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Effect of in situ annealing on the performance of spray coated polymer solar cells

Yifan Zheng [a], Ruofan Wu [b], Wei Shi [a], Zhiqiang Guan [a], Junsheng Yu [a,*]

[a] State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, PR China

[b] Department of Engineering, McGill University, Montreal, QC, Canada H3A1Y1

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ABSTRACT

Polymer solar cell (PSC) with a structure of ITO/PEDOT:PSS/P3HT:PCBM/Bphen/Ag was fabricated using spray coating method, and the influence of in situ annealing treatment on the PSC performance was studied. Comparing the performance of in situ annealed PSC with that of conventional post-annealed cell, the results showed that the in situ annealing treatment at low temperature not only corresponding to 12% enhancement of fill factor, but also resulting in 13% increase of open circuit voltage. The interpenetrating networks of P3HT:PCBM film were characterized by X-ray diffraction, and surface morphologies have been studied by atomic force microscope. The performance enhancement of PSC was attributed to the improved hole mobility of P3HT:PCBM blend and the increased interaction of active layer.

1. Introduction

Polymer solar cell (PSC) possesses many unique advantages of low-cost, environmentally friendly manufacturing and flexibility [1–5], which have attracted lots of attention in recent years. Spin coating method, with the advantage of reproducibility and accurate control of film thickness, has been widely used for fabricating high performance PSC with power conversion efficiency (PCE) approaching 10% [6]. However, spin coating method is not very suitable for large-scale production due to its limit of substrate size and materials waste [7,8]. In this case, several novel processes, such as doctor blading [9], flexographic printing [10], screen printing [11,12], slot-die or knife coating [13,14], and inkjet printing have gained considerable attention [12,15,16], since large area, continuous process, and high efficiency PSC can even be obtained. For the same purpose, spray coating method with many benefits has been introduced recently, which has high potential to be adapted into the large-scale fabrication of PSC [17–19]. First of all, high production speed and compatibility with various substrates become possible since the sprayed droplets are transferred from the spray nozzle to the substrate without direct contact to the surface [17]. Also, various materials with low solubility in less toxic solvent can be applied due to the low concentration of sprayed solution [18]. Moreover, spray process can pattern the coated film within a sub-millimeter scale by using shadow masks [19].

The photovoltaic performance based on spray coating is comparable to those made by spin coating with post-annealing treatment, which can enhance the PCE of PSC by improving the ordering of polymer blend [19–23]. Based on this treatment, recently, several groups have fabricated high efficiency PSC by spray coating with an accurate control of fabrication condition. Yu et al. achieved a PCE of 3.4% by demonstrating the practical application of spray coated PSC [19]. Moreover, Susanna et al. obtained a higher PCE of 4.1% by optimizing the parameters of the spray system through introducing a co-solvent mixture [17].

However, the main restriction for the practical application of spray coating process is the post-annealing treatment, which calls for high temperature and the utilization of nitrogen box as well as time consuming. Therefore, In this study, a simple in situ annealing method to replace the widely used post-annealing treatment was introduced, and the influence of substrate temperature on the morphology poly-3 (hexylthiophene) (P3HT): [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blend characterized by X-ray diffraction (XRD) and atomic force microscope (AFM) was analyzed. In addition, theoretic simulation using space-charge-limited current (SCLC) was carried out to test the change in hole transport mobility, and the performances of PSCs treated by in situ annealing and post-annealing were compared and analyzed in detail.

2. Experimental

The device configuration of PSC in this work is indium-tin oxide (ITO)/poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate)

* Corresponding author. Tel.: +86 28 83207157.
E-mail address: jsyu@uestc.edu.cn (J. Yu).

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(PEDOT:PSS) (40 nm)/P3HT:PCBM (220 nm)/4, 7-diphenyl-1, 10-phenanthroline (Bphen) (5 nm)/Ag (100 nm) as depicted in Fig. 1(a). ITO-coated glass substrates with a sheet resistance of 10 Ω/sq were consecutively cleaned in ultrasonic bath containing detergent, acetone, deionized water and ethanol for 10 min each step, and dried by nitrogen blow. Prior to spin coated PEDOT:PSS (Baytron P AI4083), the substrates were treated by O_2 plasma for 5 min, and PEDOT:PSS was spin coated at 2500 rpm for 60 s, resulting in an uniform film ~40 nm measured with a Dektak 150 stylus profiler. The substrates were subsequently heated on a hot plate in air at 130 °C for 30 min [2]. An 1:1 mixture of P3HT (99.9%, Aldrich) and (6,6)-phenyl-PCBM (99.9%, Lumtec) was dissolved in 1,2-dichlorobenzene (DCB). In spray coating process, an airbrush was powered by N_2 gas at 60 psi, with a relatively low pressure that ensures a fine atomization of solution. The distance between airbrush and substrate was fixed at 20 cm by holder, in which the droplet can cover the cell uniformly without leaving large aggregated droplets. Furthermore, the concentration of P3HT:PCBM solution was scrutinized from 2 to 10 mg/ml, and it was found that at a height of 20 cm with a pressure of 60 psi, 4 mg/ml solution can form the most uniformity film. The thickness of active layer is about 220 nm by spraying the 480 μl solution, characterized by Dektak 150 stylus profiler. A digital hot plate was used for the in situ annealing. Bphen as a cathode buffer layer cooperates with Ag can improve the device J_{SC}, which has been verified by our group previously [2,24]. Bphen (99%, Fluka) was thermally evaporated through OLED-V (Shenyang Vacuum Co.) thermal deposition equipment at a rate of 1 Å/s at a pressure of 3×10^{-4} Pa, formed ultrathin layer with a thickness of 5 nm [24]. Then, Ag cathode was deposited at a rate of 10 Å/s under a pressure of 3×10^{-3} Pa without breaking the vacuum. The current–voltage curves in dark and under illumination were measured with a Keithley 4200 programmable voltage–current source. A xenon lamp with an illumination power of 100 mW/cm^2 was used as an illumination source. All measurements were performed in air.

3. Result & discussion

3.1. The effect of spray rate on device performance

A schematic diagram of spray coating apparatus is shown in Fig. 1(b). A smooth dense continuous film, affected by the factors such as the atomization of droplet, the impaction of droplet to substrate and the viscosity of solution, is crucial to enhance the performance of device [19]. In this study, for the controllability and reproducibility of spray coating process, we kept other factors constant and only modulated the spray rate. To investigate how the spray rate affects the film morphology, we introduced a formula [20]

$$I \propto Q \times P^{\frac{1}{2}} \tag{1}$$

where the I is the theoretic total impact, Q is the spray rate of solution, and P is the pressure of N_2 gas. By increasing the spray rate, the total impact of droplets to substrate became bigger, resulting in stronger bonding between the sprayed wet droplets and the previous dry ones [25].

The device performance varies as the spray rate changes, and the corresponding result is shown in Fig. 2. On one hand, high spray rate (> 0.3 ml/min) causes the P3HT:PCBM droplets to be atomized with relatively more DCB, resulting in a wet film formed by the continuous droplets. Because of the long distance for evaporated DCB traveled from the bottom of P3HT:PCBM blend film to the top, a large amount of traps may appear. This will cause more charge recombination, resulting in the decrease of J_{SC}, from 9.0 mA/cm^2 to 8.25 mA/cm^2, when the spray rate increased from 0.30 ml/min to 0.40 ml/min as shown in Fig. 2. On the other hand, slow spray rate (< 0.1 ml/min) relates to the small size of P3HT: PCBM droplets, which in turn decreases the interaction between the droplets and PEDOT:PSS layer [26]. As a result, the surface of sprayed film consists of lots of small P3HT: PCBM blend droplets. These droplets turn to independent islands after DCB evaporated, leading to weak interaction between P3HT and PCBM cluster. Therefore, as shown in Fig. 2, J_{SC} is limited at a low level under a spray rate of 0.1 ml/min, corresponding to 7.52 mA/cm^2. The optimized spray rate is 0.3 ml/min, leading to a PCE of 2.70% with J_{SC} of 8.94 mA/cm^2, V_{OC} of 0.60 V and FF of 0.50.

3.2. Interface and morphology of P3HT:PCBM film

It is well known that post-annealing treatment can significantly increase the PCE of PSC by forming an ordered organization of P3HT crystal [27,28]. However, post-annealing treatment requires the hot plate at high temperature and the utilization of nitrogen box, leading to high fabrication cost. Herein, as an alternative way, the in situ annealing treatment is used, which offers the similar effect

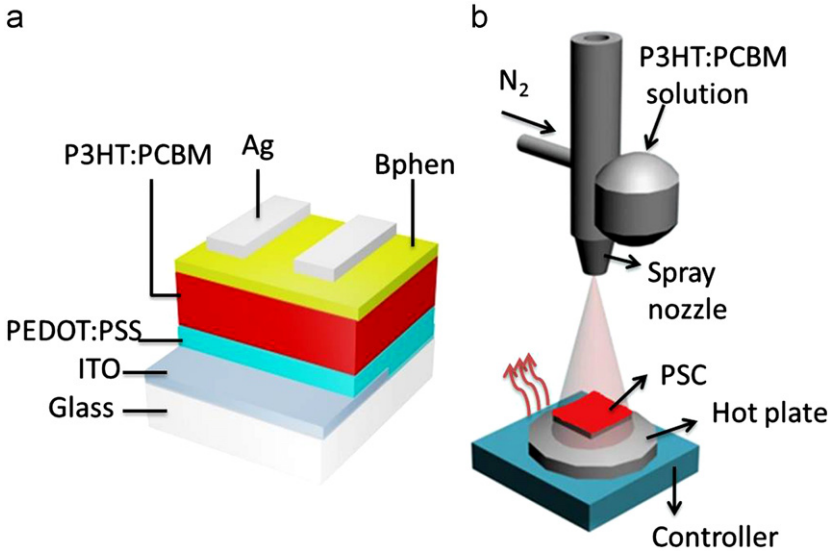

Fig. 1. Schematic of (a) spray coated PSC and (b) spray coating apparatus.