Charge carrier migration and hole extraction from MAPbI$_3$

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Abstract. Linear as well as time resolved absorption measurements were performed on 40 nm and 170 nm thick MAPbI$_3$ films with PEDOT:PSS hole extraction layer, spin-coated on quartz substrate. From linear absorption measurements exciton binding energy of 18 – 19 meV and band gap of 1.60 - 1.62 eV was deduced. Transient absorption spectra after the excitation at 1.77 eV showed a strong difference in carrier recombination dynamics for the two MAPbI$_3$ films of different thicknesses. From the analysis on the decay dynamics, hole population lifetime of 0.3 ns and 3.5 ns for 40 nm and 170 nm films, respectively, are determined. A numerical 1D diffusion model was used to model the carrier relaxation dynamics yielding hole diffusion constants of 0.025 - 0.030 cm$^2$s$^{-1}$, which results in a hole mobility of 1 cm$^2$(Vs)$^{-1}$ in these MAPbI$_3$ films.

1. Introduction

In recent years, hybrid metal halide perovskites gained significant attention in the solar cell community because of a remarkable power conversion efficiency in this material system of more than 20%.[1] Despite the rapid increase in efficiency, the exact origin for the extraordinary photovoltaic properties are still under debate. It is postulated that these are strongly correlated with anomalous MAPbI$_3$ carrier transport properties. Diffusion lengths in disordered MAPbI$_3$ films exceed 1 micrometer but mobilities are very modest, giving bimolecular recombination rates as small as in well studied single-crystalline inorganic semiconductors such as GaAs or Si:H and 5 orders lower than the mobility limited Langevin recombination model.[2] Some authors claim, that charge carriers in MAPbI$_3$ are screened by large polarons which prohibit carrier recombination and are the reason for the long carrier lifetimes observed in MAPbI$_3$.[3] Other arguments for the lifetime are based on the extraordinary defect tolerance due to the unique band structure of this material; both the conduction band and the valence band are formed from antibonding mixed Pb-I orbitals with strong ionic character, and within the band gap only shallow (benign) defects are formed.[4] Up to now, there are wide spread inconsistencies in the estimation of transport properties such as carrier mobility and diffusion constants in hybrid perovskites. Reported mobility values in MAPbI$_3$ films vary from 0.6 cm$^2$(Vs)$^{-1}$ to 80 cm$^2$(Vs)$^{-1}$ depending on the both sample preparation method and the measurement technique. [5,6]

In this study, we employ a contactless method to measure carrier transport in MAPbI$_3$ films, using transient absorption spectroscopy; this way enabled us to estimate intrinsic carrier diffusion constants by using a charge extraction layer.
2. Experimental setup
The sample structure is shown in the inset of the Figure 1a). First, PEDOT:PSS (Clevios 4083, Heraeus) was spin coated onto an ITO covered quartz glass slide. Next, a solution containing PbI$_2$ (Sigma-Aldrich) and MAI (prepared according to literature)[7] in a molar ratio of 1 : 1 was prepared and 18 mg/ml of the additive NH$_4$Cl were added. For the thick sample, a concentration of 310 mg/ml in DMF was used, while for the thinner one it was reduced to 80 mg/ml. Films were spin coated inside a nitrogen filled glovebox at 6000 rpm for 50 s and then heated at 110°C for 30 s. Small amounts of toluene were dropped around the spin-coater to create a solvent atmosphere.

Time resolved absorption as well as linear absorption experiments were performed under ambient pressure at room temperature. The time resolved absorption measurements were done using a 150 kHz Yb:KGW laser system with 80 fs resolution. Photoexcitation with the energy of 1.77 eV was used in order to create photo carriers above the band gap. Care was taken to keep the charge carrier density the same in both samples at a value of $2 \cdot 10^{18}$ cm$^{-3}$. This is important to exclude carrier density dependent recombination mechanisms, which would result in different decay times. For carrier density calculations, the carrier concentration was integrated over the sample thickness, while using the Beer-Lamberts law to estimate the excitation depth profile.

3. Experimental results and discussion
The linear absorption Tauc plots of both samples is shown in the Figure 1a), yielding onset for the direct band gap of 1.60 eV and 1.62 eV for the thicker and thinner MAPbI$_3$ film, respectively; the extracted absorption coefficient of both MAPbI$_3$ layers at the 1.75 eV is $2.5 \cdot 10^4$ cm$^{-1}$, which is in good agreement with literature values for spin coated MAPbI$_3$.[8]

![Figure 1](image.png)

Figure 1 a) Linear absorption Tauc plot of 170 nm and 40 nm thick MAPbI$_3$ layers, together with the transient absorption spectrum taken 30 ps after the 1.77 eV excitation, b) energy diagram of the studied sample, c) modelled absorption spectra of both films using the simplified Elliot formula.

The absorption spectra near the band gap of both 40 nm and 170 nm samples showed a typical exciton offset in the band gap region. To determine its contribution, the absorption spectra were modelled using the simplified Elliot formula [9]:

$$\alpha(h\omega) = [A \cdot \theta(h\omega - E_g) \cdot D_{cv}(h\omega)] \cdot \left[ \frac{\pi x e^{\pi x}}{\sinh(\pi x)} \right] + A \cdot R_{ex} \sum_{n=1}^{\infty} \frac{4\pi}{n^2} \cdot \delta \left( h\omega - E_g + \frac{R_{ex}}{n^2} \right)$$ (1)

where $R_{ex}$ is the exciton binding energy, $E_g$ the band gap, $\theta$ a step function, and $D_{cv}$ the density of states of two parabolic bands, $x = \frac{\omega}{\sqrt{(h\omega - E_g)^2}}$. Convolution with a Gaussian distribution function was applied for incorporating inhomogeneous broadening effects.
Results of this model are shown in a Figure 1c) yielding estimates for the exciton binding energy of \( R_{\text{ex}} = 19 \pm 3 \text{ meV} \) and \( 18 \pm 3 \text{ meV} \) for the two films. The observed slight differences in broadening effects (FWHM of 35 and 50 meV) can be attributed to the different disorder in MAPbI\(_3\) films.

Transient absorption (TA) experiments were carried out using above the band gap excitation at 1.77 eV. A typical TA spectrum is shown in Figure 1a); after the excitation, electrons and holes occupy the bottom of the conduction and top of the valence band, resulting in a transient population with a new quasi Fermi levels. This leads to a diminished number of available states for an optical transition resulting in a strong transient absorption peak in the region close to the band gap. The amplitude of state filling peak, assuming a rigid band picture and Pauli blocking only, is directly proportional to the number of photogenerated carriers. This is valid at delay times \( > 5 \text{ ps} \), because most of electrons and holes have equilibrated and populate the conduction band minima and valence band maxima. By monitoring the amplitude of a state filling one can get insights into the excited carrier dynamics in the material.

In this study a thin layer of PEDOT:PSS was implemented to extract holes from the MAPbI\(_3\) film. The corresponding energy diagram is shown in Figure 1b).

The decay dynamics of both films are shown in the Figure 2a). The data was fitted using a single exponential decay model with a non-decaying component \( \mathcal{C} \), \( A \cdot e^{-t/\tau} + \mathcal{C} \) and convolved with a Gaussian instrument response function. For both samples the amplitude of \( A \) and \( \mathcal{C} \) are almost equal, which supports the carrier decay mechanism we describe below. Here we assume that the carrier decay mechanism is dominated by a hole transfer from MAPbI\(_3\) to PEDOT:PSS while electrons remain in the film and contribute to the non-decaying component \( \mathcal{C} \). This indicates that only half of the carriers decay, which is consistent with the result of \( A = \mathcal{C} \), where \( A \) is proportional to the number of holes and \( \mathcal{C} \) to electrons. Interestingly, we find one order of magnitude difference in the carrier lifetimes in two films, \( \tau = 0.30 \text{ ns} \) for 40 nm and \( \tau = 3.5 \text{ ns} \) for 170 nm, even though they are prepared from the same material. Since carrier density was kept identical in both cases, the recombination time differences must originate from differences in carrier drift time, resulting from the differences in layer thickness.

To confirm this story, we numerically solved a 1D diffusion equation \( \partial n(x, t)/\partial t = D \partial^2 n(x, t)/\partial x^2 \) by varying the diffusion constant. The Beer-Lambert law \( \exp(-L \cdot \alpha) \) carrier distribution was chosen as the initial condition. The absorption coefficient \( \alpha \) was extracted from linear absorption measurements and \( L \) corresponds to the sample thickness. In the applied model, one boundary (the surface) is assumed fully reflecting \( \partial n/\partial x = 0 \) and the other (PEDOT:PSS) fully absorbing, \( n = 0 \).
Results of the numerical simulation for both samples are shown in the Figure 2b). The carrier concentration at each time step was calculated by integrating over all carriers in the modelled film. The time dependent carrier concentration was then fitted with an exponential decay function. The best match with experimental decay values was found using diffusion constants of 0.025 cm²s⁻¹ and 0.030 cm²s⁻¹ for the 40 nm and 170 nm thick films, with estimated errors of ±0.003 cm²s⁻¹. From these results we are able to extract the hole mobility \( \mu \) through the Einstein relation: \( \mu = D_e/k_BT \), where \( e \) is the electron charge \( 1.6 \times 10^{-19} \) C and \( k_B = 1.3801 \times 10^{-23} \text{m}^2\text{kg}^{-2}\text{K}^{-1} \). Using this equation, a hole mobility of 1 cm²(Vs)⁻¹ was estimated which again is in good agreement with mobility values, estimated from optical measurements such as photoluminescence decay.[10]

4. Conclusions
In this study, we have shown a simple way to extract the intrinsic carrier diffusion constants and mobilities using transient absorption experiment, combined with a simple 1D carrier diffusion model. By employing a hole extraction layer of PEDOT:PSS we were able to gain insight into the hole transport mechanisms through the excited carrier relaxation time. We found that a difference in MAPbI₃ film thickness does not affect the carrier transport properties significantly, meaning that the film quality remains the same. We estimated the hole diffusion constant of 0.025 cm²s⁻¹ for the 40 nm and 0.030 cm²s⁻¹ for the 170 nm thick MAPbI₃ film. Using diffusion constant values and the Einstein–Smoluchowski relation, resulted in an estimation for the hole mobility of 1 cm²(Vs)⁻¹.

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