, second-order (bimolecular) recombination rate constant; and $k_3$ is the non-radiative, third-order (Auger) recombination rate constant. Here, the carrier diffusivity is assumed to be the same for all charge carrier species.

To determine whether Equation 2 can also be applied to free carrier semiconductors where the external PL $\sim k_2^{ext} N^2$ (where $k_2^{ext} = k_2^{int} \cdot P_{esc}$; $P_{esc}$ is the average photon escape probability from the film),[25] we perform simulations similar to Figure 1, but with the addition of the higher-
order recombination terms as shown in (3). Figure 2 shows the mean squared displacement over a time-span of 2 ns for the scenario where the $PL \sim k_2^{ext}N^2$ and with a low simulated initial carrier density of $N_0$ of $1 \times 10^{15}$ cm$^{-3}$, where first-order recombination is the dominant decay mechanism. The shorter (2 ns) time range is typical for microscopy experiments with an optical delay stage and was also chosen to emphasize the early time dynamics where higher-order processes are expected to dominate. We apply Equation 2 to the simulated data and obtain a $D_{fit}$ of 0.0252 cm$^2$ s$^{-1}$, which underestimates $D_{sim}$ (0.05 cm$^2$ s$^{-1}$) by a factor of 2. This ~50% error primarily arises from the fact that Equation 2 was derived assuming the signal scales as $kRN$. For many 3D perovskites, the PL is intrinsically a second-order (bimolecular) process due to the recombination of free electrons with free holes (i.e $PL \sim k_2^{ext}N^2$). Taking this into account, the MSD model can be simplified to Equation 4 (see the “MSD Model for PL ~ $N^2$” subhead in the SI)

$$D = \frac{\sigma_k^2(t)-\sigma_k^2(0)}{t}$$

(4)

for the case of $PL \sim kN^2$ and the kinetics being dominated by first-order (i.e. trapping) processes. Figure 2 shows a $D_{fit}$ value of 0.0503 cm$^2$ s$^{-1}$ when Equation 4 is used to fit the data, which matches well with $D_{sim}$. We note that the additional 0.6% error in $D_{fit}$ (see table in Figure 2) stems from the flattening of the Gaussian profile due to higher-order recombination terms. As expected, this error becomes more significant at higher initial carrier densities and will be discussed in more detail below.
Figure 2. Fits to simulated photoluminescence (PL) data using Mean Square Displacement (MSD) Models for when PL \( \sim N^2 \) (i.e. \( D_{PL-N^2} = \frac{\sigma_x^2(t)-\sigma_x^2(0)}{t} \)) and when PL \( \sim N \) (i.e. \( D_{PL-N} = \frac{\sigma_x^2(t)-\sigma_x^2(0)}{2t} \)). Domain size = 2.5 x 2.5 \( \mu \)m; \( N_0 = 1 \times 10^{15} \) cm\(^{-3} \); \( k_1 = 1 \times 10^6 \) s\(^{-1} \); \( k_2 = 2 \times 10^{-10} \) cm\(^3\) s\(^{-1} \); \( k_3 = 1 \times 10^{-28} \) cm\(^6\) s\(^{-1} \); \( D_{sim} = 0.05 \) cm\(^2\) s\(^{-1} \).

2.2.1 MSD Model for High Initial Carrier Densities (\( N_0 \))

From above, it appears that the MSD Model described in Equation 2 serves as a valid approximation when the signal scales linearly with carrier density (c.f. Figure 1) and the MSD Model in Equation 4 is appropriate when the signal scales quadratically with carrier density and the kinetics are dominated by first-order processes (i.e. low excitation fluences in perovskites). In order to understand the sensitivity of Equation 4 to different initial conditions, we explore three different initial carrier densities that are commonly reported for optical microscopy measurements (see Figure S2).\(^{[17a, 19b, 22]}\) Figure 3a-c show for increasing initial carrier densities at \( t = 0 \) (\( N_0 \) is the integrated carrier density) the regions under the Gaussian excitation spot that are dominated...
(> 50% of the total recombination rate) by first-order ($k_1$, blue) and higher-order ($k_2$ and $k_3$, red/orange) recombination. As the initial carrier density increases, the area of the Gaussian profile dominated by the $k_2$ and $k_3$ terms extends further out to the tails of the Gaussian distribution.

Figure 3d-f show the time-dependent PL profiles with $D_{sim} = 0.05 \text{ cm}^2 \text{ s}^{-1}$ over the first 2 ns and the differences in broadening due to increasing fractions of higher-order recombination.

Importantly, Figure 3f highlights the flattening of the Gaussian profile at regions of higher local carrier density where recombination is faster, which is not due to the diffusion of carriers (see Figure S3).

**Figure 3.** a-c) Increasing initial carrier density at $t = 0$ ($N_0$), showing the regions under the Gaussian excitation spot that are dominated (> 50% of the total recombination rate) by first-order ($k_1$, blue) versus higher-order ($k_2$ and $k_3$, red/orange) recombination for $N_0 = 1 \times 10^{16} \text{ cm}^{-3}$, $5 \times 10^{17} \text{ cm}^{-3}$, $1 \times 10^{18} \text{ cm}^{-3}$, respectively. d-f) Time-dependent photoluminescence (PL) line profiles along the $x$-direction at $t = 0$, 1, and 2 ns for the three different $N_0$’s.
Figure 4a shows $D_{fit}$ values when Equation 4 is applied to fit the PL line profiles reported in Figures 3d-f (see Figure S4 for data over a longer time range). We report $D_{fit}$ values ranging from 0.051 cm$^2$ s$^{-1}$ (2 % error) in the low carrier density regime ($N_0 = 1 \times 10^{16}$ cm$^{-3}$) to 0.174 cm$^2$ s$^{-1}$ (248% error) in the high carrier density regime ($N_0 = 1 \times 10^{18}$ cm$^{-3}$). Figure 4b shows the range of initial carrier densities where Equation 4 accurately (< 5% error) recovers $D_{sim}$ compared to the region where significant error is introduced. Although this data highlights the fitting error that arises when $D_{sim} = 0.05$ cm$^2$ s$^{-1}$, it also suggests that the magnitude of error may be a function of the $D_{sim}$ values, as the diffusion coefficient controls the local carrier density and, hence, the dominant recombination pathways. Figure 4c shows $D_{fit}$ values with varying $D_{sim}$ for the three different carrier densities along with the resultant error. We find more significant error at lower $D_{sim}$ values, which could be expected as carriers are confined to smaller volumes leading to greater fractions of higher-order recombination. For this simulation, Figure 4c shows that the error becomes negligible (< 5%) when $D$ is above 0.02, 0.52, and 1.07 cm$^2$ s$^{-1}$ for the three different carrier densities, respectively, which is consistent with other reports.$^{[19c]}$ These results highlight the importance of conducting confocal measurements at low carrier densities (< 1 $\times$ 10$^{16}$ cm$^{-3}$), especially for perovskite samples where $D$ values typically range from 0.005 – 2 cm$^2$ s$^{-1}$ (see Figure S2). Figure S2 shows a weak positive correlation (N = 20) between carrier density and the reported diffusion coefficients, suggesting that the MSD Model may cause systematic reporting error. We note that this fitting error is still prevalent even when the non-radiative rate constant ($k_1$) is increased by three orders of magnitude to 1x10$^9$ s$^{-1}$ (see Figure S5), indicating that the material quality (i.e. defect density) does not significantly impact these results.
Figure 4. a) Mean squared displacement (MSD) plots and fits to the photoluminescence profiles shown in Figure 3d-f using the MSD Model \(\text{D}_{\text{fit}} = \frac{\sigma_x^2(t) - \sigma_x^2(0)}{t}\) for \(N_0 = 1 \times 10^{16} \text{ cm}^{-3}\) (blue circles), \(5 \times 10^{17} \text{ cm}^{-3}\) (green squares), \(1 \times 10^{18} \text{ cm}^{-3}\) (red triangles). b) \(D_{\text{fit}}\) as a function of the initial carrier density \((N_0)\) for a fixed \(D_{\text{sim}}\) of \(0.05 \text{ cm}^2 \text{ s}^{-1}\) (solid black line), the dashed black line delineates the transition to greater than 5% fitting error. c) \(D_{\text{fit}}\) as a function of \(D_{\text{sim}}\) for the three \(N_0\) values, shaded regions represent the error from the true line \(D_{\text{fit}} = D_{\text{sim}}\). (inset) Error percentages over a subset of the full \(D_{\text{sim}}\) range, where \% Error = \(100 \% \cdot |D_{\text{fit}} - D_{\text{sim}}| / D_{\text{sim}}\). Fitting error increases at high initial carrier densities and low diffusion coefficients.

3. Impact of Grain Size and Grain Boundary Behavior on Carrier Distribution Profiles
Thus far, we have only considered the evolution of the PL profile over short time ranges or when the excitation spot size (with FWHM of 660 nm) is much smaller than the grain size (5 μm). Therefore, these simulations represent the carrier transport behavior before carriers reach the grain boundaries. Given that grain size and grain boundary passivation are controllable material parameters which directly influence photovoltaic performance,[26] we next explore the role of grain size and boundary conditions (grain boundaries being reflective, transmissive, or serving as non-radiative recombination centers) on carrier transport properties. To better understand the impact of different grain sizes and grain boundary behavior on the apparent diffusion processes for a given excitation spot size, we perform simulations on 2, 3, and 5 μm sized square grains (~3x, 4.5x, and 7.5x the spot size, respectively) with reflective (i.e. no flux) grain boundaries. For this analysis, we emphasize reflective boundary conditions as several recent studies have suggested that the grain boundaries in high-quality samples may act as impermeable barriers to carrier transport.[17a, 17c, 17d, 19b, 27] Figure 5a-b show the simulated PL maps at 50 ns for the different sized grains and the MSD plots, respectively. We observe a sublinear change in the MSD for the 2 and 3 μm grain sizes as a function of time, which is due to the grain boundaries acting as solid walls and the fixed carrier density profile decaying at a similar rate across the entire grain (see Figure S6 for PL profiles). We highlight that this effect is not present in larger grains (i.e. > 5 μm) or single crystal samples and is especially prominent in smaller grains (i.e. < 3 μm), again for a $D_{\text{sim}}$ of 0.05 cm$^2$ s$^{-1}$. Importantly, this behavior appears similar to the “sub-diffusive” or nonequilibrium transport discussed earlier, and might be enticing to inaccurately fit with an $\alpha$ parameter. Such error in fitting can be avoided by studying the thermal activation of the diffusion process as well as the spatiotemporal spectra, where a slow spectral redshift is often indicative of carriers undergoing multiple trapping or hopping mechanisms.[21, 28] In addition to grain size, Figure 5c also shows the temporal evolution of the MSD for a 2 μm grain with
quenching grain boundaries and a surface recombination velocity, $S$, of 600 cm s$^{-1}$ (see Figure S6 for PL profiles).[10a] Here the change in the MSD stays nearly constant due to a non-zero carrier flux across the grain boundaries.

**Figure 5.** a) Simulated photoluminescence (PL) diffusion maps for grain sizes of 2, 3, and 5 µm at $t = 50$ ns with reflective grain boundary conditions. b) Mean squared displacement (MSD) plots of the simulations in (a) from 0 – 50 ns. c) MSD plots for 2 µm sized grains with quenching versus reflective boundary conditions. $N_0 = 1 \times 10^{16}$ cm$^{-3}$; $k_1 = 1 \times 10^6$ s$^{-1}$; $k_2 = 2 \times 10^{-10}$ cm$^3$s$^{-1}$; $k_3 = 1 \times 10^{-28}$ cm$^6$s$^{-1}$; $D_{sim} = 0.05$ cm$^2$s$^{-1}$; $S$ = surface recombination velocity = 600 cm s$^{-1}$. Color and size scale bars are the same for all images.
4. Discussion
The direct visualization of energy flow with optical microscopy offers the ability to study structure-function relationships in emerging semiconductors which possess disordered landscapes, inhomogeneities, and impurities. Accurate analysis of the diffusion coefficient in these materials requires an understanding of the dominant photophysical processes under various experimental conditions as well as the determination on how sample-specific morphology controls carrier transport. Here, we focus on the commonly deployed MSD Model, which involves monitoring the expanding carrier density distribution at sequential time intervals after photoexcitation with a focused laser spot. We identify specific scenarios where Equation 2 accurately recovers the underlying transport properties and also highlight instances when this model fails. Specifically, Equation 2 was intended for homogenous semiconductors where the measured signal scales linearly with the carrier density (i.e. excitonic molecular solids). For free carrier semiconductors that are homogeneous (i.e. single crystal or large-grain 3D perovskites) and where the measured signal scales quadratically with the carrier density, we derived a separate MSD Model captured by Equation 4, that can be applied when recombination kinetics are dominated by non-radiative, first-order processes (i.e. perovskites measured in the low-fluence regime or at the longer times of the carrier decay). As this regime is sample-specific, it can be determined by fitting the diffusion coefficient with Equation 4 over a wide range of carrier densities (c.f. Figure 4). Here, the $D$ value should be independent of carrier density under experimental conditions where higher-order effects are negligible and up to the points where carrier-carrier scattering effects begin to dominate and/or band-edge degeneracy is broken.\textsuperscript{[29]} In addition, Equation 4 can also be used for materials which possess $D$ values above a certain threshold ($\sim$1 cm$^2$ s$^{-1}$ for perovskites) and over a large range of carrier densities (c.f. Figure 4). We note that the general approaches described in this work not only apply to fluorescence
imaging, but also to transient reflection, absorption, and scattering microscopies where the measured signal directly relates to the dominant recombination mechanism.

For samples and measurements that are outside of these specific scenarios, new kinetic models should be developed which can relate the measured signal back to microscopic origins. Ideally, an MSD model taking into account the initial carrier density and higher-order recombination terms could be developed, but deriving an analytical solution to a non-linear PDE is nontrivial. Therefore, numerically solving the PDE equation described in Equation 3 serves as a good alternative option that can capture the effects of higher-order recombination processes. For materials that are not homogeneous and possess grain boundaries, structural features and interfaces can be directly input into numerical simulations. This is especially important for samples that demonstrate grain boundary behavior similar to Figure 5, where the slowing of the MSD expansion is due to carrier reflection off the grain boundaries. Here, a carrier may undergo multiple reflections before recombining, making the total distance it traveled large, despite its small displacement (i.e. vector magnitude). Therefore, reported diffusion lengths should be denoted as vector or scalar quantities, depending on the definition used. The MSD Model, which monitors the normalized changes in the carrier distribution profiles, does not differentiate between these scenarios. Without careful attention to the impact of various structural features, carrier transport could be misinterpreted as sub-diffusive or trap-dominated. Therefore, in addition to analyzing the raw (un-normalized) data, additional complementary experiments such as hyperspectral imaging and temperature-dependent measurements should be performed to further refine kinetic models.

Further addendums to PDEs like Equation 3 can be made for samples that are highly emissive, possess a small Stokes shift, and have strong band-edge absorption. In this case, photon emission
followed by subsequent photon reabsorption (i.e. photon recycling) can significantly impact the apparent carrier transport. The introduction of coupled PDEs accounting for both the photoexcited density as well as the photon density could allow for the decoupling of transport solely due to coherent or incoherent processes compared to photon recycling.

5. Conclusion
We simulate energy carrier transport processes in both excitonic and free carrier semiconductors and show that the implied material diffusion coefficient can be accurately recovered using a Mean Squared Displacement (MSD) Model of the general form, \( D_{fit} = \frac{\sigma^2(t) - \sigma^2(0)}{at} \). Although this equation is quite versatile, we also explore its limitations in capturing the impact of non-linear (i.e. bimolecular and Auger) recombination processes on the measured carrier distribution profiles. We propose a general approach to test the accuracy of the model to various experimental parameters (i.e. laser fluence) as well its sensitivity to the intrinsic material diffusion coefficient. In addition, we find that structural disorder present in many emerging semiconductors, such as grain size and grain boundary behavior, can lead to distinct carrier distribution profiles, which are not well captured by the general form of the MSD Model. We expect this work will lead to better design and optimization of device architectures for electronic and optoelectronic applications as well as bolster the efforts towards a fundamental understanding of other important transport properties such as carrier scattering times, velocities, mean free paths, and hopping rates.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Supporting Information

**Title** Accurate Determination of Semiconductor Diffusion Coefficient Using Optical Microscopy

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S1. Derivation of Mean Squared Displacement (MSD) Model

As outlined in the main article, this work is primarily concerned with the application of the MSD Model shown in Equation S1 to various material systems under different experimental conditions.

\[
D = \frac{\sigma_2(t) - \sigma_2(0)}{2t}
\]  
(S1)

In order to better understand the origins of this equation and its limitations, we outline the derivation below. We begin with the partial differential equation (PDE) which includes first-order recombination.

\[
\frac{\partial N(u,t)}{\partial t} = \nabla \cdot \left( D_{ij}(N, u, t) \nabla N(u, t) \right) - k_{tot} N(u, t)
\]  
(S2)

We assume that the material is homogenous on the length scale of the diffusion length and therefore the diffusion coefficient is 1) isotropic (i.e. \(D_{ij} = 0\) when \(i \neq j\); \(D_{ij} = D\) when \(i = j\)), 2) independent of time, 3) independent of carrier density — photoexcitation density is sufficiently low at \(t = 0\), and 4) that the diffusion along different axes is uncorrelated (i.e. the particle has no memory of the direction of its last hop) and therefore we can only consider the diffusion along one dimension:

\[
\frac{\partial N(x,t)}{\partial t} = D \frac{\partial^2 N(x, t)}{\partial x^2} - k_{tot} N(x, t)
\]  
(S3)

We consider the initial condition \((t = 0)\) where the initial carrier density profile is the Delta function at the origin, \(\delta(x_0)\). Next, we know that the photoexcited carrier will spread out uniformly from the point of excitation becoming both wider and shallower and make an educated guess of a prototypical solution.\(^1\)

\[
N(x, t) |_{\delta(t=0)} = t^{-\alpha} F(\eta)
\]  
(S4)

\[
\eta = \frac{x^2}{4Dt}
\]  
(S5)

Here, \(t^{-\alpha}\) is the size-factor that decreases the carrier density amplitude as a function of time when \(t^{-\alpha} > F(\eta)\). \(F(\eta)\) is the shape-factor that dictates the curve’s profile. The powers of both \(x\) and \(t\) are determined
based on (S3), where $x$ is associated with a second-order derivative and $t$ as a first-order derivative. The introduction of $D$ into $\eta$ makes the ratio dimensionless. The constant, $\alpha$, and the function, $\eta$, must be found.

We calculate the derivatives of this prototypical solution using the product rule where appropriate:

$$\frac{\partial N}{\partial t} = -\alpha t^{-\alpha-1} F + t^{-\alpha} \frac{dF}{d\eta} \frac{\partial \eta}{\partial t}$$

$$= -\alpha t^{-\alpha-1} F - \eta t^{-\alpha-1} \frac{dF}{d\eta}$$

(S6)

$$\frac{\partial N}{\partial x} = t^{-\alpha} \frac{dF}{d\eta} \frac{\partial \eta}{\partial x}$$

$$= \frac{xt^{-\alpha-1} dF}{2D} \frac{\partial \eta}{d\eta}$$

(S7)

$$\frac{\partial^2 N}{\partial x^2} = \frac{t^{-\alpha-1} dF}{2D} \frac{\partial \eta}{d\eta} + \frac{xt^{-\alpha-1} d^2F}{2D} \frac{\partial^2 \eta}{d\eta^2} \frac{\partial x}{\partial x}$$

$$= \frac{\partial^2 N}{\partial x^2} = \frac{t^{-\alpha-1} dF}{2D} \frac{\partial \eta}{d\eta} + \frac{x^2 t^{-\alpha-1} d^2F}{4D^2 t} \frac{\partial^2 \eta}{d\eta^2}$$

$$= \frac{t^{-\alpha-1} dF}{2D} \frac{\partial \eta}{d\eta} + \eta \frac{t^{-\alpha-1} d^2F}{D} \frac{\partial \eta}{d\eta^2}$$

(S8)

Substituting (S6) and (S8) into the PDE (S3) in the case where $k_{tot} = 0$:

$$-\alpha t^{-\alpha-1} F - \eta t^{-\alpha-1} \frac{dF}{d\eta} = D \left( \frac{t^{-\alpha-1} dF}{2D} \frac{\partial \eta}{d\eta} + \eta \frac{t^{-\alpha-1} d^2F}{D} \frac{\partial \eta}{d\eta^2} \right)$$

(S9)

We factor and cancel terms to simplify Equation S9 as much as possible:

$$t^{-\alpha-1} \left( -\alpha F - \eta \frac{dF}{d\eta} \right) = t^{-\alpha-1} \left( \frac{1}{2} \frac{dF}{d\eta} + \eta \frac{d^2F}{d\eta^2} \right)$$

(S10)

$$-\alpha F - \eta \frac{dF}{d\eta} \frac{dF}{d\eta} = \frac{1}{2} \frac{dF}{d\eta} + \eta \frac{d^2F}{d\eta^2}$$

(S11)
\[-\alpha F - \frac{1}{2} \frac{dF}{d\eta} = \eta \left( \frac{dF}{d\eta} + \frac{d^2F}{d\eta^2} \right) \quad \text{(S12)}\]

\[-\frac{1}{2} \left( \frac{dF}{d\eta} + 2\alpha F \right) = \eta \frac{d}{d\eta} \left( \frac{dF}{d\eta} + F \right) \quad \text{(S13)}\]

If we set $\alpha = \frac{1}{2}$, then the PDE becomes a simple ODE.

\[-\frac{1}{2} \left( \frac{dF}{d\eta} + F \right) = \eta \frac{d}{d\eta} \left( \frac{dF}{d\eta} + F \right) \quad \text{(S14)}\]

\[
\frac{dF}{d\eta} + F = 0 \quad \text{(S15)}
\]

This is a simple ODE that can be solved analytically:

\[F(\eta) = Ae^{-\eta} \quad \text{(S16)}\]

Substituting the solution into our prototypical solution from Equation S4.

\[N(x, t)|_{\delta(t=0)} = t^{-\alpha} F(\eta) = At^{-\alpha} e^{-x^2/4Dt} \quad \text{(S17)}\]

Where, again, we set $\alpha = \frac{1}{2}$.

\[N(x, t)|_{\delta(t=0)} = At^{-1/2} e^{-x^2/4Dt} \quad \text{(S18)}\]

We determine the normalization factor, $A$, which is the integral of a Gaussian function with respect to $x$.

\[
\int_{-\infty}^{\infty} At^{-1/2} e^{-x^2/4Dt} \, dx = 1 \quad \text{(S19)}
\]

\[A = \frac{1}{\sqrt{4\pi D}} \quad \text{(S20)}\]

Putting this all together, we arrive at the solution for the carrier density as a function of position and time. Importantly, the probability of finding an energy carrier at a position of $x$ after a time of $t$ is a Gaussian function of the form:
\[ N(x, t)|_{\delta(t=0)} = G(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad (S21) \]

Including the linear recombination term in Equation S3 the equation becomes.

\[ N(x, t)|_{\delta(t=0)} = G(x, t) = e^{-k_{tot} t} \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad (S22) \]

The exponential prefactor with \( k_{tot} \) strongly impacts the recombination rate, but is independent of \( x \). Therefore, all positions across the carrier density profile decrease the same relative amount leading to no impact on the spatial broadening of the distribution. Taking this into account, the measured signal intensity is often normalized to isolate the expansion of the carrier density distribution.

**S1.1. Convolution with Gaussian Initial Condition**

Next, we consider the initial condition which, for a confocal microscopy experiment, is an Airy disk that can be approximated as a Gaussian function

\[ N(x, 0) = N_0 e^{-x^2/2\sigma_x^2} \quad (S23), \]

where \( N_0 \) is the integrated carrier density.

The time evolution of the carrier density is therefore the convolution of the initial carrier density with the evolving Gaussian profile as shown in Equation S24.

\[ N(x, t) = N(x, 0) \ast G(x, t) = \frac{N_0}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} e^{-x^2/2\sigma_x^2} e^{-x^2/4Dt} dx \quad (S24) \]

Conveniently, the convolution of two Gaussians functions with variances of \( \sigma_A^2 \) and \( \sigma_B^2 \) is \( \sigma_A^2 + \sigma_B^2 \).

\[ N(x, t) = \frac{N_0}{\sqrt{4\pi Dt}} e^{-\left(x^2/(2\sigma_x^2+4Dt)\right)} \quad (S25) \]

The variance of Equation S25, which is the excited carrier distribution \( (\sigma^2_{N,x}) \), is
\[ 2\sigma_{N,x}^2(t) = 2\sigma_x^2 + 4Dt \] (S26)

and is often written as the mean squared displacement (MSD)

\[ MSD = \langle x(t)^2 \rangle - \langle x(0)^2 \rangle = \sigma_{N,x}^2(t) - \sigma_x^2 = 2Dt \] (S27)

Rearranging for the \( D \)

\[ D = \frac{\sigma_{N,x}^2(t) - \sigma_x^2}{2t} \] (S28)

Oftentimes, we do not have direct access to the local carrier density or the initial condition and measure a spectroscopic signal (i.e. such as photoluminescence) to gain insight into these distributions, as commented by others,\(^2\) the true variance is the measured signal intensity (\( \sigma_{int}^2 \)) convolved with the point spread function (\( \sigma_{PSF}^2 \)) of the measurement setup.

\[ \sigma_{int}^2(t) = \sigma_{N,x}^2(t) + \sigma_{PSF}^2 = \sigma_x^2 + 2Dt + \sigma_{PSF}^2 \] (S29)

The MSD is

\[ \sigma_{int}^2(t) - \sigma_{int}^2(0) = \sigma_x^2 + 2Dt + \sigma_{PSF}^2 - (\sigma_x^2 + 2D(0) + \sigma_{PSF}^2) \] (S30)

\[ \sigma_{int}^2(t) - \sigma_{int}^2(0) = 2Dt \] (S31)

\[ D = \frac{\sigma_{int}^2(t) - \sigma_{int}^2(0)}{2t} \] (S32)

**S2. MSD Model for PL ~ N^2 when \( dN/dt \sim -kN \)**

Following the general approach described in Equations S23-S32, if the measured signal intensity scales as \( N^2 \), then Equation S22 becomes

\[ \text{PL} \sim N^2(x,t) = e^{-2k_{tot}t} \frac{1}{4\pi Dt} e^{-x^2/(2Dt)} \] (S33)

Convolving with the initial condition defined in Equation S23:
\[ e^{-2k_{tot}t} \frac{N_0}{4\pi D t} e^{-\left(\frac{x^2}{(2\sigma_x^2+2Dt)}\right)} \]  

(S34)

The variance of Equation S34, which is the excited carrier distribution \((\sigma_N^2)\), is

\[ 2\sigma_{N,x}^2(t) = 2\sigma_x^2 + 2Dt \]  

(S35),

which, following Equations S28-S32, can be simplified to

\[ D = \frac{\sigma_{int}^2(t)-\sigma_{int}^2(0)}{t} \]  

(S36).

S3. Recombination/Diffusion Model

As described in the main article, Equation S37 describes the spatiotemporal carrier density in two dimensions with the inclusion of higher-order recombination terms.

\[ \frac{\partial N(u,t)}{\partial t} = \nabla \cdot (D_{ij}(u) \nabla N(u, t)) - k_1 N(u, t) - k_{2int} N(u, t)^2 - k_3 N(u, t)^3 \]  

(S37)

Where the spatial coordinates are represented by the vector \( u = (x, y) \), \( N(u, t) \) is the spatially and temporally-dependent carrier density, \( D_{ij}(u) \) is the diffusion coefficient tensor, \( \nabla \) is the gradient operator, \( k_1 \) is the non-radiative, first-order (monomolecular) recombination constant; \( k_{2int} \) is the internal radiative, second-order (bimolecular) recombination rate constant; and \( k_3 \) is the non-radiative, third-order (Auger) recombination rate constant. Here the carrier diffusivity is assumed to be the same for all charge carrier species. For our simulations, \( D = 0.05 \text{ cm}^2\text{s}^{-1} \), \( k_1 = 1 \times 10^6 \text{ s}^{-1} \), and \( k_{2int} = 2 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \), and \( k_3 = 1 \times 10^{-28} \text{ cm}^6\text{s}^{-1} \) unless otherwise stated. We also assume that diffusion along the z-dimension can be ignored for sufficiently thin, homogeneous samples. We note that many polycrystalline films do possess heterogeneity over the length scale of the film thickness, which can more accurately be described by a 3-dimensional partial differential equation.3

S3.1. Gaussian Initial Condition
For the majority of the simulations in this work, we approximate the excitation spot with a Gaussian function defined in Equation S23, but in two-dimensions. For the simulation, we input the experimentally measured laser excitation profile parameters ($\sigma_x = \sigma_y = 314$ nm) and center the excitation source at the origin ($x = y = 0$). A pre-factor $(2\pi \sigma_x^2)^{-1}$ is also introduced in front of the exponent as normalization constant to ensure that the spatial integral equals $N_0$.

S3.2. Airy Disk Initial Condition

We also consider the excitation profile for a diffraction-limit spot in confocal microscopy, which is often described by an Airy disk. The functional form of an elliptical Airy disk excitation profile is given by Equation S38:

$$G(r, 0) = \frac{N_0}{I_0} \left( \frac{2J_1(1.22\pi r)}{1.22\pi r} \right)^2$$

(S38)

Where $J_1$ is the Bessel function of the first kind, $r = \sqrt{\left(\frac{x}{x_0}\right)^2 + \left(\frac{y}{y_0}\right)^2}$, $x_0$ is the $x$-coordinate along the $x$-axis where the first zero occurs, and $y_0$ is the $y$-coordinate along the $y$-axis where the first zero occurs, $I_0 = \iint_A B(r) dx dy$ where $B(r) = \left( \frac{2J_1(1.22\pi r)}{1.22\pi r} \right)^2$ and $A$ is the domain area of the simulation.

S3.3. Boundary Conditions and Photoluminescence Signal

For simulating the time-resolved PL maps and profiles we consider both no flux (i.e. reflective) boundary conditions in Equation S39 as well as quenching boundary conditions in Equation S40 with a surface recombination velocity ($S$) of 600 cm s$^{-1}$.4

$$\frac{\partial N(u, t)}{\partial x} \bigg|_y = \frac{\partial N(u, t)}{\partial y} \bigg|_y = 0$$

(S39)
\[
\frac{\partial N(u,t)}{\partial x} \bigg|_\gamma = \frac{\partial N(u,t)}{\partial y} \bigg|_\gamma = -\frac{S}{D} N(\gamma, t) \quad (S40)
\]

where \(\gamma\) is the vector that denotes the spatial coordinates of the grain boundaries. The solutions to these equations (i.e. \(N(u,t)\)) are evaluated using a time-domain, finite-element analysis in the MATLAB PDE toolbox. For the radiative, first-order recombination processes described in Figure 1 and S1 the PL is calculated using Equation S41:

\[
PL(t) = k_{rad} N(u, t) \quad (S41)
\]

For the rest of the simulations throughout the work, the PL is the external radiative second-order recombination rate constant multiplied by the square of the time-dependent carrier population as shown in Equation S42:

\[
PL(t) = k^{\text{ext}}_2 N(u, t)^2 \quad (S42)
\]
Figure S1. a-c) Simulated photoluminescence (PL) diffusion maps at time ($t$) intervals of $t = 0$, 10, and 20 ns. The initial excitation condition is an Airy disk and the dynamics follow first-order ($k_{tot}$) recombination kinetics (Domain size = 5 x 5 µm; $N_0 = 1x10^{16}$ cm$^{-3}$; $k_{tot} = 1x10^6$ s$^{-1}$; $D_{sim} = 0.05$ cm$^2$ s$^{-1}$; PL $\sim k_R N$, where $k_{tot} \sim k_R$). d) Temporal line profiles along the x-direction, indicated by the red dashed line shown in (a). e) Gaussian variance as function of time along with a fit using the Mean Squared Displacement Model, where $D_{fit} = \frac{\sigma^2(t) - \sigma^2(0)}{2t}$. The change in the initial condition introduces a 6% error in the diffusion coefficient fit ($D_{fit} = 0.053$ cm$^2$ s$^{-1}$) compared to the pre-defined $D_{sim}$ value input into the partial differential equation.
Figure S2. a) Literature survey of the reported diffusion coefficients as a function of initial carrier density ($N_0$) with a Pearson coefficient ($R$) of 0.30 ($N = 43$), indicating a weak positive correlation. Square data points indicate fits using the Mean Squared Displacement (MSD) Model, X-shaped data points indicate fits to a partial differential equation (PDE), hour-glasses-shaped data points indicate a fit using a combination of the MSD Model and a PDE. Black data points indicate $D$ values for polycrystalline films and blue data indicate $D$ values for single crystal samples. b) Data points for the MSD Model only with $R = 0.44$ ($N = 20$), indicating a weak positive correlation. The $N_0$ values range from $1 \times 10^{16}$ to $3.8 \times 10^{19}$ cm$^{-3}$ and the fitted diffusion coefficient values range from 0.005 to 2.4 cm$^2$ s$^{-1}$. Numbers to the right of the data points are the corresponding references.
Figure S3. a-c) Time-dependent simulated photoluminescence (Sim. PL) line profiles along the $x$-direction at $t = 0, 1,$ and 2 ns for the case where $PL \sim k_{\text{rad}} N$, and $N$ is simulated using equation (1) in the main article. d-f) Temporal PL line profiles where $PL \sim k_{\text{ext}}^2 N^2$, and $N$ is simulated using equation (3) in the main article or (S37). Non-diffusive broadening behavior at high initial carrier densities is not observed in a-c) and is therefore due to higher-order recombination processes present in d-f).
Figure S4. a) Gaussian variance plots and fits to the photoluminescence (PL) profiles in Figure 3d-f in the main article using the Mean Squared Displacement Model for $N_{0,\text{total}} = 1 \times 10^{16}$ cm$^{-3}$ (blue circles), $5 \times 10^{17}$ cm$^{-3}$ (green squares), $1 \times 10^{18}$ cm$^{-3}$ (red triangles). b) Identical plot from (a) over a 50 ns time-window. The differences in the variances as a function of time are evident regardless of the time range analyzed.
Figure S5. $D_{fit}$ using the Mean Squared Displacement Model as a function of $D_{sim}$ for $N_{0,\text{total}} = 1 \times 10^{16}$ cm$^{-3}$ (blue), $5 \times 10^{17}$ cm$^{-3}$ (green), $1 \times 10^{18}$ cm$^{-3}$ (red) when the non-radiative, first-order recombination constant ($k_1$) is set to $1\times10^6$ s$^{-1}$ (solid lines) versus $1\times10^9$ s$^{-1}$ (dashed lines). Fitting error is evident in both scenarios, indicating that the perovskite material quality does not significantly impact the key findings of this work.
Figure S6. Time-dependent simulated photoluminescence (PL) line profiles along the $x$-direction at $t = 0, 12.5, 25,$ and $50$ ns for a) no flux (i.e. reflective, equation (S39)) compared to b) non-zero flux (i.e. quenching, equation (S40)) boundary conditions. Domain size = 2 x 2 $\mu$m; $N_0 = 1 \times 10^{16}$ cm$^{-3}$; $k_1 = 1 \times 10^6$ s$^{-1}$; $k_2 = 2 \times 10^{-10}$ cm$^3$ s$^{-1}$; $k_3 = 1 \times 10^{-28}$ cm$^6$ s$^{-1}$; $D_{sim} = 0.05$ cm$^2$ s$^{-1}$ and $S= 600$ cm s$^{-1}$ for b). In (a) the sublinear change in the variance is due to the grain boundaries acting as solid walls and the nearly fixed carrier density profile decaying at a similar rate across the entire grain.
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