Solar Energy Materials & Solar Cells 130 (2014) 20–26

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

The study of solvent additive effects in efficient polymer photovoltaics via impedance spectroscopy

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ARTICLE INFO

Article history:
Received 13 March 2014
Received in revised form
12 May 2014
Accepted 24 May 2014

Keywords:
OPV
Impedance spectroscopy
Bulk heterojuction
Interface

ABSTRACT

1, 8-Diiodooctane (DIO) has been known for its role of improving the polymer morphology and enhancing performance of polymer bulk heterojunction (BHJ) solar cell. In this work, the impedance spectroscopy was used to investigate the interface of poly(4,8-bis-alkyloxybenzo(1,2-b:4,5-b′)dithiophene-2,6-diyl-alt- (alkyl thieno(3,4-b) thiophene-2-carboxylate)-2,6-diyl) (PBDTTT-C):PC$_{70}$BM in BHJ with DIO as additive. Based on our results, we were able to simulate the device into an equivalent circuit model, which allows us to conveniently analyze the organic/organic interfacial contact in the organic photovoltaic (OPV) device. Thus, we demonstrate that the impedance spectroscopy can an effective approach in characterizing the donor/acceptor interfaces, such that a direct correlation can be established between the morphology and the device performance of BHJ devices.

1. Introduction

Organic photovoltaics (OPVs) have attracted considerable attention in the past decade because of their unique advantages over their inorganic counterparts, such as low-cost fabrication, compatible with flexible substrates, and roll-to-roll processing [1]. Polymer photovoltaic cells are based on the donor/acceptor concept that Frankel excitons with large binding energy are split at the donor/acceptor interfaces due to chemical potential difference [2]. The BHJ structure has been widely used, in which the donor and acceptor are blended, forming intimate contact on molecular level that allows excitons to reach the D/A interfaces for dissociation into free charges. Normally polymers are used as electron donor, while fullerene C60, C70, and their derivatives, such as PCBM, are given as electron acceptors [3–10]. Therefore, some high efficient OPVs have been published in single junction [11–14] and tandem devices [15–19]. In order to maximize power conversion efficiency (PCE), it is important to form interpenetrating networks for both the purpose of exciton dissociation and charge transport [20]. The morphology on microscale is strongly depending on the processing parameters, such as blending ratio, solvent, and annealing, through which an optimal morphology can be reached.

One effective method is to use high boiling-point solvent additive to control morphology. For example, 1,8-octanedithiol (OT) [21], a high-boiling-point minor solvent with favorable solubility only for PCBM, is able to cause a phase separation in both P3HT:PCBM and PCPDTBT:PCBM BHJ films at optimal scale. Its poor solubility for polymers forces the precipitation of polymer component during the evaporation of major solvent. Similar solvent additives [22–26] also works well, causing dramatic improvement in the efficiency.

Hence the understanding of how the additive works and how to make the connection between film morphology and electrical properties becomes much important. Morphology study on micro- and nano-scales involves various tools in order to gain insight in the phase separation, and aggregation behaviors of individual molecules or conjugated unites [27–32]. On the other hand, morphological characteristics dictate the optical and electrical properties in the polymer:fullerene blend films. Electrical characteristics of OPV devices are normally characterized by several tools [33–37]. These methods reveal detail information on the charge dynamics in the OPV cells, giving empirical guidelines for morphology modification [38]. However it is still difficult to directly probe the charge generation and recombination at the donor/acceptor interfaces on the molecular level. The correlation between the film morphology and the electric properties of OPV devices therefore remains unclear.

In OPV devices, several interfaces form upon direct contacts of individual components, and each interface plays an important role [39]. Assuming Ohmic contacts for charge collection by both anode

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http://dx.doi.org/10.1016/j.solmat.2014.05.049
0927-0248/

and cathode in optimal device architectures, the donor/acceptor interfaces and film morphology in polymer blend films are therefore of significant importance to maximize photovoltaic efficiency. Here, we employ impedance spectroscopy (IS) to investigate the organic/organic interfaces under various morphological scenarios induced by solvent additives. It allows us to link the morphology to the electrical properties of the OPV cells.

IS has been widely used in determining the electric characteristics through simple equivalent circuit models in many optoelectronic devices like dye sensitized solar cells (DSSC) [40], organic light emitting diodes (OLEDs) [41], organic thin film transistors (OTFTs) [42], and OPVs [43,44]. In our case, the interfaces of the OPV devices can be considered as simple elements such as resistances and capacitances in circuit models. With the representation of the elements, the electric properties of the BHJ can be connected to current density–voltage (J–V) characteristics of the devices. More importantly, the interface between the donor and acceptor in the BHJ can directly relate to the morphology of the BHJ. Hence, IS can be a powerful method to connect the morphology of the BHJ and the performance of the devices.

PBDTTT-C is among the earliest polymers achieving over 6% efficiency in OPVs [45]. It has clear response to solvent additive, making it an ideal model system to study both morphology and electrical properties in polymer films. Yet it is not well understood, even neglected, due to the overwhelming progress of the field of polymer solar cells. In this work, we used IS method and equivalent circuit model to characterize photovoltaic cells based on PBDTTT-C, and scrutinize the relationship between the morphology and the device performance under the influence of 1, 8-Diiodooctane (DIO) solvent additive.

2. Experimental setting

The OPV devices have a structure of Indium Tin Oxide (ITO)/poly (3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS)/ PBDTTT-C:P70BM/Calcium (Ca)/Aluminum (Al). First, ITO-coated glass substrates were cleaned sequentially in acetone, isopropanol, and DI water by ultrasonic cleaner. The cleaned ITO substrates were exposed to ozone for 15 min in a UV ozone system. Then, the PEDOT:PSS was dropped on each substrate (about 30 nm) and annealed at 120 °C for 15 min. The PBDTTT-C:PC70BM layer was deposited about 90 nm on the PEDOT:PSS by spin-coating the blend chlorobenzene and 1,2-dichlorobenzene solution with 10 mg/mL PBDTTT-C and 15 mg/mL PC70BM with or without 3% volume ratio of DIO in nitrogen filled glove box. At last, the Ca and Al were deposited by thermal evaporation with the rate of 0.05 nm/s and 0.2 nm/s and the thickness of 20 nm and 100 nm under $\sim 10^{-6}$ Torr, respectively. The device active area was 0.1 cm^2 for all the solar cell devices discussed in this work. Device characterization was measure under simulated AM1.5G irradiation (100 mW/cm^2) using a xenon-lamp-based solar simulator. The IS measurements were implemented using a Hewlett-Packard precision LCR meter 4284 A. The frequency range was from 100 Hz to 1 MHz, and the DC bias of each device was set at the value of the voltage that drives the device at 1 mA/cm^2 in the dark with the magnitude of the alternative signal at the value of 30 mV. The obtained IS data were fitted with EIS spectrum Analyzer in terms of appropriate equivalent circuits.

3. Results and discussion

3.1. *J–V characteristics*

The J–V curves of the PBDTTT-C:PC$_{70}$BM-based devices in cholorobenzene (CB) or dicholorobenzene (DCB) solution and with or without and with DIO additive are shown in Fig. 1, and the corresponding performance parameters of the devices are listed on the table inserted in Fig. 1. Using CB only as solvent to processing the polymer:fullerene blend films, the device shows a PCE of 3.08%. DCB has a much higher boiling point of 180 °C than that of CB (130 °C), yielding a better PCE of 4.2%, with improved short circuit current density (J_{sc}) and fill factor (FF). The morphological difference between the devices made with CB and DCB due to the different boiling points can determine the phase separation, the domain formation and the intermolecular packing of polymer chains and PCBM molecules during the drying process of the films. It is obvious to see the dramatic improvement in PCE, which can be explained from the morphological changing by DIO. Also by adding DIO in both CB and DCB, the devices processed from both solvents show almost identical J–V characteristics and PCE, with lower open circuit voltage (V_{oc}) but higher J_{sc} and better FF, in comparison with those of OPV devices without any additive.

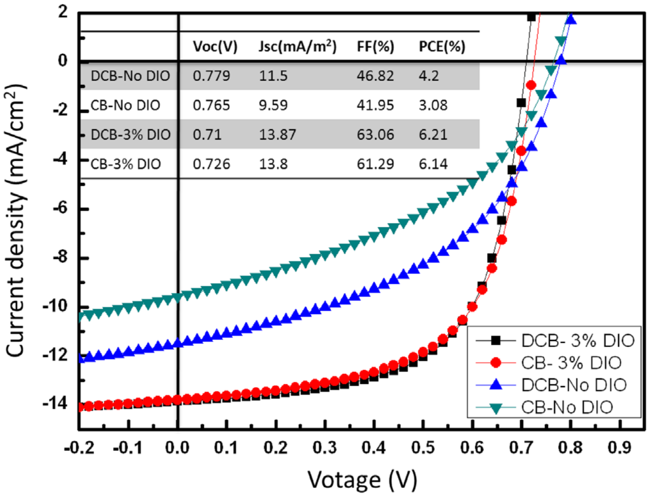

Fig. 1. J–V curve of PBDTTT-C:PC$_{70}$BM-based OPV devices in different conditions. The inset listed the performance of each device.

3.2. *TEM analysis and phase images of AFM*

Fig. 2 shows the transmission electron microscopy (TEM) images and atomic force microscopy (AFM) phases image of PBDTTT-C:PC$_{70}$BM film in CB or DCB solution and with or without 3% DIO. In the images, the prominent area should be the crystallization of PC$_{70}$BM, and the other area is the series of PBDTTT-C chains. The prominent units become smaller by doping 3% DIO into the CB or DCB implying that the aggregation of the PC$_{70}$BM decreases in scale apparently. Moreover, since the domain size of PC$_{70}$BM decreases, the improved phase separation was expected by doping with 3% DIO in both CB and DCB. Hence, adding DIO reduces the size of the domains in the film, and it gives longer time for the molecules to reorganize and assemble into smaller but finer phase separation. With better phase separation, the electron–hole pair would be easily dissociated since more interface area between donor and acceptor molecules is obtained. Besides, with reduced domain size and less phase separation, it would be easier for the excitons to diffuse to the donor/acceptor interfaces, and to generate free carriers. It also results in the fine interpenetrating networks in the whole bulk heterojunction and forms pathways for efficient charge transport and collection. Hence, charge extraction and injection are significantly enhanced, as strongly indicated the improved J_{sc} and FF.

With the confirmed photovoltaic performance which is consistent with previous reports [46] on PBDTTT-C:PC70BM with and without DIO, we thus started electrical characterization of the