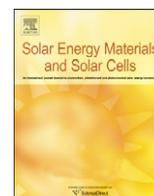




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Facile hot solvent vapor annealing for high performance polymer solar cell using spray process

Yu-Ching Huang^{a,*}, Hou-Chin Chia^a, Chih-Min Chuang^a, Cheng-Si Tsao^a,
Charn-Ying Chen^a, Wei-Fang Su^{b,**}

^a Institute of Nuclear Energy Research, Longtan, Taoyuan 325-46, Taiwan

^b Department of Materials Science and Engineering, National Taiwan University, Taipei 106-17, Taiwan

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ABSTRACT

In this paper, the use of hot solvent vapor (HSV) annealing is demonstrated to improve the performance of polymer solar cells (PSCs) fabricated by the spray process. The blend of poly(3-hexylthiophene) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT/PCBM) is used as a photoactive layer of the solar cell. Compared to the conventional solvent vapor annealing, the HSV annealing can eliminate the formation of intra-droplet boundary during the spray process and optimize the nanostructure of the film quickly (≤ 5 min). The study of conducting atomic force microscopy (C-AFM) reveals that the HSV annealed film exhibits smooth film surface and homogenous conductivity distribution. Moreover, an enhanced light harvesting and increased crystallinity of P3HT in the active layer are observed by UV-vis absorption and X-ray diffraction (XRD). With subsequent thermal annealing, the power conversion efficiency of solar cell made from the HSV annealed film is reached at 3.61%. This HSV annealing technique can be implemented into the fabrication of high efficient large-area PSCs using the spray process.

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1. Introduction

Polymer solar cell (PSC) has potential to become next generation of low cost and flexible solar cell due to its ease of processing from solution into large area [1–4]. Due to relatively low power conversion efficiency (PCE) of PSC fabricated from P3HT/PCBM, the enhancement of PCE has been obtained by design and synthesis of new conjugated polymer [5–7] and fullerene derivatives [8–10]. A PCE of about 9% was achieved recently [11]. Furthermore, the morphology of active layers is critical to the overall PCE improvement of PSCs. A bi-continuous network of bulk heterojunctions (BHJs) is formed in the active layer, so an efficient charge transport can occur [12–15]. Due to the small exciton diffusion length (on the order of ~ 10 nm) [16,17], the nanoscale morphology of BHJs is important to the solar cells performance [18–22]. Several approaches have been proposed to manipulate the phase-separated nanostructures, including thermal annealing [23–25], solvent mixture [26,27], slow growth [28,29] and solvent vapor annealing [30–32]. Therein, thermal annealing is the most effective approach to enhance the PCE of solar cells. However, most of the

previous studies have focused on the optimization of nanostructured thin films (≤ 250 nm) processed by the spin-coating technique, which is not suitable for mass production. To facilitate the mass production, in-line compatible deposition methods have been developed [33–39]. The spray process has been emerged as a low cost fabricating process for large-area devices because of its high throughput rate and low material waste. However, it is difficult to control the film thickness below 250 nm with desired morphology using the spray process.

In addition, the PCE of the PSC fabricated by the spray process is also limited by the series resistance (R_s) resulting from the presence of inter-droplet boundary in sprayed films. The problem has been reduced with improved PCE by using co-solvent [35,40], multi-source deposit [41] and spraying solvent over layer [42]. These results were obtained by optimizing the film drying kinetics, i.e. controlling the film drying time within 10 min. If we could further control the film drying kinetics, we would achieve higher enhancement in PCE.

In this paper, we demonstrated a facile method, hot solvent vapor (HSV) annealing, to control the sprayed film morphology. Traditional solvent vapor annealing takes about 1 h to accomplish. Conversely, the HSV annealing takes only a few minutes to eliminate the inter-droplet boundary and reduce the R_s because the hot solvent vapor can effectively penetrate the films. Moreover, the surface morphology and the internal structure of the films can be

* Corresponding author. Tel.: +886 3 4711409x6426.

** Corresponding author. Tel.: +886 2 33664078.

E-mail addresses: huangyc@iner.gov.tw (Y.-C. Huang), suwf@ntu.edu.tw (W.-F. Su).

uniformly re-constructed by HSV annealing. After the HSV annealing, a ~20% improvement in PCE was achieved (2.12%) as compared to that of the as-sprayed film. Furthermore, the PCE of HSV annealed device with subsequent thermal annealing was further increased to 3.61%. Our study could pave a way to the fabrication of high efficient spray solar cells using the spray process.

2. Experimental

2.1. Materials

P3HT and PCBM are supplied from Rieke Metals, Inc. PEDOT:PSS is supplied from Baytron company. All the solvents used in this study are supplied from Aldrich company.

2.2. Active layer deposited by spray process

The P3HT/PCBM solution was first prepared by dissolving 2 mg of P3HT and 2 mg of PCBM in 1 ml of chlorobenzene (CB), stirred overnight at 45 °C in a glove box. Prior to the film fabrication, the ITO glass substrate was ultrasonically cleaned in a series of organic solvents (methanol, acetone, and isopropanol) and then treated with UV/ozone for 10 min. Poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid, PEDOT:PSS (Baytron AI 4083), was used as a hole transport layer (HTL). A 40-nm-thick layer of PEDOT:PSS was deposited on a cleaned ITO glass substrate by spin-coating at 5000 rpm for 1 min and drying at 120 °C for 20 min. The active layer was spray-coated in ambient conditions using an ExactaCoat system equipped with an AccuMist 120 kHz ultrasonic atomizing nozzle (Sono-Tek Corporation). Fig. 1 shows the schematic diagram of this system which is constructed by combining an ultrasonic atomizing nozzle with a controlled jet of air from the flat jet air deflector. An auto-solution injection controller (Fig. 1a) controls the injected flow rate of P3HT/PCBM solution into the ultrasonic nozzle from a solution inlet (Fig. 1c). The ultrasonic nozzle as shown in Fig. 1e can atomize P3HT/PCBM solution into droplets of about 15 μm in size. To spray the droplets of P3HT/PCBM onto the PEDOT:PSS coated ITO substrate, an air stream is flowed into flat jet air deflector (Fig. 1d) from an air inlet (Fig. 1b). The air stream allows low or high-impact of the atomized droplets onto the substrate by tuning the pressure of air stream from the air deflector. In our study, the injected flow rate of P3HT/PCBM solution was 0.1 ml min⁻¹ and the pressure of air stream was ~0.6 MPa. The ultrasonic nozzle tip was kept at 10 cm distance from the substrate. In this spray condition, the thickness of P3HT/PCBM films was ca. 300 nm.

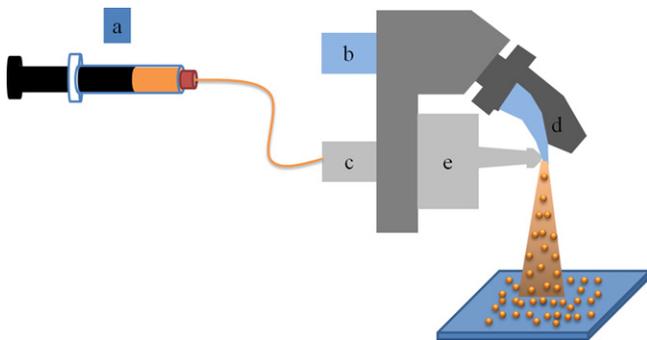


Fig. 1. Schematic diagram of spray-coater: (a) Auto-solution injection controller: control the injected flow rate of P3HT/PCBM blend solution; (b) air inlet: allow air stream to flow into air deflector; (c) solution inlet: allow P3HT/PCBM blend solution to be injected into ultrasonic nozzle; (d) flat jet air deflector: control air stream pressure to allow low or high-impact of the atomized spray onto the substrate; and (e) ultrasonic nozzle: atomized P3HT/PCBM blend solution into droplet.

2.3. Annealing treatment

For HSV annealing, 1,2-dichlorobenzene (DCB) was heated at various temperatures (45 °C~75 °C) in a Petri dish. P3HT/PCBM films were put into the Petri dish filled with hot DCB vapor for a few minutes and the surface of films would gradually become wet. After HSV annealing, the films were left to dry for roughly 1 min in ambient. For thermal annealing, the films were thermally annealed at 130 °C for 10 min in a glove box before cathode deposition.

2.4. Active layer characterization

The formation of intra-droplet boundary during the spray process was studied by an optical microscope (OM, Leica Microsystems, DM1750M). The morphology and conductivity of films were characterized using conducting atomic force microscope (C-AFM, Veeco, CP-II). A Pt/Ir₅ coated tip used in C-AFM setup serves as a mobile electrode to record morphology and local electric property simultaneously. UV–vis absorption spectroscopy (PerkinElmer Lambda 35) was used to monitor the absorption spectra of films. The thickness and surface profile of films were measured using a stylus profiler (AlphaStep D-100, KLA Tencor). A high resolution X-ray diffractometer (Rigaku TTRXA 3) was used to study the crystallinity of P3HT.

2.5. Device fabrication and characterization

After annealing treatment, the films were deposited with Ca and Al as cathode using thermal evaporation. ~30 nm of Ca and ~100 nm of Al were sequentially deposited at a high vacuum of 5×10^{-6} torr. The device area was determined by the covered cathode area because we did not etch the anode of ITO. In our study, the area of solar cells was 0.30 cm². The *J*–*V* characterization was evaluated under A.M. 1.5 illumination (100 mW/cm²) using a solar simulator (Abet technologies, Model # 11000). The EQE spectra were recorded under the illumination of a xenon lamp and a monochromator (Enlitech, QE-R).

3. Results and discussion

All the films of active layer of solar cells were prepared by the spray process; we called them as-sprayed films. The names of as-sprayed films after different treatments are defined as following: TA means thermal annealed film; the HSV annealed films were labeled according to the solvent vapor temperature and annealing time. For instance, the 45 °C 2 min HSV annealed film means the as-sprayed film was treated by the HSV at 45 °C for 2 min.

3.1. Morphology evolution and local electric property of HSV annealed films

The morphology of HSV annealed films at different conditions was studied by optical microscopy as shown in Fig. 2. Fig. 2a shows the as-sprayed P3HT/PCBM film which exhibits a heterogeneous morphology. An obvious droplet boundary was observed in the film which would generate a barrier to slow charge transport. The amount of droplet boundary was decreased sharply after solvent vapor annealing at 45 °C for 2 min, but there were few droplet boundaries remained (Fig. 2b). The droplet boundaries were further reduced by increasing the annealing time to 4 min (Fig. 2c). When the solvent vapor temperature was increased to 55 °C, the droplet boundary was eliminated regardless of 2 min (Fig. 2d) or 4 min (Fig. 2e) annealing time. Previous studies [38,39] have pointed out

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