Recombination in Perovskite Solar Cells

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Abstract

Metal-halide perovskites have recently started to become a major topic in photovoltaics because of their high efficiency and ease of preparation. One of the main ingredients for their high efficiency seems to be their peculiar defect physics and extremely long charge carrier lifetimes that are often probed by techniques such as transient photoluminescence. Here we discuss typical experimental transient photoluminescence data on $CH_3NH_3PbI_3$ thin films and discuss the impact of different physical processes on the shape of these transients. We develop a model to describe the transients that includes a redistribution of charge carriers at early timescales, recombination in the bulk of the material by radiative and non-radiative (Shockley-Read-Hall) recombination and diffusion to the surface of the device followed by surface recombination. We conclude that recombination at early timescales and high laser intensities is due to radiative recombination and possibly even Auger recombination, the recombination at long timescales is due to non-radiative recombination either in the bulk or at the surface. Based on the thickness of the films and the estimated minimum mobilities, we can provide upper limits for the surface recombination velocity of the perovskite glass and perovskite – N_2 interfaces to be on the order of 10 cm/s, i.e. an extremely low value for not intentionally passivated surfaces.

Introduction

Transient photoluminescence (trPL) is a suitable method to study the recombination dynamics of metal halide perovskites due to their high luminescence yield and (for photovoltaic materials) high band gap of around 1.6 eV for the most frequently studied compound $CH_3NH_3PbI_3$. These two aspects make luminescence decays of $CH_3NH_3PbI_3$ thin films comparably easy to detect e.g. with gated Si detectors. TrPL decays have therefore been frequently reported in the literature on perovskites but relatively little work has been dedicated to a sound theoretical treatment and analysis of the decays.[1]

In this contribution, we will therefore attempt to fill this gap by taking into account the different mechanisms affecting the PL intensity at different times during the transient and try to establish models that are suitable to describe the effects and better interpret the data.

Results and Discussion

For the trPL experiment, samples are grown on glass substrates and were measured in a cuvette filled with nitrogen in order to exclude effects of oxygen or water. Thus, the samples have two surfaces – one to glass, one to N_2 – neither of which are intentionally passivated. However, the samples were annealed in air, which may have a positive effect on the surface passivation. So the initial expectation would be that these surfaces are active recombination centers. The typical thickness of the films is about 300 nm.

After photoexcitation of the sample with a pulse dye laser at 496 nm, the decays are recorded with a gated iCCD camera (iStar DH720 from Andor Solis) that is attached to a Spex 270m monochromator (Horiba Jobin Yvon), i.e. the trPL decays are obtained spectrally resolved. However, the spectrum doesn't change as a function of time and therefore only the time response and the dependence on the pulse energy are taken into account in the model.

The doping level of perovskite thin films is currently not well understood. There are some reports that conclude that both n-type and p-type doping are possible and others that show that at least in $CH_3NH_3PbI_3$ the doping density should be negligibly low. Our results can be explained well without doping, therefore we restrict ourselves in the following to the case of high level injection, i. e. we assume that the concentration of photogenerated charge carriers exceeds the concentration of free charge carriers due to doping.

The photoexcitation will result in a nonhomogenous distribution of charges due to Lambert-Beers law. At early times, the charge carrier distribution will redistribute itself and become more homogenous.[2,3] For the case of high level injection, $\Delta n = \Delta p$ and $\phi_{PL} \propto \Delta n^2$. Thus, at early time scales, the luminescence emission from the surface of the film that faces the laser should be rather strong and decay quickly during this redistribution process. While the redistribution process will keep the average Δn and Δp the same, the average Δn^2 will be reduced. Based on a simple model of charge redistribution,[2,3] one can estimate at what times the redistribution should be completed based on values for mobility and device thickness. Figure 1 shows the simulated initial decay for different values of the mobility. We conclude that for typical reported mobilities, the redistribution happens at sub ns timescales that cannot be resolved in our setup but that might be accessible with other setups with higher time resolution.

After the redistribution has happened, bulk and surface recombination can happen. Surface recombination and Shockley-Read-Hall (SRH) recombination should be linear with light intensity while radiative or Auger recombination should be non-linear for the case of high level injection. Figure 2 shows normalized injection level dependent decay curves measured on our samples. The shape of the transients clearly depends on the laser intensity, therefore giving evidence for non-linear recombination mechanisms. We model the decays using the rate equation

$$\frac{\partial}{\partial t}\boldsymbol{\Delta n} = -\boldsymbol{k}\cdot\boldsymbol{\Delta n}^2 - \frac{\boldsymbol{\Delta n}}{\boldsymbol{\tau_{SRH}}} - \boldsymbol{C}\cdot\boldsymbol{\Delta n}^3. \qquad (1)$$

The lines in Fig. 2 show the quality of the fits of Eq. (1) to the data. The evidence for Auger recombination is however relatively weak, while it is clear that at least linear (SRH) and quadratic terms (radiative) must contribute to the shape of the decays. The linear (SRH) decay dominates at long times and has a lifetime of approximately 1 µs. This lifetime can be interpreted in two different ways. Either as a bulk recombination rate via deep defects. In this case, the lifetime resulting from the fit would be about 1.1 µs. Alternatively, the long part of the decay can be interpreted as a diffusion process of charges to the surface followed by recombination at the interface between perovskite and the glass substrate or the N_2 atmosphere in the cuvette. If this process dominates, the lifetime τ_{SRH} in Eq. (1) would have to be interpreted as[4]

$$\boldsymbol{\tau_{SRH}} \cong \frac{\boldsymbol{d}}{\boldsymbol{2S}} + \frac{\boldsymbol{1}}{\boldsymbol{D}}\left(\frac{\boldsymbol{d}}{\boldsymbol{\pi}}\right)^{\boldsymbol{2}}. \qquad (2)$$

Here *d* is the film thickness (ca. 300nm), *D* is the diffusion constant and *S* is the surface recombination velocity. If we follow this interpretation, the second term in Eq. (2) will be negligible due to the high mobility and low thickness combination present here. Thus the *d*/(2*S*) term will dominate and yield an extremely low value for S of about 10 cm/s. Thus, the perovskite surfaces seem to self-passivate themselves. However, a currently still open question is how to access the surface recombination velocity of the relevant interfaces in a device (i.e. TiO_2-perovskite or perovskite—PCBM, etc.) and evaluate their impact on V_{oc}.

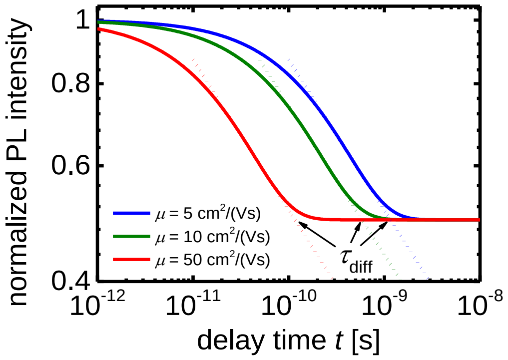

Figure 1: Expected initial decay due to redistribution of the charge carrier profile in samples under high-level injection for different mobilities (layer thickness *d* = 311 nm).

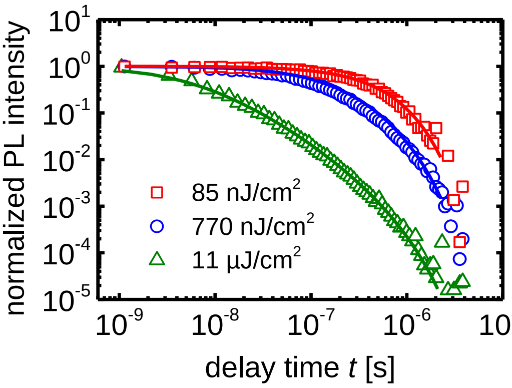

Figure 2: Measured PL decays normalized to the value at early times for different pulse energies. Experimental data (symbols) is compared to fits to the model given by the solution to Eq. (1).

References

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