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Comparison of recombination models in organic bulk heterojunction solar cells

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ABSTRACT

Recombination in bulk-heterojunction (BHJ) organic solar cells is the key loss mechanism, and it directly affects characteristic parameters such as power conversion efficiency, short-circuit current, open-circuit voltage, and fill factor. However, which recombination mechanism dominates the loss in organic materials is unclear at present. In this work, we simulate state-of-art BHJ solar cells using five recombination models, including direct recombination, Langevin recombination, charge transfer state recombination, trap-assisted recombination, and recombination via tail. All processes are strongly dependent on charge carrier mobility and exhibit a similar recombination distribution in active layer. For high mobilities, all models present a similar behavior along with the increased mobilities, whereas, there are slight differences in open-circuit voltage between trap/tail model and other ones at lower mobilities, resulting from the interaction between photo-carriers and dark-carriers.

1. Introduction

Because of the low-cost fabrication of large area and the possibility to use flexible substrates, researches on organic solar cells have been increasing rapidly in recent years, and the device efficiencies have increased from 3% to close to 10% [1]. BHJ organic solar cells have attracted much attention due to their technological application [2,3]. Such a structure helps to study which operating mechanism governs solar cell's overall performance, and establishes the achievable values for short-circuit current J_{sc}, open-circuit voltage V_{oc}, and fill factor FF.

The power conversion efficiency (PCE–η) of a solar cell is given by the well-known relation $\eta = J_{sc}V_{oc}\,FF/P_{in}$, where P_{in} is the incident solar power. In order to improve PCE of BHJ organic solar cells, it is important to know the loss mechanisms to determine limits of PCE. PCE is dominated by three main loss factors, i.e. non-radiative recombination along the distributed heterointerfaces, inefficient collection of photogenerated excitons, and parasitic absorption of the contact layers [4]. Recombination has been recognized as the key loss mechanism in organic solar cells and causes a reduction in J_{sc} and FF and a corresponding loss of PCE [5,6].

Several recombination mechanisms have been proposed and implemented in numerical models for BHJ cells [7–10] the charge transfer (CT) state model developed by Koster et al. [11] has been widely used and shown good match between simulations and experimental data of BHJ cells under illumination. However, in dark current–voltage characteristics, many models fail to reproduce the diode ideality factor (n_{id}), as the limitation of considering direct band recombination [12]. Kirchartz et al. [13] proposed to consider trapping and recombination via exponential tails in valence and conduction band, which can well reproduce the ideality factor of dark characteristics.

However, which recombination mechanism dominates the loss in organic materials is an open question, and the possibility that the recombination is codetermined by several mechanisms has been proposed [14–16]. We notice that these works on different models mainly aim at different physical properties of solar cells. In present work, we would systematically study influences of different models on physical properties of BHJ cells. Such work is helpful to judge which recombination mechanism is dominant in solar cells, and is fairly valuable.

In this paper, we focus on five recombination models popular in literature, i.e., direct recombination model (Constant), Langevin recombination model (Langevin), charge transfer state model (CT), trap-assisted model (Trap), and recombination via tail model (Tail). The experimental illuminated current–voltage curve of an OC_1C_{10}-PPV/PCBM device is fitted by Trap model and Tail model, and other physical properties are calculated with both the two models and other three models. We present a comparison of recombination rate distributions in active layer and exhibit the behaviors of PCE, J_{sc}, V_{oc}, and FF as a function of mobilities, which can be used as a reference to determine the recombination mechanism in BHJ solar cells.

2. Fundamental formula

Drift-diffusion modeling of organic solar cells has been demonstrated to be a powerful tool [11] to explain the influence

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of various effects on current–voltage characteristics (J–V curve). For a macroscopic simulation in steady state, the Poisson equation, the continuity and drift-diffusion equations for electrons and holes have to be solved,

$$-\frac{\partial^2\varphi(x)}{\partial x^2}=\frac{q}{\varepsilon}[p(x)-n(x)], \tag{1}$$

where $n(x)$ and $p(x)$ are the concentrations of free electron and holes, respectively, $\varphi(x)$ is the electrical potential, q is the elementary charge, and ε is the dielectric constant.

$$\frac{\partial J_n(x)}{\partial x}=qU(x) \tag{2a}$$

$$\frac{\partial J_p(x)}{\partial x}=-qU(x),, \tag{2b}$$

Eqs. (2a) and (2b) are the continuity equations for electrons and holes, respectively in steady state. $J_n(x)$ and $J_p(x)$ are the electron and hole current densities, respectively and $U(x)$ denotes the net generation rate, i.e., the difference between generation rate G and recombination rate R of free carriers, $U(x)=G(x,n,p)-R(x,n,p)$. G is a function of position and is mainly determined by absorption of sunlight, and weakly dependent on densities of carriers. So we take it as constant, as done by many authors [11–13,17]:

$$J_n(x)=-qn(x)\mu_n\frac{\partial\varphi(x)}{\partial x}+qD_n\frac{\partial n(x)}{\partial x}, \tag{3a}$$

$$J_p(x)=-qp(x)\mu_p\frac{\partial\varphi(x)}{\partial x}-qD_p\frac{\partial p(x)}{\partial x}, \tag{3b}$$

where $\mu_{n,p}$ are the electron and hole mobilities, and $D_{n,p}$ are the carrier diffusion coefficients. $D_{n,p}$ are assumed to obey the Einstein relationship $D_{n,p}=\mu_{n,p}V_t$, with thermal voltage $V_t=k_BT/q$, where k_B is Boltzmann's constant and T is absolute temperature. All the variables above are related to the spatial coordinate x normal to the surface; q, ε, $\mu_{n,p}$, and $D_{n,p}$ relate all the variables to each others.

In Ref. [11], Koster et al. have clarified that both contacts of BHJ cells are Ohmic, and the Ohmic nature is supported by space-charge limited current (SCLC) behavior [18,19] measured on two materials. Recently, Kirchartz et al. [20] studied influence of surface recombination on performance of BHJ cells. They [20] estimated the surface recombination velocity, $S=7\times10^5$ cm/s, a very large value, from Monte Carlo simulation results [21], and compared numerical results in two cases with surface recombination velocities $S\to0$ and $S\to\infty$, respectively. They pointed out that the Ohmic contact is equivalent to the infinite velocity $S\to\infty$, and the corresponding numerical results are in better agreement with relevant experimental data. Therefore, it is reasonable to adopt following boundary conditions corresponding to Ohmic contacts proposed by Koster et al. [11] in our simulations:

$$n(0)=N_c,n(L)=N_c\exp\left(-\frac{E_g}{k_BT}\right), \tag{4a}$$

$$p(L)=N_v,p(0)=N_v\exp\left(-\frac{E_g}{k_BT}\right) \tag{4b}$$

where Eqs. (4a) and (4b) are the boundary conditions for electron carriers density and hole carriers density, respectively. Here we assume that anode (hole contact) and cathode (electron contact) are located at $x=0$ and $x=L$, respectively. E_g is the energy difference between LUMO (the lowest unoccupied molecular orbital) of the acceptor and HOMO (the highest occupied molecular orbital) of the donor functions of the semiconductor, and $N_{c,v}$ are the effective density of states of conduction and valence band.

Neumann et al. [22] confirmed that the classical Einstein relation is valid for the organic semiconductors, and the classical Einstein relation supports nondegenerate Boltzmann statistics for density of carriers. Recently, Wetzelaer et al. [23] also verified experimentally the validity of the classical Einstein relation in organic semiconductors by studying the diffusion-driven currents of single-carrier diodes. So in terms of present references [22,23], the organic semiconductors can be treated as nondegenerate and Boltzmann statistics can be used. Correspondingly, the intrinsic charge carrier density n_i satisfies the formula $n_i=\sqrt{N_cN_v}\exp(-E_g/2V_t)$. The boundary condition for the electrical potential can be written as [11]

$$\varphi(d)-\varphi(0)=V_{bi}-V_a, \tag{4c}$$

V_{bi} is the built-in voltage and V_a is the applied voltage. With appropriate boundary conditions, the Poisson and continuity equations can be solved iteratively by a numerical scheme proposed by Gummel [24] as well as Scharfetter and Gummel [25].

3. Recombination models

3.1. Bimolecular recombination

Recombination takes place directly between free electrons and holes. It is governed by both charge carrier densities n and p, with the direct recombination constant γ and the intrinsic charge carrier density n_i:

$$R=\gamma(np-n_i^2), \tag{5}$$

Classic Langevin recombination describes the recombination prefactor γ as a function of μ; thus, the Langevin recombination prefactor is [26]

$$\gamma_L=\frac{q(\mu_n+\mu_p)}{\varepsilon}, \tag{6}$$

However, a recombination process described by Eq. (5) results in an ideality factor $n_{id}=1$, and cannot account for the typical ideality factors of organic solar cells $n_{id}>1$, which is deduced from experimental data [13].

3.2. Recombination via CT states

The so-called charge transfer (CT) state is introduced by Koster et al. [11]. This model is an extension of Langevin model. It is based on metal–insulator–metal (MIM) picture, where the active layer of BHJ is considered as an effective semiconductor that has properties of both donor and acceptor materials. The final expression of net generation rate is given by Koster et al. [11]

$$U=PG-(1-P)R_{CT}, \tag{7}$$

where R_{CT} is the Langevin recombination, $R_{CT}=\gamma_L(np-n_i^2)$ and P is the probability of electron–hole pair dissociation [11].

As the total time needed for both carriers to reach interface is dominated by the slower one, Koster et al. concluded that Langevin recombination prefactor in polymer/fullerene solar cells is not dominated by the fastest charge carrier but by the slowest one [27]. Thus, the sum of the mobilities is replaced by $\min(\mu_n,\mu_p)$.

3.3. Shockley–Read–Hall recombination and recombination via tail

The theory of recombination via a single-electron trap has been developed by Hall [28,29] and Shockley and Read [30]. The net recombination through a trap level is determined by the net result of two capture and two emission processes. Recombination through a localized state occurs if a state occupied by a hole