Recombination effects in perovskite solar cells

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***Abstract*— Schockley-Read-Hall recombination model was used to describe the performance of organic photovoltaics. J-V curves under illumination and in the dark were successfully reproduced using this model. Effects of electron and hole trap density on simulated performance were also investigated and it was found that electron traps play a dominant role in limiting the achieved efficiency.**

I. Introduction

Recently hybrid organic-inorganic lead halide perovskites have emerged as new generation of thin-film photovoltaic cells with great promise, exhibiting not only efficiency over 22% but also lower fabrication cost [1]. Although there is large efficiency improvement within these few years, understanding of crucial mechanism which can describe the generation, diffusion and recombination of carriers inside perovskite solar cell is just only emerging. The charge-carrier recombination via different processes can be generally described through the equation

$$\frac{dn}{dt} = G - k_1 n - k_2 n^2 - k_3 n^3 \quad (1)$$

where G is generation rate of charge density, k_1, k_2 and k_3 are monomolecular, bimolecular and Auger recombination rate constants respectively. These rate constants, extracted from photoconductivity transients recorded for several commonly used perovskite including $MAPbI_3$ [2], showed that k_1 (s^{-1}) is significant. Monomolecular charge-carrier recombination is related to process involving free and trapped carriers, which depends on trap-assisted recombination. Trap-assisted recombination was also shown to be dominant mechanism in perovskite solar cells [3]. In organic photovoltaic cells (OPVs), the Shockley-Read-Hall (SRH) recombination model has been used. It has been shown that SRH model can describe the behaviors of an OPV device, including both steady state and transient behavior which is far away from equilibrium [4]. In SRH model, the free-to-trapped carrier recombination was described. Thus, this SRH model was applied and evaluated on perovskite solar cell with simulated data obtained in this work using software general-purpose photovoltaic device model (gpvdm).

In the model, finite-difference drift-diffusion model is used to account for both SRH recombination and free carrier transport in the perovskite layer. Carrier transport can be obtained in 1D transport model through solving the Poisson's equation for internal potential distribution, bipolar drift-diffusion equations and carrier continuity equations for current flux from top to bottom electrode [4]. On the other hand, SRH model of trapping, de-trapping and recombination of carriers can be described through equation for electron density for a certain trap level

$$\frac{dn_t}{dt} = r_{ec} - r_{hc} - r_{ee} + r_{he} \quad (2)$$

where r is rate of carriers (first subscript letter e/h for electrons or holes) being captured or escaped (second subscript letter c/e for capture and escape) from or to free carrier population [4].

To obtain experimental data, perovskite solar cell device was fabricated with conventional structure with fluorine doped tin oxide (FTO)/TiO_2/$MAPbI_3$/Spiro-OMeTAD/MoO_3/Al. $MAPbI_3$ was prepared through 1 step solution-processed spin-coating. The device achieves reasonable performance with short circuit current density (J_{sc}) of 21.9 mA cm^{-2}, open circuit voltage (V_{oc}) of 1.03V, fill factor (FF) of 0.70 resulting in power conversion efficiency of 15.8%.

II. Results and Discussion

The J-V curves under light and dark conditions were fit to the model. Parameters that are free to change are listed in Table I while parameters that are kept constant are in Table II. From using the fit parameters from Table II, J-V curves under light and dark conditions can be fit to the model. This is an indication that the SRH model incorporated can correctly describe the recombination in perovskite devices. From the results of the fitting, it can be noted that both open circuit voltage and fill factor can be reproduced under simulated solar illumination of 1 sun. Figure 1 shows the fitting of simulated results for both dark and light J-V curve.

TABLE I. Parameters for Fitting Experimental Data

Description	Value
Left contact electron density	1 x 10^{26} m^{-3}
Right contact hole density	1 x 10^{26} m^{-3}
Effective electron trap density	8 x 10^{23} m^{-3}eV^{-1}
Effective hole trap density	2 x 10^{22} m^{-3}eV^{-1}
Slope of electron exponential tail	20 meV
Slope of hole exponential tail	20 meV
Effective free electron denisity of states	9 x 10^{23} m^{-3}
Effective free hole denisity of states	5 x 10^{22} m^{-3}
Free electron mobility	1.5 x 10^{-3} m^{2}V^{-1}s^{-1}
Free hole mobility	1.5 x 10^{-3} m^{2}V^{-1}s^{-1}
Free electron to Trapped electron	5 x 10^{-19} m^{-2}
Trapped electron to Free hole	1 x 10^{-13} m^{-2}
Trapped hole to Free electron	5 x 10^{-19} m^{-2}
Free hole to Trapped hole	5 x 10^{-20} m^{-2}

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TABLE II. CONSTANT MODEL PARAMETERS

Description	Value	Source
Perovskite thickness	300 nm	Measured using SEM
LUMO mobility edge	-3.90 eV	[5]
HOMO mobility edge	-5.45 eV	[5]
Shunt Resistance	$3.7 \times 10^4\,\Omega$	Obtained from dark J-V curve
Contact Resistance	50.7 Ω	Obtained from light J-V curve
Permittivity of perovskite	6.5	[6]

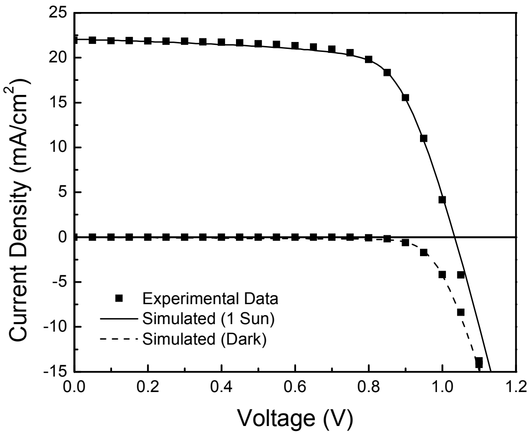

Fig. 1. Simulated J-V curve under 1 sun illumination and in the dark compared with experimental data obtained.

After successfully fitting the perovskite light and dark J-V curves, effects of effective carrier trap density on devices performance was simulated. As shown in Figure 2, the performance of devices will drop with increasing effective electron trap density. All the device parameters J_{sc}, V_{oc} and FF decrease with increasing electron trap density, which leads to rapid drop in performance.

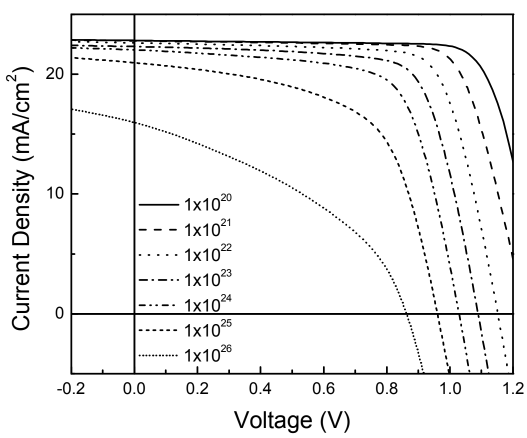

Fig. 2. Simulated J-V curves for different effective electron trap densities.

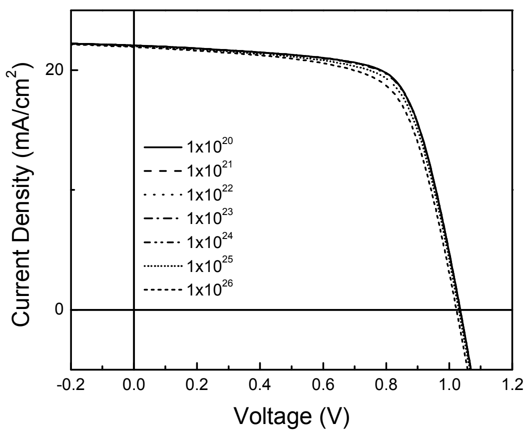

Fig. 3. Simulated J-V curves for different effective hole trap densities.

On the other hand, the variation of hole trap density in the same range as electron trap density will not have significant effect on the performance of perovskite solar cell as shown in Figure 3. Fill factor only drops slightly when hole trap density was set to 1×10^{26} $m^{-3}eV^{-1}$. This is in agreement with the report that electron traps should be the factor responsible for dominant trap-assisted recombination observed in perovskite solar cells, that is confirmed though measurements of hole-only and electron-only devices [3]. Thus the power conversion efficiency should be improved with the reduction in electron trap density or minimization of the non-radiative recombination in perovskite solar cells.

III. CONCLUSION

In this work, experimental results including J-V curves under light and dark condition were successfully fit to the model. This model incorporates trapping, de-trapping and recombination of charges which can provide a good simulation of the performance on $MAPbI_3$ perovskite solar cell. Electron trap density significantly affected the device performance, where the J-V curves exhibited negligible changes with varying hole trap density over a wide range. This indicated that the electron traps are the dominant traps responsible for the trap-assisted recombination.

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