Solar Energy Materials and Solar Cells 180 (2018) 76–82

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Classical modelling of grain size and boundary effects in polycrystalline perovskite solar cells

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ARTICLE INFO

Keywords:
Perovskite solar cell
Polycrystalline solar cells
Matthiessen rule
Grain size
Grain boundary
Drude-Smith model

ABSTRACT

A theoretical approach based on the Matthiessen rule for scattering lifetime is presented to formulate the effective characteristics of polycrystalline solar cells. Application of this method to Perovskite solar cells obtains polycrystalline bulk defect density for diverse grain sizes along with the determination of surface recombination velocity at grain boundaries. Unlike previous works on Silicon based solar cells that use an independently weighted average equation for extracting mobility, we introduce a variation of Drude-Smith model for calculating the mobility from carrier lifetime and defect density. In agreement with the experiments, introduced method reveals sub-picosecond background scattering times associated with phonon-lattice vibrations. Obtained carrier diffusion length spans over multi-micron to multi-millimeter scale for grain sizes ranging from 100 nm to 1 mm. Calculated monomolecular recombination lifetimes explains elevated Photoluminescence Yield and peak position in larger grain sizes. Presented method is verified by feeding extracted parameters into Drift-Diffusion equations and fitting with reported experimental photovoltaic conversion efficiency data. Finally, through employing a Gaussian distribution for grain sizes, we also study the reduction of device efficiency caused by non-uniform grain size distribution as a more realistic case.

1. Introduction

Perovskites constitute a new class of organic-inorganic materials which has actively contributed in the recent breakthrough of solar cell research. Since their first introduction in 2009 as a dye sensitizer [1], they have shown rapid development and giant boost in their Photovoltaic Conversion Efficiency (PCE) above 22% [2,3]. Shallow and benign defect states, ambipolar conductivity, long carrier diffusion lengths, high optical absorption and scalable fabrication methods that are independent of elaborate facilities put them among the major candidates to replace first generation Si solar cells [4–6].

Among efforts to improve their efficiency, less troublesome fabrication of larger grains through inexpensive solution or vapour based depositions is also in the focal point of growing research in this field. It is well-established that larger grains posses less boundaries and therefore result in a reduced defect density. Since carrier recombination lifetime in perovskites is mainly limited by the Shockley-Read-Hall (SRH) monomolecular recombination, this reduction leads to improved values for the carrier mobility as well. Consequently, decreased rate of monomolecular to bimolecular recombination in samples with larger grains shows enhanced Photoluminescence (PL) emission [7,8]. Additionally, red-shifted band gap associated with altered lattice strain and bond stress in larger grains further assists photon absorption and carrier generation [9]. Grain boundaries in Perovskite Solar Cells (PSCs) act as ion migration routes and thus scaling down these boundaries can modify the undesired hysteresis as one of the most important challenges in these materials. Likewise, reduced boundaries are favoured because ion redistribution and moisture penetration through these routes lower the device durability and functionality [10,11]. There are various methods to obtain larger grain sizes in PSCs such as altered or non-stoichiometric precursor concentration [12,9,13], additive components [11], solvent annealing [14], high pressure [15] and hot casting [16]. Unlike first and second generations of solar cells, fabrication of larger grains in PSCs has higher conceivability and thus requires detailed consideration. However, despite enormous and fast growing experimental efforts toward PSCs with lowered grains boundaries, there are insufficient theoretical studies assisting these investigations. Variation in grain size generally affects the defect density, carrier mobility, capture cross section, band gap and PL emission [17]. Existing theoretical studies on polycrystalline Silicon

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https://doi.org/10.1016/j.solmat.2018.02.026
Received 11 December 2017; Received in revised form 13 February 2018; Accepted 16 February 2018

or organic materials mostly benefit from a derivation of Matthiessen rule for effective mobility which is also known as weighted average method [18,19] and employ an empirical relation for defect density [20]. Others that use Matthiessen rule for scattering time and derive a relation for defect density are unable to account for mobility [21,22]. Simultaneous application of Matthiessen rule for both scattering time and mobility would result in too many fitting parameters, far away from an analytical investigation.

In what follows, we present an analytical method for modelling the grain size effects in PSCs. Starting from Matthiessen rule for scattering lifetime, we arrive at a simple relation for variation of defect density. Then the influence of altered defect density on the monomolecular and PL emission is discussed and the dependency of PL yield and its emission peak on grain size are investigated as well. Next, through examination of the Drude model and showing its limitations, we employ a variation of Drude-Smith model with a reduced decay time to extract mobility from scattering time. After determination of the carrier scattering time and mobility, carrier diffusion length is elucidated for diverse grain sizes. There is also a simulation section where the introduced model is verified by feeding obtained characteristic parameters into Drift-Diffusion equations and calculated PCEs are compared with the existing experimental data. Finally, by employing a Gaussian distribution for the grain sizes, we address the behaviour of a more realistic case in PSC fabrication.

2. The model

The presented model is based on Matthiessen rule for the effective decay rate of carrier lifetime in polycrystalline semiconductors as [23]:

$$\frac{1}{\tau_{poly}} = \frac{1}{\tau_{mono}} + \frac{1}{\tau_{gb}} \tag{1}$$

where τ_{poly}, τ_{mono} and τ_{gb} represent SRH defect assisted recombination lifetime in polycrystalline, single crystalline and on grain boundaries, respectively.

2.1. Defect density

Despite the existence of higher orders of recombination pathways in PSCs, dominant reduction in carrier density occurs due to the SRH defect assisted monomolecular recombination [24]. Lower density of carriers as well as semi-constant value of higher orders in diverse grain sizes allow us to consider Eq. (1) only for defect densities [25]. However, other decay processes will be included as we expand the model in the following sections. Decay rates are related to defect density (N), capture cross section (σ) and thermal velocity of carriers (V_{th}) via [26]:

$$\begin{aligned} \tau_{poly(mono)} &= \frac{1}{\sigma_{poly(mono)}\ V_{th}\ N_{poly(mono)}} \\ \tau_{gb} &= \frac{l_g}{S_{gb}} = \frac{l_g}{\sigma_{mono}\ V_{th}\ N_{gb}} \end{aligned} \tag{2}$$

Denoting grain size with l_g, surface recombination velocity and defect density on grain boundaries are included as S_{gb} and N_{gb}, respectively. Implementation of Eq. (2) in Eq. (1) gives:

$$N_{poly} = \frac{\sigma_{mono}}{\sigma_{poly}} \left(N_{mono} + \frac{N_{gb}}{l_g} \right) \tag{3}$$

Capture cross section ratio ($\sigma_{mono}/\sigma_{poly}$) is obtained by the relation for Schottky barrier as [26,22]:

$$\sigma_{poly} = \sigma_{mono}\ e^{-\Delta E/k_B T} \tag{4}$$

Where, k_B refers to Boltzmann constant, T to temperature and ΔE depicts the variation of defect state (trap) energy regarding the Fermi level. Eq. (3) is the general form for what has been used to calculate the effective defect density in polycrystalline semiconductors without $\sigma_{mono}/\sigma_{poly}$ term [22]. However, due to the reportedly confirmed red-shifted band gap around 0.1 eV between single and polycrystalline PSCs [17], this ratio shall not be neglected in equations.

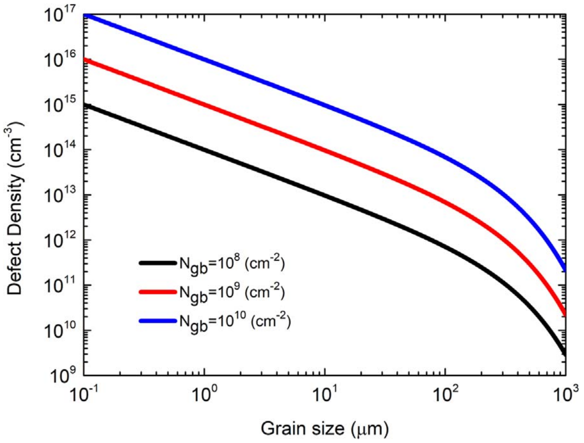

Fig. 1. defect density (N_{poly}) versus grain size (l_g) with different values for grain boundary defect densities (N_{gb}).

Since traps in PCSs are described approximately 170 meV above the Valance Band (VB), in agreement with previous studies, it is possible to employ the red-shifted value of the band gap as $\Delta E = 100\ meV$ [27,28]. This leads to one order increase in the capture cross section of polycrystalline PSC compared to that of monocrystalline. N_{mono} for single crystalline perovskite is set to $3.6 \times 10^{10}\ cm^{-3}$ as reported by Dong et al. [7] and confirmed by Liu et al. [8]. Through Eq. (3) a plot of defect density versus grain size is depicted in Fig. 1. Regrading the reported values for single and polycrystalline PSCs [8,7,27], interface defect density on grain boundaries (N_{gb}) is gauged around $10^9\ cm^{-2}$.

2.2. PL quantum yield

Other than the monomolecular recombination rate ($k_1 = 1/\tau_{poly}$), total scattering lifetime in PSCs for moderate carrier densities (n) is also depends on the bimolecular (k_2) and Auger (k_3) rates as well [29]:

$$\frac{1}{\tau_{total}} = k_1 + nk_2 + n^2 k_3 \tag{5}$$

In comparison to the monomolecular recombination rate that arises from SRH defect assisted trapping of the carriers, bimolecular decay takes place as a result of electron-hole wave function overlap, and Auger pathway stands for the energy and momentum transfer to the other carriers. Due to the lower carrier concentration in PSCs under the standard illumination, probability of first order recombination rate (k_1) is much higher than k_2 and k_3. Considering the fact that k_2 and k_3 are intrinsic property of the material, they are slightly changed in different grain sizes. Hence, we employ constant values for bimolecular and Auger recombination rates as $k_2 = 1 \times 10^{-10}\ cm^3/s$ and $k_3 = 1 \times 10^{-28}\ cm^6/s$ [25]. Bimolecular recombination pathway is also called radiative decay rate and PL quantum yield (Φ) is defined as its ratio to the total recombination rates [29]:

$$\Phi = \frac{nk_2}{k_1 + nk_2 + n^2 k_3} \tag{6}$$

PL quantum yield reaches its peak value when carrier density n equals $\sqrt{k_1/k_3}$. For carrier densities below 10^{16} monomolecular defect assisted SRH recombination eclipses other pathways, where Auger loss dominates for carrier densities above 10^{19}. Between these two regimes the bimolecular rate has the dominant role. Knowing grain size dependency of k_1 by Eq. (3), PL quantum yield is drawn based on grain size variation in Fig. 2. Obviously, reduction of trap assisted recombination in PSCs with larger grains leads to a higher probability of radiative