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Full paper

Kinetic Monte Carlo modeling on organic solar cells: Domain size, donor-acceptor ratio and thickness

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ABSTRACT

Organic solar cells have received a lot of attention in the last few decades. Extensive experimental work has been conducted to improve organic solar cell performance. However, a much more realistic and accurate model needs to be developed that can simulate and predict photovoltaic performance for organic solar cells. In this work, a Kinetic Monte Carlo (KMC) model was developed to simulate the morphological variation of organic solar cells and its effects on photovoltaic parameters. This model is currently based on P3HT: PCBM system and can be easily extended to any low bandgap polymer solar cells. The novelty and advancement of this work is that this new KMC simulation model can simulate three different parameters including domain size, donor-acceptor ratio and active layer thickness in the same model and predict the efficiency of organic solar cells on the variation of these parameters. This simulation model has been validated by photovoltaic performance from fabricated devices. The optimized parameters of simulation and fabrication are correlated and the simulation results are in agreement with the experimental results. With the assistance from this model, researchers may be able to simplify the complex fabrication processing by identifying optimal conditions such as domain size, donor-acceptor ratio and active layer thickness via this new simulation model.

1. Introduction

Organic solar cells which are made up of intermixed blend of polymer and fullerene materials showed great potential because of their light weight, flexibility and low manufacturing cost. Organic solar cells have achieved an efficiency over 12%. Simulation models including Simulink and COMSOL multiphysics are being developed in different fields such as electrical AC/DC, heat transfer, battery cell dynamics, chemical reactions and fluid mechanics which facilitate the research and development of new materials and ultimately save the cost and materials [1]. Modeling of organic solar cells can be a powerful tool to simulate different fabrication conditions and parameters, and ultimately simplify the fabrication processing and reduce material and fabrication cost. For the simulation of complex 3D morphology of organic solar cells, partial differential equations and closed form mathematical equations are really difficult. Therefore, the probabilistic and statistical approach using Monte Carlo (MC) simulation is utilized which use repeated random sampling to determine different properties of physical and chemical phenomena. KMC which can simulate the time evolution of processes is the most suited for the modeling of 3D donor/acceptor blend morphologies, charge transport mechanisms and recombination and generation of charge particles as real natural phenomena. The first report describing basic features of KMC was from Young et al. in 1996 which revealed vacancy migration in the binary ordered alloys: simple cubic and face centered structures [2]. KMC requires a lot of resources, memory, and simulation time which can be made possible through the high performance computing facility to implement on real devices.

Some work on MC Simulation was performed by Watkins et al. in 2005 on the morphology of organic solar cells [3]. They performed Dynamic MC modeling of 3D organic solar cells to study the dependence of internal quantum efficiency on device morphology. Another 2D analysis of organic solar cell morphology and its dependence on device are performed by Lei et al. in 2008 and it showed the trade-off between efficiency and chance of electron-hole recombination on different steps of phase separation while maximizing the interfacial areas [4]. However, 2D analysis alone cannot be supposed to give the actual and real world physics of 3D bulk heterojunction (BHJ) devices.

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Kimber et al. studied the 3D gyroid structure to obtain high efficiency conjugated polymer solar cells via MC simulation [5]. MC simulation on Forster resonance energy transfer in 3D nanoscale performed by Maqsood et al. in organic BHJ morphologies showed that exciton dissociation probability in evenly distributed 20 nm domain sized blend was higher than that in ordered and graded 20 nm domain blends [6]. Groves et al. used MC simulation to study geminate pair dissociation in polymer-polymer solar cells. They found that geminate separation was improved when domain size increased from 4 nm to 16 nm [7]. Yang et al. studied photovoltaic parameter of copper phthalocyanine (CuPc) and C_{60} using MC simulation methods [8]. However, all morphological parameters of BHJ are not addressed from these models. KMC simulation of dark and illuminated current-voltage (I-V) characteristics of 3D organic solar cells was done by Baidya et al. in 2013 and it showed that electron-hole recombination at the donor/acceptor interface was the origin of dark IV and shape of illuminated I-V curves [9]. Thus, the interfacial area between donor and acceptor plays an important role on current generation due to charge recombination. Khodakarimi et al. in 2016 [10] studied the effect of interfacial layer by adding a P3HT layer on the BHJ using MC simulation. In addition, the phase-field model is another flexible method for studying interfacial width between the domains of BHJ [11]. This approach used Cahn-Hilliard equations to solve the problem of morphology evolution such as surface wetting [12] and solvent evaporation [13]. Therefore, there is a need to develop a model to simulate more parameters that reflect photovoltaic parameters of organic solar cells. These parameters including domain size, active layer thickness, donor/acceptor ratio, addition of some additive materials, annealing conditions have been identified and optimized in fabrication experiments for achieving higher efficiency in different polymer solar cells. It has been basically found that domain size of active layer is changed by changing the annealing temperature, solvent drying conditions as well as the concentration of polymer-fullerene blend. Active layer thickness can be changed by changing the spin speed and donor/acceptor ratio is simply changed by changing the weight of donor and acceptor [14–21].

In this work, we developed a KMC model to simulate the morphological variation of organic solar cells and its effects on photovoltaic parameters such as open circuit voltage (Voc), short circuit current density (Jsc), fill factor (FF) and power conversion efficiency (PCE). This model is currently based on P3HT: PCBM system and can be easily extended to any low bandgap polymer solar cells. The novelty and advancement of this work is that this new simulation model can simulate three different parameters including domain size, donor-acceptor ratio and active layer thickness in the same model and predict the efficiency of organic solar cells on the variation of these parameters. The simulated results were validated by the photovoltaic performance from fabricated devices.

2. Modeling procedures

For simulation, a 3D BHJ device of certain dimension was created and divided into several cubes of 1 nm^3 volume each representing either donor or acceptor material (Red for donor and blue for acceptor as shown in Fig. 1). The 10 nm strip from each side of x - dimension was assigned as charge transport layers and the active layer was sandwiched between these two transport layers. Initially, the fixed number of donor and acceptor sites that makes certain volume ratios was randomly distributed throughout the volume of the device. The variation in the number of donor and acceptor sites was related to the donor-acceptor ratio by volume and could be ultimately converted to weight ratio.

The Monte Carlo Metropolis algorithm was implemented to the distribution of sites and phase separation of donor and acceptor at different steps of morphology evolution [22]. Fig. 1 shows different random steps of morphology evolution. Initially, the system had randomly distributed sites of donor and acceptor. The interfacial area and surface energy were very high at the beginning. Phase separation started and the blend formed separate clusters of donor and acceptor. Consequently, interfacial area decreased as morphology evolved from Fig. 1a to d because the system tended to minimize its surface energy by forming clusters of donor and acceptor separately as governed by metropolis algorithm.

The domain size of morphologies was calculated by considering the position of donor and acceptor in the (x, y, z) coordinates. Fig. 1a has a domain size of ~ 2 nm and Fig. 1b has a domain size ~ 5 nm. Similarly, the domain size of Fig. 1c and d can be approximated to be ~ 20 nm and 30 nm, respectively. The control of morphology evolution on Metropolis algorithm provided a method to engineer the domain size of active layer blend in this simulation. After the generation of morphology, neighbor sites within 3 nm of each site were tracked and assigned with exciton exponent radius and charge exponent radius that would be used later in the hopping rate calculations. The HOMO/LUMO energy levels were distributed in sites with Gaussian distribution [23] and band bending phenomenon was implemented by modifying HOMO/LUMO levels with the linear effect of built-in voltage [9]. The morphological parameters such as active layer thickness was altered by changing x-dimension of the device; donor/acceptor ratio was changed by varying the number of donor and acceptor sites in the volume of device; and domain size was changed by controlling morphology evolution generation algorithm.

Transport layers were made highly doped with free charge carrier densities of 10^{18} cm^{-3} so that it could attain ohmic contacts between the active layer and charge transport layer. The donor-acceptor sites were randomly distributed in the device with a density of 10^{-21} cm^{-3}. [9] The LUMO/HOMO levels of donor were assigned as −2.74 eV/−4.76 eV and those of acceptor was assigned as −3.91 eV/−5.93 eV [24]. The LUMO/HOMO levels were distributed to each site with the Gaussian distribution of standard deviation of 0.05 eV as described by Baessler et al. as follows.

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}}\exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right) \quad (1)$$

where N is density of sites within a given device geometry, ε is mean energy value (HOMO/LUMO levels), σ is the deviation from the mean energy level.

Hole transport layer and electron transport layer were assumed to be made up of same materials as donor and acceptor, respectively. Because of this, the work function of anode and cathode could be chosen close to the donor HOMO (−4.76 eV) and acceptor LUMO (−3.91 eV) so that the effective built-in voltage (V_{bi}) was 0.85 eV. If V_A is the applied voltage to the device, then the potential distribution inside the active layer of the device was designed to vary on x-direction linearly from 0 V to (V_{bi} -V_A) along the active layer in x-direction of the device [25]. There appeared a band bending within BHJ which was further described by Baidya et al. [9] The variation of potential energy with respect to x-axis is given by the following equation.

$$\Psi(x) = V_0 - \frac{V_0}{L}x \quad (2)$$

where $\Psi(x)$ is the potential energy, $V_0 = V_{bi} - V_A$, x is the distance considered from the starting point of active layer and L is the thickness of active layer.

The major physical processes addressed in the simulation model were exciton generation after photo-excitation, exciton hopping towards the interface of donor and acceptor clusters, exciton dissociation at the donor-acceptor interface, exciton recombination if the exciton does not reach the interface within its lifetime, hole hopping in donor material and electron hopping in acceptor material, charge recombination and charge injection or extraction from or to electrodes [26]. Exciton generation due to photon illumination is given by the following equation.