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Effect of solvent annealing on the crystallinity of spray coated ternary blend films prepared using low boiling point solvents

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ABSTRACT

The effects of different post treatments on the spray coated P3HT:PPV:PCBM for an active layer in polymer solar cell were investigated using atomic force microscopy (AFM), UV–vis spectroscopy, photoluminescence (PL) spectroscopy and X-ray diffractometer (XRD). The annealing temperatures were varied from 130 °C to 150 °C and the annealing time was kept constant for 10 min. The RMS roughness of the sample that dried in the ambient condition was lower compared to other samples. This explained that the samples that undergo solvent and thermal annealing treatment had higher crystallinity of P3HT or phase separation in these samples is mostly favored. The peak absorption for P3HT:PPV:PCBM thin film is higher compared to P3HT:PCBM thin film. The better defined shoulders can be observed in the samples with solvent annealing treatment. The XRD spectra showed that the structure of the samples will evolve with high thermal annealing temperature (150 °C) due to a weak intermolecular force in P3HT molecules. This will contribute to the low crystallinity of the films which consequently affects the absorption properties of the films.

1. Introduction

The typical active layer bulk heterojunction solar cell consists of one electron-donating unit (e.g. P3HT and PPV) and one electron-acceptor unit such as PCBM. Blending two types of electron-donating unit is believed can alter the absorption properties of the semiconducting polymer and the morphological properties of the film. The fabrication and study of polymer blends has been a natural extension of polymer science because different aspects of the constituent polymer materials can be combined to create new compounds with wider potential applications [1]. A lot of researches have been done on the binary and ternary blend systems to tailor the active layer architecture into the optimal condition for exciton diffusion and separation [2–11].

Campoy-Quiles et al. [3] blended PCBM with regio regular (RR-) P3HT and regio random (RRa-) P3HT and found that this ternary blend is very efficient for controlling the morphology of the active layer Besides, RRa-P3HT is reportedly to improve the charge generation and the open circuit voltage with minimum cost, owing to its charge mobility. Other study by Ruderer et al. [2] showed that the addition of dye in P3HT:PCBM could expand the absorption range as compared with the binary P3HT:PCBM system. Yang et al. [4] on the other hand found that with the addition of TiO_2 nanotubes into the P3HT:PCBM blends, the absorbance of the active layer was reduced while maintaining the charge collection and transportation same as binary systems P3HT:PCBM. The improvement in the electron mobility can also be observed in the ternary systems. Kim and his group [12] studied the influence of electron donating polymer addition (i.e. MDMO-PPV) and thermal annealing on the performance of P3HT:PCBM. They observed that the open circuit voltage (V_{oc}) of the ternary blends is higher compared to binary blends (thermal annealing at 70 °C). However, higher thermal annealing temperature (110 °C) led the ternary blend device to show largely reduced in short circuit current density but this value is very close to the binary systems. The result is supported by the optical absorption that showed the increment in P3HT crystallization upon thermal annealing at 110 °C.

The performance of the polymer solar cell (PSC) depends critically on the properties of the materials and the processing conditions; both have a direct impact on the morphology of the film

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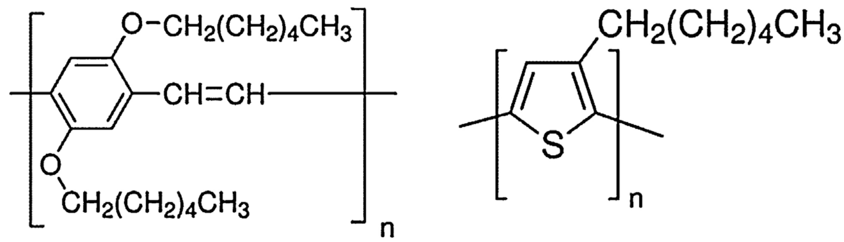

(a) (b)

Fig. 1. Molecular structure of (a) PPV and (b) P3HT.

[13]. Several methods have been employed to alter the morphology of the films. These include the addition of the processing additives [14–16], thermal annealing at specific temperature [17–19], the use of solvent mixture, controlling the solvent evaporation rate [20] and synthesizing a new narrow bandgap copolymer [21–23]. Solvent annealing approach is one of the methods that can be used to control the morphology of the active layer in the PSC. This method attempts to slow down the solvent evaporation rate during active layer preparation, producing the nanomorphology between the two compounds which significantly affects the efficiency of exciton separation as well as the charge transport in the blended films [19,24]. General speaking, thermal annealing improves the crystallinity within the phase separated networks and thereby facilitates charge transport to the electrodes [5].

In this work, poly (2,5-dihexyloxy-1,4-phenylenevinylene) (PPV) and poly-3, hexylthiophene (P3HT) and C61-butyric acid methyl ester (PCBM) were used to study the effects of ternary mixing on the morphology and optical properties of the active layer. PPV offers good mechanical and processing properties besides showing excellent luminescent abilities compared to other light emitting conjugated polymers [1]. The P3HT has been extensively used for electric and photovoltaic application due to its easy availability, excellent solubility in common organic solvents and high mobility [1,6]. Although it is known that the addition of PPV will interrupt the chain packing of P3HT, thus reducing the crystallinity of the polymer, no systematic study has yet been conducted up to date to look into the effects of solvent annealing and thermal annealing of the spray coated ternary systems on the optical and morphological properties of the films. The effects of solvent annealing and thermal annealing on the optical and morphological properties of the thin films were investigated using UV–vis spectrophotometer, photoluminescence (PL) spectroscopy, X-ray diffractometer (XRD) and atomic force microscopy (AFM). It is expected that the findings will provide insights in developing PSC with improved power conversion efficiencies.

2. Experimental

Poly (2,5-dihexyloxy-1,4-phenylenevinylene) (PPV) and poly-3,hexylthiophene (P3HT) from Sigma Aldrich were used as received. The molecular structures of both polymers are presented in Fig. 1. Both of these polymers were used as the electron donating unit. C61-butyric acid methyl ester (PCBM) from Sigma Aldrich was used as an electron acceptor unit. All of these polymers were dissolved in 2 ml toluene in 1:1:1 weight ratio. The solution were stirred using a magnetic stirrer at 500 rpm for 48 h in room temperature. Then, the thin films were prepared by spray coating the polymer solution on pre-cleaned glass or quartz substrates. The spray coating parameters such as distance between substrate and nozzle, spray duration and air pressure were set at 7 cm, 10 s and 1 bar, respectively. The thickness of the thin films is in the range of 200–300 nm, measured using surface profiler.

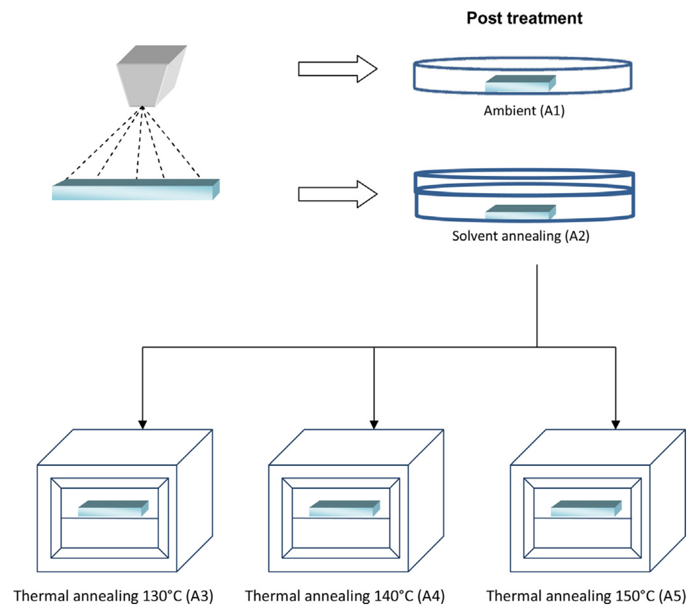

Fig. 2. Post treatment procedure.

The glass substrates were cleaned sequentially with a detergent, deionized water, ethanol, methanol and acetone. Afterwards, the substrates were dried in an oven. After the spray coating, the wet film was subjected to different post treatments to determine the effects on the morphological and topographical properties of the films. Fig. 2 illustrated the thin films fabrication and post treatment procedure. For the first sample, the wet films were dried in ambient condition (referred to as A1). Second sample, the wet films were put in a Petri dish for 15 min for solvent annealing treatment (A2). Third sample, after the annealing process, the device was further baked at 130 °C (A3), 140 °C (A4) and 150 °C (A5) for 10 min. The UV–vis absorption spectra of the polymer films were taken with Shimadzu UV-3101-PC. The topographical properties of the polymer films were obtained using microscopy Atomic Force Microscopy (AFM) with the tapping mode while XRD spectra were measured using Rigaku.

3. Results and discussion

3.1. Topographical and morphological properties of the ternary blend systems

To observe the topographical and morphological properties of the active layers, AFM has been performed on the spray coated thin film. Fig. 3 shows the topographical images for P3HT:PPV:PCBM spray coated from toluene-based solution which was dried at ambient condition, with solvent annealing and thermal annealing