Effect of mixture ratio on the performance of MDMO-PPV:PCBM bulk heterojunction solar cells: A numerical study

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ABSTRACT

This paper presents a systematic numerical simulation of variation of blending ratio and cathode work function dependence of poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-para-phenylene vinylene) (MDMO-PPV):phenyl-C61-butyric acid methyl ester (PCBM) bulk heterojunction (BHJ) solar cells performance for MDMO-PPV concentration between 0 and 100 mol percentage and cathode work function interval 3.7–4.7 eV. From our studies it became evident that the open-circuit voltage (V_{oc}), short-circuit current (J_{sc}) and fill factor (FF) decrease with the increasing cathode work function. It is shown that J_{sc} increases almost linearly with the increasing MDMO-PPV concentration from 0 to 60 mol%, and then decreases. With the increasing of MDMO-PPV concentration, FF augments gradually to 76.56% and then plunges to 19.53%. It is also demonstrated that when MDMO-PPV is larger than 45 mol%, the enhancing MDMO-PPV mol percentage is detrimental for the device performance.

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1. Introduction

Polymer-based photovoltaic (PV) cells have attracted a great deal of attentions because of their potential use for realizing low-cost, solution-processable, large area and flexible solar cells [1–6]. Bulk heterojunction (BHJ) is a blend of the donor and acceptor components in a bulk volume which forms a nanoscale, bicontinuous, and interpenetrating network which excitons dissociate into electrons and holes at donor–acceptor interface and transport through to the electrodes, respectively. BHJ solar cells based on blends of poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-para-phenylene vinylene) (MDMO-PPV) and phenyl-C61-butyric acid methyl ester (PCBM) bulk heterojunction belong to the most promising candidates for this application. However, compared with traditional inorganic photovoltaic cells, the polymer-based devices are still limited in their performance because of the drawbacks such as the weak absorption in the visible long-wavelength, poor charge transport, and low stability [7–11]. Essential parameters which determine the power conversion efficiency of thin film photovoltaic devices are the short-circuit current (J_{sc}), the open-circuit voltage (V_{oc}), and the fill factor (FF). It has been shown that the J_{sc} is sensitive to the film morphology, solvent type, or deposition method [12,13]. Mihailetchi et al. [14] have demonstrated that V_{oc} is determined by the work function difference of electrodes in experiments for non-Ohmic contacts and Ohmic contacts.

Koster et al. [15] presented a metal–insulator–metal (MIM) model which quantitatively addresses the role of contacts, drift, and diffusion of charge carriers, charge carrier generation and recombination. Kemerink et al. [16] reported that optimal performance of photovoltaic cells generally requires the presence of Ohmic electron and hole contacts. However, an Ohmic electron contact is usually non-Ohmic for holes, and vice versa, different contacts for electrons and holes are used in most optimized devices, thus Schottky contacts are indispensable for many organic solar cells. Regarding the performance of organic solar cells, many experimental and theoretical investigations have been done, but the effect of mixture ratio is still unclear. In this article, we study the effect of mixture ratio on J_{sc}, V_{oc}, and FF of organic BHJ solar cells by using numerical methods.

2. Device model

The device is described by using the MIM picture. The model used in this article contains drift and diffusion of charge carriers, and the effect of space charge on the electric field in the device.

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2.1. Basic equation

The basic equation used in this simulation is the Poisson equation:

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{q}{\varepsilon_0 \varepsilon_r}[n(x) - p(x)] \tag{1}$$

where q is the elementary charge, relating the potential $\psi(x)$ to the electron and hole densities $n(x)$ and $p(x)$, respectively, and the dielectric constant (ε_r) described as

$$\varepsilon_r = \zeta \varepsilon_{r-DOP} + (1-\zeta)\varepsilon_{r-HOS} \tag{2}$$

where ζ is the mixture ratio, which is defined as the molar ratio of the donor to the totals. ε_{r-DOP} and ε_{r-HOS} are the dopant and host dielectric constant, respectively.

In order to solve the basic equation, a set of equations are needed relating the current densities to the potential and the carrier densities. Incorporating both drift and diffusion of charge carriers:

$$J_n = -qn\mu_n \frac{\partial}{\partial x}\psi + qD_n \frac{\partial}{\partial x}n \tag{3a}$$

$$J_p = -qp\mu_p \frac{\partial}{\partial x}\psi - qD_p \frac{\partial}{\partial x}p \tag{3b}$$

where D_n and D_p are the carrier diffusion coefficients, which obeyed Einstein relation:

$$D_{n,p} = \mu_{n,p}\frac{k_B T}{q} \tag{4}$$

where k_B is Boltzmann's constant, T is the absolute temperature,

LUMO $g_L(E)$ and HOMO $g_H(E)$ display Gaussian profiles [17]:

$$g_L(E) = \frac{(1-\zeta)N_{HOS}}{\sqrt{2\pi}\sigma_{L-HOS}}\exp\left(-\frac{(E-E_{L-HOS})^2}{2\sigma_{L-HOS}^2}\right)$$
$$+ \frac{\zeta N_{DOP}}{\sqrt{2\pi}\sigma_{L-DOP}}\exp\left(-\frac{(E-E_{L-DOP})^2}{2\sigma_{L-DOP}^2}\right) \tag{5a}$$

$$g_H(E) = \frac{(1-\zeta)N_{HOS}}{\sqrt{2\pi}\sigma_{H-HOS}}\exp\left(-\frac{(E-E_{H-HOS})^2}{2\sigma_{H-HOS}^2}\right)$$
$$+ \frac{\zeta N_{DOP}}{\sqrt{2\pi}\sigma_{H-DOP}}\exp\left(-\frac{(E-E_{H-DOP})^2}{2\sigma_{H-DOP}^2}\right) \tag{5b}$$

where E is the energy of states, N_{HOS} and N_{DOP} are the total density of states DOS of the acceptor and the donor, σ_{L-HOS} (σ_{H-HOS}) and σ_{L-DOP} (σ_{H-DOP}) are the variances of the acceptor DOS and the donor DOS distribution, respectively. E_{L-HOS} (E_{H-HOS}) and E_{L-DOP} (E_{H-DOP}) are the mean energy level of LUMO (HOMO) of the acceptor and donor, respectively (Fig. 1).

To obtain a unique solution of the model for non-Ohmic contact boundary conditions, it is necessary to specify the potential and carrier densities at both contacts. Let x denotes the position within the device, and $x = 0$ represents the location at the anode/organic interface. By application of Fermi statistics for the occupation of the energy states, an expression for the electron and hole densities at both contacts ($x = 0$ and $x = d$) are derived:

$$n_0 = n(0)$$
$$= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \frac{((1-\zeta)N_{L-HOS}/\sigma_{L-HOS})\exp(-(E-E_{L-HOS}-\delta\phi_a)^2/2\sigma_{L-HOS}^2) + (\zeta N_{L-DOP}/\sigma_{L-DOP})\exp(-(E-E_{L-DOP}-\delta\phi_a)^2/2\sigma_{L-DOP}^2)}{1+\exp((E-W_a)/k_B T)}\,dE \tag{6a}$$

$$p_0 = p(0)$$
$$= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \frac{((1-\zeta)N_{H-HOS}/\sigma_{H-HOS})\exp(-(E-E_{H-HOS}-\delta\phi)^2/2\sigma_{H-HOS}^2) + (\zeta N_{H-DOP}/\sigma_{H-DOP})\exp(-(E-E_{H-DOP}-\delta\phi)^2/2\sigma_{H-DOP}^2)}{1+\exp((W_a-E)/k_B T)}\,dE \tag{6b}$$

$$n_d = n(d)$$
$$= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \frac{((1-\zeta)N_{L-HOS}/\sigma_{L-HOS})\exp(-(E-E_{L-HOS}-\delta\phi_c)^2/2\sigma_{L-HOS}^2) + (\zeta N_{L-DOP}/\sigma_{L-DOP})\exp(-(E-E_{L-DOP}-\delta\phi_c)^2/2\sigma_{L-DOP}^2)}{1+\exp((E-W_c)/k_B T)}\,dE \tag{6c}$$

$$p_d = p(d)$$
$$= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \frac{((1-\zeta)N_{H-HOS}/\sigma_{H-HOS})\exp(-(E-E_{H-HOS}-\delta\phi_c)^2/2\sigma_{H-HOS}^2) + (\zeta N_{H-DOP}/\sigma_{H-DOP})\exp(-(E-E_{H-DOP}-\delta\phi_c)^2/2\sigma_{H-DOP}^2)}{1+\exp((W_a-E)/k_B T)}\,dE \tag{6d}$$

and the $\mu_{n,p}$ is the electron (hole) mobility, respectively, which are mixture ratio dependent see of Fig. 10.

Organic semiconductor thin films are either amorphous, or polycrystalline in structure, which is disordered in energy in comparison with regular crystals. The essential effect of disorder is to split the electronic transport orbital bands of the corresponding regular crystal lattice into a series of localized states. To a good approximation, the energy distributions of the density of states of

Here $\delta\varphi_a$ ($\delta\varphi_c$) is the image-force lowering of the energy barrier at the anode/organic (cathode/organic) interface, which depends on the electric field. The boundary conditions for the potential read:

$$\Psi(0) = -U_{bi} \tag{7a}$$

$$\Psi(d) = 0 \tag{7b}$$

where U_{bi} is the built-in potential.