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Modeling and simulation of bulk heterojunction polymer solar cells

Chunjun Liang [a,*], Yongsheng Wang [a], Dan Li [b], Xingchen Ji [b], Fujun Zhang [a], Zhiqun He [a]

[a] Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, China
[b] School of Science, Beijing Jiaotong University, Beijing 100044, China

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ABSTRACT

This review summarizes the optical and electrical models of bulk heterojunction (BHJ) polymer solar cells (PSCs) and numerically simulates and analyzes the performance of the PSCs. A complete simulation of a conventional BHJ device based on the polymer P3HT is presented and results are compared with the experimental data. Key factors affecting the device performance, including the photo absorption, quantum efficiency, short-circuit current, fill factor, and open-circuit voltage of the device, are analyzed and summarized. Simulations on inverted, semitransparent, and large-area PSCs are performed and findings are compared with experimental results. Simulations reveal the effects of optical spacer layers, different thicknesses, carrier mobilities, light intensities, contact barriers, effective bandgaps, recombination coefficients, and energy-level bending on the quantum efficiency, short-circuit current, fill factor, and open-circuit voltage of the PSCs. Differences between conventional and inverted geometry, opacity and semitransparency, and small and large-area PSCs are discussed based on the simulations. A power conversion efficiency of 11.0% is predicted for the PSC based on P3HT. Results suggest the need to further reduce the series resistance in large-area PSCs.

1. Introduction

Polymer solar cells (PSCs) serve as renewable sources of electrical energy because of their many advantages, which include low cost of fabrication [1–4] and easy processing on flexible substrates [5–9]. The performance of PSCs has been greatly improved by introduction of the bulk-heterojunction (BHJ) concept [10–15] as an active layer where electron donor and acceptor materials are mixed in a solution and cast into a thin film sandwiched between two electrodes. The power-conversion efficiency of state-of-the-art PSCs has exceeded 9% for single cells and 10% for tandem cells in recent published research [16,17].

Materials innovation is one of the major forces driving the performance of PSCs. MEH-PPV, P3HT, PCPDTBT and PCDTBT are some important electron-donor polymers in the history of PSCs research [18]. The most impressive high-performance polymers are those composed of thieno[3,4-b]-thiophene (TT) and benzodithiophene (BDT) alternating units [16,19,20], which are the first donor system capable of reaching power conversion efficiency of 7–9%. The C60 derivative PCBM is the most widely used electron-acceptor material in PSCs. However C70 derivatives exhibit better absorption than those of C60. Replacing C60 derivatives with C70 derivatives often enhances photocurrent by around 10%. Another important approach for improving PSC performance is by replacing the conventional acceptor PCBM with a new soluble C60 derivative (ICBA), the lowest unoccupied molecular orbital (LUMO) energy level of which is 0.17 eV higher than that of PCBM; this approach leads to higher open-circuit voltages and enhanced power conversion efficiencies [21,22].

Besides great progress on donor and acceptor materials [18,23–27], device processing techniques and their corresponding influence on the performance of PSCs have been investigated intensively. The most prominent processing steps for PSC devices include growth-rate control [28], solvent annealing [29], solvent additive [30,31], and thermal annealing [32–34]; these approaches are effective approaches for increasing optical absorption and carrier mobilities in the active blends [35]. Another approach involves the use of a relatively thin (100 nm) layer of the active blend to yield satisfactory device performance [36–38]. Small thickness, however, leads to insufficient optical absorption in the active blend layer. Kim et al. [39] introduced the concept of an optical spacer, a thin layer inserted between the active layer and the reflective electrode, to increase photo absorption in the active layer through the optical interference effect. The properties of the electrodes [40–43], the buffer layer [44–46], and the device area [47–49] have great impacts on the performance of PSCs.

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* Corresponding author. Tel.: +86 10 51688675.
E-mail address: chjliang@bjtu.edu.cn (C. Liang).

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Device architectures for PSCs have been diversified. Conventional PSCs refer to architectures consisting of a transparent conducting metal oxide coated with a PEDOT:PSS hole-transporting layer followed by the active BHJ layer. A low work function metal electrode (Al, Ca/Al) is evaporated on top as an electron-collecting electrode to complete the device [50–55]. An inverted PSC refers to an architecture wherein the nature of charge collection is reversed [6,56–81]. The device ITO/ZnO/P3HT:PCBM/MoO_3 (or PEDOT:PSS)/Ag is a typical inverted PSC [82,83]. This architecture exhibits stability [84–86] and processing [87,88] advantages over its conventional counterpart. Semitransparent or transparent PSCs [43,89–98] and solution processed large-area PSCs [3,99,100] are some important ongoing developments in the field of PSCs.

Experimental results show that the performance of solar cells is a function of multiple variables, such as the absorption coefficient, layer thickness, carrier mobility, contact barrier, energy bandgap, recombination coefficient [101–104], and device architecture [16]. These factors impart a remarkable influence on the performance of a BHJ PSC. A comprehensive understanding of the physics of the device, including the relationships between processing technique and device performance as well as differences between normal and inverted geometries, opaque and transparent devices, and small- and large area devices, is necessary for device optimization and further improvement. Modeling and numerical simulation are powerful tools for exploring the physics of the device and provides key insights into the internal mechanisms of PSCs. These tools also allow the extrapolation of possible but undiscovered device concepts.

We review the progress on the modeling and simulation of BHJ PSCs. A comprehensive and intuitive discussion of device performance is provided to help further endeavors toward device optimization. In the second section, a brief review on the development optical and electrical models is given. The simulation of a conventional PSC is presented with a basic model in the third section, and key factors that affect the device performance, specifically, the photo absorption, quantum efficiency, short circuit current (I_{sc}), fill factor (FF), and open circuit voltage (V_{oc}) of the device, are analyzed and discussed. Simulations of inverted, semitransparent PSCs, and large-area PSCs are also performed and discussed. Results are compared with the experimental data from related works and discussed accordingly. Finally, a summary is provided in the fourth section.

2. Device models of BHJ PSCs

A typical PSC is shown in Fig. 1(a), where the incident light passes through a transparent substrate and its successive layers; the light reflects back at the metal electrode. Excitons are formed and undergo dissociation into free electrons and holes in the BHJ layer after light absorption. The charge carriers are driven by an internal electric field and collected by the electrodes before recombination. The optical model is applied to calculate the numbers of the absorbed photon in the multilayer structure, and the electrical model is used to address the carrier generation and collection process of the photovoltaic structure.

2.1. Optical model

Because the layer thicknesses in organic solar cells are comparable with the wavelength of sunlight, the optical interference effect should not be ignored in the multilayer structure, especially when the highly reflective metal electrode is used. The mathematical treatment for optical interference in multiple-layer thin-film stacks has long been established [105]. The optical transfer-matrix theory introduced by Heavens [106] was applied to organic heterojunction solar cells by Pettersson et al. [107] and others [108,109]. The basic concepts of the method are briefly described here. A complete description of the method is presented in Ref. [107] and a free Matlab program is presented by the authors of Ref. [109].

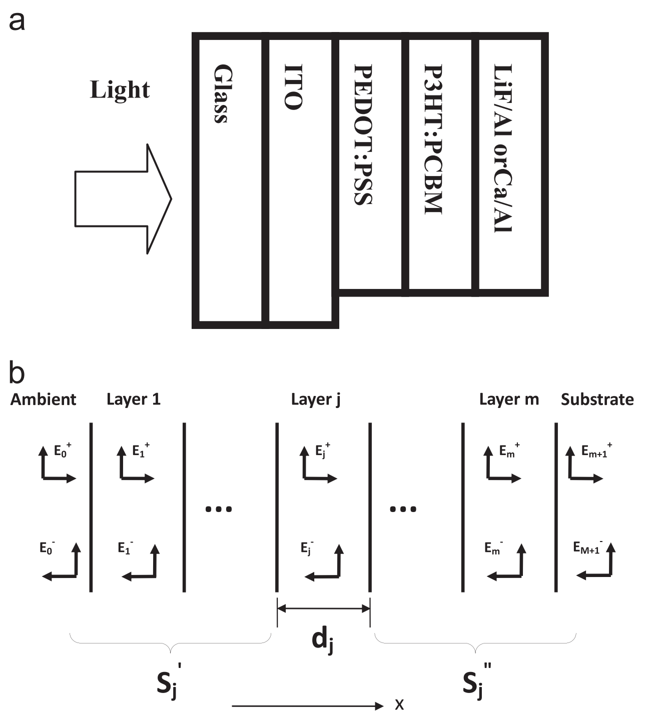

Fig. 1. (a) Device configuration of a typical bulk-heterojunction polymer solar cell. (b) A multilayer structure having m layers between a semi-infinite transparent substrate, an ambient substrate, and a semi-infinite substrate. Each layer j has a thickness of d_j and its optical property is described by its complex index of refraction. The optical electric field at any point in layer j is represented by two components: one propagating in the positive and one in the negative x direction, E_j^+ and E_j^-, respectively.

Consider a plane wave incident from the left on a multilayer structure having m layers between a semi-infinite transparent ambient and a semi-infinite substrate as schematically described in Fig. 1(b). Each layer j ($j=1, 2, \ldots, m$) has a thickness d_j and optical properties described by a complex index of refraction. The optical electric field at any point in the system can be resolved into two components: one propagating in the positive x-direction and one in the negative x-direction, which, at a position x in layer j, are denoted $E_j+(x)$ and $E_j-(x)$, respectively. The total electric field in an arbitrary plane in layer j at a distance x to the right of boundary $(j-1)|j$ is given by

$$E_j(x) = E_j^+(x) + E_j^-(x) \tag{1}$$

The energy absorbed at position x in the layered structure is proportional to the product of the square of the modulus of the electric field, the refractive index, and the absorption coefficient at the actual position x. Thus, $|E|^2$ versus position x in the film directly represents the number of absorbed photons at each point. The absorbed optical power in layer j at position x at normal incidence is finally given by

$$Q_j(x) = \alpha_j T_j I_0 \left[e^{-\alpha_j x} + \rho''^2_j e^{-\alpha_j (2d_j - x)} + 2\rho''_j e^{-\alpha_j d_j} \cos\left(\frac{4\pi\eta_j}{\lambda}(d_j - x) + \delta''_j \right) \right] \tag{2}$$

where I_0 is the intensity of the incident light, T_j is the internal intensity transmittance, and ρ''_j and δ''_j are the absolute value and the argument of the complex reflection coefficient for the second subsystem (see Ref. [107]), and α_j is the absorption coefficient.