

Contents lists available at ScienceDirect

### Solar Energy Materials & Solar Cells



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

## Effect of two-step annealing on the performance of ternary polymer solar cells based on P3HT:PC<sub>71</sub>BM:SQ



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#### ARTICLE INFO

Article history: Received 23 January 2014 Received in revised form 25 April 2014 Accepted 7 May 2014 Available online 5 June 2014

Keywords: Polymer solar cells (PSCs) Ternary blends P3HT:PC71BM:SQ Solvent annealing Thermal annealing

#### ABSTRACT

The effect of two-step annealing, including solvent annealing and further-step thermal annealing on the inverted ternary polymer solar cells (PSCs), which are composed of poly(3-hexylthiophene-2,5-diyl) (P3HT):[6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM):2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQ), was systematically investigated. The film morphology of ternary blends was characterized by X-ray diffraction and atomic force microscope. The results showed that a dramatic enhancement of power conversion efficiency from 1.32% to 4.42% was obtained due to the improved light harvesting, optimized self-assembled morphology and thermally induced crystallization of ternary blends. Especially, the optimized temperature of the thermal annealing process was remarkably decreased to 80 °C. It was also found that the two-step annealing process was crucial in achieving high performance, which could not only control the domain size of SQ but also maintain a well-ordered nanoscale structure within the ternary blends of P3HT:PC<sub>71</sub>BM:SQ.

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#### 1. Introduction

Polymer solar cells (PSCs) have attracted significant interest with many merits of low cost, light weight, high flexibility and versatility of chemical structures [1–4]. To date, the power conversion efficiency (PCE) of PSCs approaching 10% has been achieved by altering polymer material, device architecture and fabricating technique [5]. One attractive strategy toward improving the PCE is to dope the third composite into the polymer: fullerene binary blends to fabricate ternary PSCs [6-8]. Unlike the tandem PSCs with a complex layer-by-layer structure, the ternary PSCs inherit the major advantages of conventional single bulk heterojunction PSCs. Additionally, incorporating the third component in binary blends can broaden the photon absorption range by offering an additional absorber [9], enhance the exciton harvesting through Forster resonance energy transfer process [10], and improve the charge transport by providing high charge mobility material [11]. To improve the PCE of ternary PSCs, numerous treatments such as blend ratio control [12], solvent modification [13], processing additives [14], and annealing treatment [9,15], which are all effective methods to enhance the PCE of binary PSCs, have been directly used to optimize the phase separation and

http://dx.doi.org/10.1016/j.solmat.2014.05.026 0927-0248/© 2014 Elsevier B.V. All rights reserved. crystallization of ternary blends. Among them, Taylor et al. achieved a PCE of 4.5% based on poly(3-hexylthiophene-2,5-diyl) (P3HT):[6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM):2,4-bis[4-(N,N-iisobutylmino)-2,6-iydroxyphenyl] squaraine (SQ) blends by solvent annealing [10]. Koppe et al. achieved a 7-fold increase of PCE through the formation of bi-continuous interpenetration network by thermal annealing [9], and Mikroyannidis et al. found that thermal annealing can increase the crystallization of both polymer donors in the ternary blends [15].

Although the individual solvent annealing or thermal annealing can improve the PCE of ternary PSCs [16–18], nanoscale structure control in the ternary blends is more difficult than that in the simple binary blends due to the miscibility and the diversity of chemical properties of different materials. For instance, the optimized thermal annealing temperatures ( $T_{TA}$ ), i.e., 150 °C and 50 °C for the binary blends of P3HT:[6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) and SQ:PC<sub>71</sub>BM, are quite different [19,20]. Thus, if the  $T_{TA}$  higher than 100 °C is used to treat the P3HT:PC<sub>71</sub>BM:SQ blends, the molecular aggregation of SQ will lead to negative effect on the performance of ternary PSCs [20]. Thus, the effect of thermal annealing on the performance of P3HT:PC<sub>71</sub>BM:SQ ternary PSCs needs further investigation.

In this work, the effect of two-step annealing, including solvent annealing and further-step thermal annealing, on the performance of P3HT:PC<sub>71</sub>BM:SQ ternary PSCs was studied. Especially, the optimized photovoltaic performance of ternary PSCs was obtained

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at a  $T_{TA}$  lower than 100 °C. The mechanism of two-step annealing was investigated based on the film morphology of ternary blends characterized by X-ray diffraction (XRD) and atomic force microscope (AFM). Also, the external quantum efficiency (EQE) spectra were analyzed to reveal the variation of photocurrent.

#### 2. Experimental

The chemical structures of organic materials are shown in Fig. 1(a). and the device with an inverted structure is indium tin oxide (ITO)/ ZnO (30 nm)/P3HT:PC71BM:SO (150 nm)/MoOx (15 nm)/Ag (100 nm) as depicted in Fig. 1(b). The ITO-coated glass substrates with a sheet resistance of 10  $\Omega$ /sq were cleaned consecutively in an ultrasonic bath containing detergent, deionized water, acetone and isopropyl alcohol for 10 min each step, and finally dried in an oven for 1 h. The ZnO precursor solution was spin-coated on top of the ITO-glass substrates. After baking at 200 °C for 60 min in ambient, the substrates were transferred to a nitrogen-filled glove box ( < 1 ppm O<sub>2</sub> and H<sub>2</sub>O). A solution containing a mixture of P3HT (99.9%, Riek metals):PC71BM (99.9%, Lumtec):SQ (1:1:0.06, weight ratio) in 1, 2-dichlorobenzene (DCB) with a concentration of 30 mg/ml was spin-coated on the top of the ZnO thin layer. After that, the substrates coated with the active layer were dried in a covered Petri dish for 20 min, and then were dried under various  $T_{TA}$  for 10 min ( $T_{TA}$ =60, 80, 100, 120 °C). MoO<sub>X</sub> (99.98%, Aldrich) layer was deposited onto the substrates at a rate of 1-2 Å/s at a pressure of  $3 \times 10^{-3}$  Pa in vacuum, followed by the deposition of Ag anode at a rate of about 10 Å/s under a pressure of  $3 \times 10^{-3}$  Pa without breaking the vacuum. The typical area of PSCs was 0.02 cm<sup>2</sup>. All the devices were encapsulated with UV-sensitive resin, and exposed to ultraviolet light for 5 min.

A light source integrated with a xenon lamp (CHF-XM35, Beijing Trusttech) with an illumination power of 100 mW/cm<sup>2</sup> was used as a solar simulator [21,22]. The current–voltage curves in the dark and under simulated AM 1.5G solar illumination were measured with a Keithley 4200 programmable voltage–current source, and the EQE spectra were measured under the lump light passing through a monochromator. The ultraviolet–visible (UV–vis) absorption spectra of the active layer on quartz substrates were measured using a Shimazu UV1700 system. The film preparation conditions for AFM (MFP-3D-BIO, Asylum Research) and XRD (D1-HR XRD, Bede, Inc.) measurement were kept the same as the device fabrication for comparison.

#### 3. Result and discussion

#### 3.1. Absorption spectra

The UV-vis absorption spectra of pristine films of P3HT,  $PC_{71}BM$  and SQ are shown in Fig. 2(a). The absorption spectra of

P3HT and SQ exhibit an apparent complementary absorption in the range from 400 nm to 750 nm, which are ideal constituents for ternary PSCs. The UV–vis absorption spectra of P3HT:PC<sub>71</sub>BM:SQ blend films treated by various annealing processes are shown in Fig. 2(b). The peak of absorption intensity at the wavelength of about 675 nm is ascribed to SQ. It can be seen that the as-cast ternary blend film shows the lowest light absorption. When treated by solvent annealing and further-step thermal annealing, the absorption spectra of ternary blend films are significantly improved. In terms of solvent annealing, an obvious enhancement of absorption intensity in whole absorption range can be observed due to the self-assembly of ternary blends, which was consistent with those of both P3HT:PC<sub>61</sub>BM and SQ:PC<sub>71</sub>BM PSCs [16,23].

With respect to further-step thermal annealing, the relative absorption intensity in the region of 400–630 nm slightly increases along with the increase of  $T_{TA}$ . The enhancement of light absorption is derived from the thermally induced crystallization of



**Fig. 2.** (a) UV–vis absorption spectra of pristine films of P3HT, PC<sub>71</sub>BM and SQ. (b) UV–vis absorption spectra of P3HT:PC<sub>71</sub>BM:SQ blend films treated by various annealing processes. Here, solvent annealing and thermal annealing are denoted as SA and TA, respectively.



Fig. 1. (a) Chemical structures of P3HT, PC<sub>71</sub>BM and SQ. (b) Schematic structure of PSCs in this work.

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