Supporting Information

Monitoring Charge Carrier Diffusion Across Perovskite Film with Transient Absorption Spectroscopy

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1 Additional information on modelling transient reflectance and transmittance signals

1.1 Roughness layer

![Graphs](image)

Figure S1: Initial distribution of charge carrier density (a) without roughness and (b) with roughness. The distribution is stretched in the roughness layer because of lower relative volume of perovskite at the surface. The charge carrier density at the surface is $2 \cdot 10^{18} \text{cm}^{-3}$.

The roughness was modelled as a nanocone which was also split into multiple layers for the transfer matrix. The refractive index $n$ in each layer was calculated as

$$n = \sqrt{V_{frac} \cdot n_{film}^2 + (1 - V_{frac})n_{air}^2}$$  \hspace{1cm} (1)
where $V_{frac}$ is the relative volume of perovskite and $n_{film}$ and $n_{air}$ refractive indexes of perovskite and air.

Diffusion and charge carrier density distribution was simulated using Matlab pdepe-function\(^1\) in one dimension. The simulation assumed a flat film, so the charge carrier distribution in the roughness layer was estimated by calculating the total volume of perovskite as function of depth and stretching the distribution accordingly (Figure S1). The total volume with and without roughness layer was kept approximately the same: Thickness of bulk perovskite was 527 nm without roughness and 496.5 nm with roughness, and height of nanocone (roughness) was 90 nm. Cone with this height has the same volume as 30 nm flat cylinder, $30 \text{ nm} + 496.5 \text{ nm} \approx 527 \text{ nm}$, so the total volume is roughly the same with and without roughness. 90 nm roughness is reasonable in these kind of perovskite films (Figure S2).

![Figure S2: An example of a typical FAMACs perovskite thin film cross-section.](image)
1.2 Modelling steps

We have provided Matlab codes for each modelling step as part of supporting info. The modelling steps are:

1) First we roughly approximated the thickness of the film from steady state transmittance and reflectance. At this point we assumed flat film without surface roughness. Then we fine-tuned the thickness for transient simulations by simulating the transient reflectance and transmittance and comparing them to measured transient data around 1 ns delay time. We used the spectral change in refractive index acquired in our previous paper\textsuperscript{2} as the initial estimation for photoinduced change in refractive index. Thickness mainly determines the position of the signal peaks and zero-spots in transient reflectance signal, so thickness can be determined by aligning those.

2) We estimated the change in complex refractive index by using a transfer matrix based fitting program. We again used measured data at 1 ns delay time for the fitting.

3) We simulated how the change in charge carrier distribution changes the transient reflectance response over time. We calculated the starting distribution from absorption of the film at the pump wavelength and film thickness, and simulated the change in distribution over time; The initial distribution depends on film thickness and absorbance and subsequent changes in distribution over time depend on diffusion coefficient and charge carrier lifetime. We then simulated transient reflectance and transmittance signals with these charge carrier distributions, essentially simulating how the transient signal evolves over time.

4) Addition of roughness layer: At this point the simulated signal matched the experimental data at long delay times but not at short delay times (depending on wavelength, Figure S4), so we added a roughness layer to the model and increased its thickness until the simulated and measured signals matched at short delay times as described in the main article. We kept the average thickness the same while adding more roughness, and the charge carrier density distribution in the roughness layer is shown in Figure S1. Addition of roughness induced only minor changes to simulated transient signal at long delay time, but we
corrected those by redoing the complex refractive index fit after determining the suitable roughness thickness.

5) Fitting of diffusion constant was then done simply by minimizing square root error between simulated and measured signals at each wavelength. Diffusion constant was the only fitting parameter at this point as the other parameters (thickness, change in refractive index and roughness) had each been determined separately.

Figure S3: Simulated (a) charge carrier density distributions and (b-d) resulting transient reflectance and transmittance signals at wavelengths 880, 936 and 1040 nm respectively as in Figure 2 of the main text but without recombination. The recombination mainly influences the signal in nanosecond scale.
Figure S4: Transient signal simulations without roughness at (a) 866 nm, (b) 936 nm and (c) 1046 nm. The diffusion constant was 2 cm$^2$s$^{-1}$. The initial peak in transmittance response is caused by hot carriers and their cool down within 1 ps.
1.3 Visible range simulations

In the visible range the roughness layer makes the reflectance simulation less accurate (Figure S5). This could be explained by the difference in the ratio of the excitation wavelength to characteristic roughness feature size: smaller wavelengths are better at distinguishing roughness features, experiencing sharp change in refractive index instead of gradual change. However, even if flat surface is used the simulation is still very inaccurate: The signal decays in linear fashion (in logarithmic scale) while the simulation insists that there should be an initial increase in signal and the long delay times (>100 ps) are not a good match either. This implies that there are additional factors affecting visible range transient reflectance response.

![Figure S5: Visible range transient reflectance simulation at 480 nm. Simulated signals had diffusion constant of 164 nm$^2$ps$^{-1}$.](image)

Comparing visible range to NIR, high versus low absorption, the visible range transient reflectance signal only depends on what happens on the surface whereas in NIR the signal depends on the entire perovskite layer. Visible range is hence affected by surface phenomena, such as surface recombination$^3$ and traps, that do not necessarily appear in NIR signal. Wavelengths near the bang-gap are also more difficult to analyse because of extreme change.
in absorption compared to other wavelengths, and absorption may be low enough to allow reflectance from film-glass interface to also play a role in TA and TR signals. All of these factors lead to the conclusion that analysis of transient reflectance and charge carrier diffusion is much easier at wavelengths where the sample has very low absorption.

2 Visible range steady state and transient absorption

Figure S6: Transient absorption response in visible range.
Figure S7: Sample absorbance. The small peak around 950 nm is caused by reflectance (thin film interference). Measurement reference was air.

3 Experimental details

3.1 Time-resolved terahertz spectroscopy

Time-Resolved Terahertz Spectroscopy is a pump-probe technique which is described in detail in the reviews\textsuperscript{4,5} and our particular setup in article by Hempel et al.\textsuperscript{6}

A pump pulse (with wavelength of 402 nm and photon flux of $4 \cdot 10^{12}$ photons/cm\textsuperscript{2} per pulse) photo-excites a charge carrier concentration $\Delta n$ in semiconductor. The electric field $E(f)$ of the following terahertz pulse oscillates at terahertz frequencies $f$ and includes a drift of the photo-excited charge carriers. The corresponding current $I(f) = e\mu(f)\Delta nE(f)$ can be described by a frequency-dependent mobility $\mu \sum(f)$, which is the sum of the electron mobility and of the hole mobility. It is a complex quantity as its phase describes the phase...
delay between driving terahertz field and oscillating current.

During the interaction, energy is transferred from the terahertz pulse to the charge carriers, which can be understood as free carrier absorption of the terahertz radiation. The change in the transmission $\Delta T/T$ of terahertz probe pulse is measured in the TRTS setup and can be analyzed for the mobility $\mu \sum(f)$ of the photo-excited charge carriers by the so-called “thin film approximation” in Equation (2).

$$\mu \sum = -\frac{\varepsilon_0 c (1 + n)}{\Delta n_s} \frac{\Delta T/T}{1 + \Delta T/T}$$  \hspace{1cm} (2)

The photo-excited sheet carrier concentration $\Delta n_s$ of $4 \cdot 10^{12}$ electrons/cm$^2$ per pulse is calculated for the photon flux of the pump pulse and its reduction by the reflection at the sample, which is shown in Figure S8. The reactive index $n$ of the glass substrate at frequencies of 0.5 THz is 2.55.

![Figure S8: Reflection of the sample measured by a PerkinElmer UV-vis spectrometer.](image)

The sum mobility of photo-excited electrons and holes is shown in Figure S9. The real part has only a slight frequency-dependence. Therefore, it can be extrapolated to DC-value ($f = 0$) of $65 \pm 10$ cm$^2$(Vs)$^{-1}$. Such a DC-value is relevant quantity for application
in solar cell or LEDs, which are operated at DC-conditions. This value is in line with our previous publication on MAPbI$_3$ (40 cm$^2$(Vs)$^{-1}$) and the results of other TRTS groups\textsuperscript{8} (ca. 20 – 80 cm$^2$(Vs)$^{-1}$).

![Figure S9: Sum mobility of photo-excited electrons and holes measured by time-resolved terahertz spectroscopy. The real part is extrapolated to the DC-value, which is the relevant quantity for application in solar cells or LDEs.](image)

### 3.2 Transient absorption spectroscopy equipment

The samples were excited by laser pulses generated by Libra F, Coherent Inc., coupled with Topas C, Light Conversion Ltd. A white continuum generator (sapphire crystal for NIR and heavy water for visible range) was used to produce the probe beam. The TA responses were measured using an ExciPro TA spectrometer (CDP, Inc.) equipped with a CCD array for the visible spectral range (460–770 nm), and an InGa diode array for the near-infrared wavelengths.

### 3.3 Sample fabrication

Soda-lime glass substrates (Thermo Scientific\textsuperscript{TM}) were washed by sonication for 15 min with Mucasol solution 2% in water, isopropanol and acetone respectively. After 15 min of O$_3$...
and ultraviolet (UV) treatment, the samples were taken to a N₂-filled glovebox for the perovskite spin coating. Regarding the FAMACs-perovskite solution, stock solutions of PbI₂ (1.5 M, TCI) and PbBr₂ (1.5 M, TCI) in anhydrous dimethylformamide (DMF) / dimethyl sulfoxide (DMSO) = 4:1 (v:v, Sigma-Aldrich) were previously prepared and heated again overnight at 60°C in a thermostaker before use. Methylammonium (MA) bromide and formamidinium (FA) iodide powders (dyenamo) were weighed out in two separate vials and then the proper volume of PbI₂ (PbBr₂) stock solutions was calculated and added to the vials containing the FAI (MABr) powder to get a stoichiometry of FAI:PbI₂ (MABr:PbBr₂) of 1:1.09. Before deposition, the solutions were mixed as follows: FAPbI₃:MAPbBr₃ = 85:15 (v:v). Further CsI (1.5 M, Sigma-Aldrich) from a stock solution in DMSO was eventually added to the precursor solution to produce a final composition with the stoichiometry (CsI)₀.₀₅[(MAPbBr₃)₀.₁₅(FAPbI₃)₀.₈₅]₀.₉₅. 80 µL of perovskite solution was then drop-casted on the 2.5×2.5 cm² substrate and spin coated in a two-step program at 1000 rpm for 10 s and 6000 rpm for 20 s. 5 s prior to the end of the program, 100 µL of anhydrous chlorobenzene was poured on the spinning substrate. Subsequently, the sample was annealed at 100°C for 1 h.

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