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Quantitative characterization of phase separation in the photoactive layer of polymer solar cells by the phase image of atomic force microscopy

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ABSTRACT

We have quantitatively characterized the phase separation of poly(3-hexylthiophene) (P3HT):C61-butyric acid methyl ester (PCBM) blend films and studied the effect of phase separation of photoactive layer on the performance of polymer solar cells. A mixed solvent of dichlorobenzene and chlorobenzene was adopted to prepare the P3HT:PCBM blend films, and a series of blend films with different morphologies were obtained by adjusting both the volume ratio of dichlorobenzene to chlorobenzene and the solvent annealing time. The surface morphology and phase distribution were measured by atomic force microscopy (AFM). The interface length between the domains of donor and acceptor, which is extracted from the AFM phase image of blend film, was used to quantitatively characterize the phase separation of photoactive layer. It was found that the short-circuit current density (J_{SC}) of bulk heterojunction solar cells is proportional to the interfacial area of two phases, while it has a negligible effect on the open-circuit voltage. These results indicate that the larger interfacial area of donor and acceptor phases is beneficial to the exciton dissociation and carrier transport resulting in a significant increase of J_{SC} and power conversion efficiency.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) composed of a blend of a conjugated polymer and a fullerene derivative have attracted considerable interest of both academic and industrial researchers because of their large area, flexibility, light weight, and low cost. The BHJ structure provides a distributed junction between donor and acceptor materials, and the two components should phase separate on a suitable length scale to allow maximum ordering within each phase. The morphology and phase separation of the photoactive layer, governing the dissociation of photo-generated excitons and the transport of charge carriers, play a crucial role in the device performance. The ideal morphology of BHJ solar cell is defined as a bi-continuous composite of donor and acceptor with a maximum interfacial area for exciton dissociation and a domain size on the order of several nanometers to tens of nanometers, matching the exciton diffusion length [1]. Therefore, the blend film morphology has to be carefully tailored to optimize the total efficiency of PSCs [2–5]. However, it remains a challenge to maximize light absorption, charge separation, and transport while maintaining the necessary size scale and continuity constraints of the morphology of these blends [6].

The morphology of the photoactive layer is intrinsically determined by the thermodynamic miscibility between donor polymers and fullerene acceptors, the crystallinity of the active materials, and the molecular weight of donor polymers [7,8]. Besides those intrinsic factors, the blend morphology can also be controlled by several extrinsic factors, such as choice of solvent [8–11], solvent evaporation rate [12,13], thermal annealing [13,14], and solvent annealing [15–17]. These different approaches tend to facilitate the formation of phase separated morphology with crystalline donor and acceptor domains, leading to improved photovoltaic device performance [13]. Among them, both mixed solvent system [18–21] and solvent annealing have received much attention because of their capability in controlling crystallinity, solubility, and miscibility of the donor and acceptor components as well as the domain size and the local composition distribution at the donor/acceptor (D/A) interface.

One of the most commonly investigated PSCs is that based on a BHJ blend active layer of poly (3-hexythiophene) (P3HT) as a donor and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as an acceptor, whose morphology is well studied relative to other organic photovoltaic materials [3]. It is well known that chlorobenzene (CB) is mostly used as solvent of P3HT:PCBM because it has good solubility for both of them and can produce a smooth film. However, due to the fast evaporation of CB in P3HT:PCBM blend films, the crystallinity and the orientation of P3HT are restrained by the short timescale and do not form an interpenetrating bi-continuous percolation network for charge transport.

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Because the slow evaporation of a high boiling point solvent provides enough time to plasticize the polymer and allows it to crystallize slowly, dichlorobenzene (DCB), which possess a higher boiling point (180 °C), is a good alternative to CB for preparing P3HT:PCBM blend films [17]. Nevertheless, it is hard to obtain a uniform photoactive layer on top of the poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) buffer layer from a solution of P3HT:PCBM in pure DCB since significant shrinkage of the film occurs during the drying process due to its large surface tension [22]. Using a mixed solvent of DCB and CB is a possible way to increase the solvent evaporation time and obtain a uniform film. On the other hand, solvent annealing provides an alternative method to control morphology in a more convenient manner, which causes a morphological equilibration of films at room temperature without thermal damage.

To investigate the effect of morphology on the performance of PSCs, various techniques have been adopted to characterize the phase separation of active layer, such as atomic force microscopy (AFM) [23–27], transmission electron microscopy [26–29], grazing-incidence x-ray diffraction or scattering [25,30–32], small-angle neutron scattering [17,32], and photoluminescence and Raman spectroscopy [2,33]. Among them, AFM is one of the most important tools to characterize the phase separation and has been widely used since the nanoscale morphology and domain formation of blend films can be directly observed by using the phase image of AFM. Although all of these reports have shown the correlation between blend morphology and photovoltaic device performance, a comprehensive picture of the influence of morphology on the device performance is still lacking due to the absence of quantitative analyses. The purpose of this work is to provide a method for quantitatively characterizing the phase separation of photoactive layer of BHJ solar cells.

In this work, to explore the effect mechanism of morphology on performance of BHJ solar cells, the phase separation of photoactive layer was evaluated quantitatively by the phase image of AFM. A mixed solvent of DCB and CB was adopted to prepare the P3HT:PCBM blend films, and a series of blend films with different morphologies were obtained by adjusting both the volume ratio of DCB to CB and the solvent annealing time. The surface morphology and phase distribution were measured by AFM, and the interface length between the domains of donor and acceptor, which is extracted from the AFM phase image of blend film, was used to characterize quantitatively the phase separation of photoactive layer. It was found that the circuit current density (J_{SC}) of BHJ solar cells was proportional to the interfacial area of two phases, while it had a negligible effect on the open-circuit voltage (V_{OC}). These results are helpful for understanding and controlling the morphology of P3HT:PCBM mixture, which is essential to improve the power conversion efficiency (PCE) of the resultant PSCs.

2. Experimental

2.1. Preparation of blend films and polymer solar cells

The indium-tin-oxide (ITO)-coated glass substrates were cleaned sequentially by ultrasonic treatment in detergent, de-ionized water, acetone and isopropyl alcohol, and dried with nitrogen. PEDOT:PSS (Baytron P VP AI 4083, H.C. Stark) was spin-coated onto the cleaned ITO substrates at 4000 rpm for 40 s and then thermally annealed at 130 °C for 15 min in air, resulting in a ~35 nm thick anodic buffer layer. In order to systematically control solvent evaporation rate, P3HT (average molecular weight: approximately 50000, region-regularity: 91-94%, Rieke Metals, 12 mg/ml) and PCBM (Lum Tec. Co. Ltd, 12 mg/ml) was dissolved in the binary CB/DCB mixed solvent composed of 0, 10%, 40%, 70%, 80%, and 100% DCB. Next, the samples were transferred into a nitrogen-filled glove box, and a ~120 nm active layer is fabricated by spin-coating a blend solution of P3HT and PCBM. In the case of mixed and pure DCB solvents, solvent annealing was carried out by keeping the wet P3HT:PCBM films in a covered Petri dish immediately after spin-coating. Due to the slower evaporation rate of DCB, for the solvents with higher DCB concentrations, it takes longer time to plasticize the polymer. The solvent annealing was completed until the blend film was transformed from the liquid (orange) to the solid (dark purple) phase. The solvent annealing time (t_a) was controlled by varying spin-coating time, i.e., the longer spin-coating time means the shorter t_a. For example, for the mixed solvent with 70% DCB, the blend film was spin-coated at 700 rpm for 40, 55 and 70 s, respectively, and the resultant t_a is 30, 18 and 10 min, respectively. Further increase of the spin-coating time to 105 s, the P3HT:PCBM blend film was continuously dried by nitrogen without solvent annealing, which is referred as the as-cast film. During the solvent annealing process, the temperature in the glove box keeps a constant. To complete the corresponding BHJ solar cells, 100 nm Al was deposited on the photoactive layer by thermal evaporation under a vacuum of 10^{-4} Pa with a rate of 0.5 nm/s as a cathode. For the pure CB solvent, the blend film was completely dry by spin-coating at 700 rpm for 40 s, and the completed device was thermally annealed at 130 °C for 20 min on a hotplate under nitrogen ambient. The device structure is ITO/PEDOT:PSS/P3HT:PCBM/Al, and each device has an area of 0.04 cm^2.

2.2. Characterization

The film thickness was measured by a high-resolution surface profiler (KLA-Tencor P-6). Surface morphologies and phase distribution of the P3HT:PCBM blend films were characterized by AFM with an NT-MDT Solver P47 using a semi-contact mode. To quantitatively evaluate the phase separation of photoactive layer, the AFM phase images were analyzed by ImageJ software, from which the interface length between the domains of P3HT and PCBM was obtained. The ultraviolet-visible (UV-Vis) absorption spectra of PEDOT:PSS/P3HT:PCBM films on silica substrates were recorded with a Varian Cary 5000 spectrophotometer in a double-beam mode. The current density–voltage (J–V) characteristics of PSCs were taken using a Keithley 2400 source measure unit under 100 mW·cm^{-2} illumination (AM 1.5G). In each ITO substrate, 8 solar cells were fabricated, which is defined by the overlapped area of the Al layer and ITO layer. Among 8 solar cells in the same ITO substrate, if the maximum PCE deviation is less than 5% in at least 6 solar cells with higher PCE values, then their performance parameters will be recorded. The highest PCE values in the records were adopted here for comparison. The external quantum efficiency (EQE) was measured using a lock-in amplifier with a current preamplifier under short-circuit conditions after illuminating the cells with monochromator.

3. Results and discussion

These previous investigations indicate that forming a phase separated morphology of the P3HT:PCBM mixture and maintaining bi-continuous percolation paths are essential to increase charge carrier mobility and charge collection, both of which improve the ultimate power conversion efficiency of PSCs [1]. To characterize the phase separation of photoactive layer, we measured the surface morphology and phase image of the P3HT:PCBM blend films using AFM. The AFM height images of the P3HT:PCBM blend films with and without solvent annealing are shown in Fig. 1(a) and (b), respectively. These films were prepared with the 70% DCB mixed solvent. A root-mean-squared (RMS) roughness of 0.96 nm is obtained within the scanning area of 1μm×1μm for the as-cast film, while the film with 18 min solvent annealing is much rougher with an RMS roughness of 2.17 nm, as shown in Fig. 1(b). The P3HT chains self-organize into ordered structure after solvent annealing, as a result, the roughness of blend films increase, which is also considered to be an indicator of phase separation [15,34].

Fig. 1(c)–(f) displays the phase images of P3HT:PCBM blend films that were solvent annealed for 0, 10, 18, and 30 min, respectively. AFM phase images of two-component blend film provide information regarding the surface hardness and the identity of the fullerene- and