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Morphological control and performance improvement of organic photovoltaic layer of roll-to-roll coated polymer solar cells



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ABSTRACT

We systematically investigated the thermal effects of drying process as well as thermal annealing on morphology and performance of inverted polymer solar cells (PSCs) fabricated by roll-to-roll (R2R) slot-die coating. Power conversion efficiency (PCE) of PSCs layer is strongly influenced by bulk heterojunction (BHJ) active layer. Compared to the conventional annealing process, we demonstrate that the drying process for transforming the wet active layer into solid-state film (an early polymer crystallization step) in the R2R process is a critical control of morphological evolution to the desired structure. We have demonstrated that a significant improvement in performance of inverted PSCs can be achieved by tuning the parameters in the drying process prior to the annealing process. This study provides the mechanistic understanding of how the drying and annealing processes affect the morphological evolution regarding to the crystallinity, BHJ structure and interface between layers. Moreover, with respect to environmental concerns, halogen-free are carried out as an alternative solvent to halogenated solvents. We successfully incorporate halogen-free solvent, *o*-xylene, with an elevated drying temperature for improving the performance of R2R slot-die coated inverted solar cells.

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1. Introduction

Polymer solar cells (PSCs) have attracted tremendous attention over the past decade and have been deemed to a promising photovoltaic technology due to their benefits such as light weight, low manufacturing cost, and compatibility with flexible and large-area applications [1–3]. The power conversion efficiency (PCE) of PSCs with a single bulk heterojunction (BHJ) structure consisted of conducting polymers as electron donor materials blended with fullerene derivatives as electron acceptor materials has been achieved 8–10% [4,5]. Furthermore, the PCE of PSCs has reached more than 10% with a multijunction structure, such as tandem and triple-junction PSCs [6–9]. With the rapid growth of PSCs' performance, many researching groups have focused on the field related to the commercialization of PSCs in recent years, for instance device stability [10–12] and large-area fabrication [1,13–17]. An inverted structure has been studied extensively to obtain a long device operation time [18]. In the inverted PSCs, the charges drift to opposite electrodes in comparison with conventional PSCs. Therefore, inverted PSCs allow the use of high work function metals as top electrode, such as Ag and Au, which are less air-

sensitive. In addition, an electron transport layer (ETL), such as zinc oxide (ZnO) [19] and caesium carbonate (Cs_2CO_3) [20], is used to cover on the transparent indium tin oxide (ITO) electrode, to replace poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) to prevent from etching ITO electrode due to the acidic nature of PEDOT:PSS.

Large-area coating of PSCs have been developed to facilitate the mass production, such as spray [14,21], inkjet printed [22], gravure printing [23,24], slot-die and screen printing processes [25–28]. One of the most attractive advantages of PSCs is the high mechanical flexibility that is suitable for roll-to-roll (R2R) processing technique. The R2R processing technique has been used to fabricate PSCs due to its fast process [1,29]; however, it is still challenging to achieve a high PCE. Among these processes, slot-die coating is the most widely used in the R2R process for the large-area production of PSCs due to its reproducibility, high coating quality and high throughput. Recently, several studies have been demonstrated the ability to fabricate large-area PSCs by slot-die coating [17,26,30–34]. Although substantial studies have been performed on the development of conventional PSCs fabricated by slot-die process, the high-efficiency inverted slot-die-coated PSCs are still critically lacking [35,36]. The literature pointed out that the PCE of PSCs layer is strongly influenced by BHJ active layer or polymer crystallinity [37–42]. The BHJ structure is a phase-separated interpenetration network and can be tailored by various treatments, such as thermal annealing [37], addition of

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nanoparticles [38], change of acceptor components [39,40] and additive [42]. The BHJ structure can also be tailored by the radical oxidation with nitrogen plasma treatment [43]. The plasma treatment can provide the high energy of ions diffusing into the surface layer to produce the high-area surface and serve as the defects/doping inside the structure (inducing the other reactions to form local BHJ structure). In comparison with the spin-coating process, the slot-die coating process is a relatively slow thin-film formation and then crystal growth process. The films fabricated by spin coating are usually dried in a few seconds because the substrate is rotated at high speed. However, the drying rate and drying temperature of the films deposited by the slot-die or blade coating could cause a different mechanism (P3HT crystallization and PCBM aggregation) during drying process from wet film to dry film, which influence the subsequently thermal annealing effect [44]. Many factors affect the drying process, such as the mass solvent of the coating materials, solution concentration, deposit amount of the solution and coating rate. Therefore, we can optimize the performance of slot-die coated devices by controlling the film formation and the subsequent crystallization growth more effectively, but such a manuscript cannot be conducted in the spin coat process. Basically, few studies [17,45] reported how to thermally tailor BHJ structure in the R2R slot-die coating process different from the well-known annealing treatment for spin-coating process.

In this study, high-efficiency inverted PSCs consisted of the blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) were fabricated by R2R slot-die coating process. The past researches only focused on the effect of conventionally thermal annealing on the performance. There are very few studies demonstrating how the drying process as the first pre-treatment affects the performance. We illustrated herein that the control of the drying process from wet film to dry film plays an important role in tailoring the device performance; even these P3HT/PCBM dry films were treated with the same thermal annealing process. We also investigated the factors, including the drying temperature for solidification of wetly coated film into dry film (control of the early crystallization), determining the performance of inverted PSCs, absorption behavior and nanostructure evolution. Our results show an improvement in performance of inverted PSCs coated at a high drying temperature of 110 °C. Halogenated solvents, such as chloroform (CF), chlorobenzene (CB) and 1,2-dichlorobenzene (DCB), are widely used as the host solvent of photoactive layer due to the high solubility. However, halogenated solvents are not acceptable in the mass production because of their toxicity, corrosive property and environmental concerns. In recent, halogen-free solvents are studied for an alternative to halogenated solvents [46]. In this study, we successfully incorporated halogen-free solvent, o-xylene, in the slot-die coating process and obtained an equivalent performance to that of PSCs fabricated by halogenated solvents.

2. Experimental

2.1. Materials

The ITO-coated polyethylene terephthalate (PET) substrate was purchased from Optical Filters Ltd (EMI-ito 15, surface resistance of 15 Ω/square). Zinc acetate and aluminum acetate were obtained from Alfa Aesar and Aldrich, respectively. The surfactant Zonyl FS-300 was purchased from Fluka. Polyethylenimine ethoxylated (PEIE) received from Aldrich was diluted in 2-methoxyethanol into 0.4 wt% of solution. We prepared the precursor of aluminum doped zinc oxide (AZO) solution by dissolving zinc acetate (1 g), aluminum acetate (0.015 g) and Zonyl FS-300 (0.06 g) in 10 g of

deionized water (DIW). The as-prepared AZO precursor was filtered through a 0.45 μm filter, and then diluted with DIW by the volume ratio of 1:1. After that, the AZO precursor was mixed with 20 vol% of PEIE to form a hybrid solution of AZO:PEIE₂₀. P3HT (MW~35,000, PDI and RR are ~2 and 90%, respectively) and PCBM were provided by Rieke Metals. We prepared the active layer solution by dissolving 12 mg of P3HT and 12 mg PCBM in 1 ml chlorobenzene (CB) or o-xylene solution.

2.2. R2R slot-die coating process for PSC fabrication

We slot-die coated the ETL and photoactive layer by using Coatema R2R system (Coatema smartcoater, Germany). Because our laboratory-scale R2R equipment is not suitable for full-R2R process, the PET/ITO substrate was cut into 10 × 10 cm² and it was spliced in the machine. The widths of web and slot-die coater are 14.2 and 10 cm, respectively. All the coating speed used for each layer is 1 m/min. The solution output rates for ETL and active layer are 0.8 and 1.2 ml/min, respectively, using a mask of 100 μm thickness. Prior to the ETL deposition, the flexible ITO-coated PET substrate was treated with air plasma at the web speed of 1 m/min. The experimental procedure, photographs of Coatema R2R system and device structure were described previously [25]. There are two ovens we used here. One oven with a length of 50 cm is installed in the R2R system for drying the active layer from wet film to dry film. We called it as R-oven. The other one, called A-oven, is set in ambient atmosphere. To stably keep the temperatures of ovens, we pre-heated these ovens for 40 min before testing. For the photovoltaic devices fabrication, we dried the deposited ETL at 150 °C for 10 min in the A-oven. The deposited wet active layer was dried at various temperatures in the R-oven, and then thermal annealed (TA) at 130 °C for 10 min in the A-oven. The dried thicknesses of ETL and active layer are about 60 and 150 nm, respectively. We thermally evaporated hole transport layer (HTL) of MoO₃ and silver electrode on the active layer in a separate thermal evaporator. The thicknesses of MoO₃ and silver were 5 nm and 100 nm, respectively. The structure of the devices is PET/ITO/ETL/active layer/MoO₃/Ag. The device area is defined by the metal electrode with the area of 1 × 0.3 cm². It is noteworthy to mention that all the R2R coating processes were conducted in air.

2.3. Performance measurement and structural characterization

Current density–voltage curves were measured by using a solar simulator (Abet technologies, Model # 11,000) under A.M. 1.5 illumination (100 mW/cm²) and ambient condition. All slot-die coated layers for the relevant tests were fabricated in the same batch, and the devices were not encapsulated. The thicknesses of films were measured by a profilometer (Alpha Step D-100, KLA Tencor). Surface roughness and morphology of the blend films were analyzed by atomic force microscopy (AFM, Digital Instruments, Nanoscope III). The UV–vis absorption and photoluminescence (PL) spectra of the P3HT:PCBM films were obtained using a UV–vis spectrometer (Perkin Elmer Lambda 35) and a spectrofluorometer (Perkin Elmer FS-55). The R_s and R_{sh} of PSCs were evaluated based on the measured $J-V$ curves.

3. Results and discussion

Nanomorphology of photoactive layer plays a critical role in its performance. In the R2R slot-die coating process, the BHJ nanomorphology is strongly influenced by the thermal effects of two steps: (1) drying process to evaporate the solvent for forming the solid-state film (i.e., early polymer crystallization) and

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