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Performance improvement of large-area roll-to-roll slot-die-coated inverted polymer solar cell by tailoring electron transport layer

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ABSTRACT

For attaining the commercialization, the large-area roll-to-roll (R2R) slot-die-coated inverted polymer solar cells (PSCs) would be promising. The electron transport layer (ETL) plays an important role in scale-up development from small PSCs. In this work, the active layer comprising poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and sol–gel zinc oxide (ZnO) ETL were slot-die coated on flexible PET/ITO substrate as reference based on the R2R process. Aluminum-doped ZnO (AZO) instead of ZnO was also adopted. For further improving the performance of large-area PSC, we used polyethylenimine ethoxylated (PEIE) material to tailor the nanostructure of ZnO and AZO ETLs for reducing the surface traps on ETLs using two approaches: (1) ZnO/PEIE bilayer formed by sequential deposition and (2) ZnO:PEIE hybrid composite as ETLs. The present work would demonstrate the optimum material (fabrication) parameters and how the performance of the R2R large-area slot-die coated PSC can be improved by modifying the ZnO- and AZO-based ETL structures. We also perform the various measurements and structural characterization to understand the relationship among R2R slot-die coating process, charge transport properties, film structure and photovoltaic performance as increasing the device areas from 1×0.3 cm^2 (power conversion efficiency: 2.69%) to 1×1 cm^2.

1. Introduction

Polymer solar cells (PSCs) increasingly attract the interest among the solar cells due to the advantages of low weight, low cost, flexibility, easy fabrication, low energy-pay-back time, etc. [1,2]. Due to these advantages, PSCs have great expectations for commercialization referring to minimum materials waste, scalability, high throughput and mass-production. However, most of PSC researches focused on the small-area devices fabricated by spin-coating. Until now, relatively few works developed toward the target of commercialization because of the performance reduction of PSCs devices fabricated by large-area process. There have existed several coating or printable processes used for large-area PSC fabrication, such as spray coating [3,4], ink-jet printing [5,6] and roll-to-roll (R2R) processes, doctor-blade coating [7], screen printing [8] and slot-die coating [9–20]. Among these processes, slot-die coating is the most potential candidate for the large-area and solution-processed process toward commercialization currently.

On the other hand, stability of the PSCs is an important issue for the PSC commercialization. Inverted PSC has much better stability than that of conventional PSC because its structure has no contact between poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) layer (as hole transport layer) and ITO layer (electrode), and a low work-function Al cathode [21]. Thus, the inverted PSC becomes necessary for the future commercialization. In the usual inverted PSC structure, the electron transport layer (ETL) comprising ZnO nanoparticles is deposited on ITO cathode. However, the use of ZnO layer causes the problems reducing the power conversion efficiency (PCE) because of (1) many traps/defects on the surface of nanoscale ZnO particles (trapping the electrons and thus causing high series resistance) [22], (2) change of interfacial morphology between ETL and active layer [22], and (3) difficulty controlling the layer thickness depending on the particle size [23,24]. In addition, the PCE of conventional PSCs usually decreases as the device extended from small-area cell to large-area module because of the increasing sheet resistance or internal defects. However, the introduction of ZnO ETL into the inverted PSCs would further amplify the PCE degradation because of its limiting conductivity, especially when the OPV device is scaled up. Therefore, the modification and improvement of ZnO ETL play critical roles in the development of the commercially large-area inverted PSCs.

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In the present work, the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as active layer and ZnO as ETL were both slot-die coated on flexible PET/ITO substrate through roll-to-roll (R2R) process. Moreover, aluminum-doped ZnO (AZO) instead of ZnO was also adopted in this work for attaining easy fabrication (water-based) and conductivity improvement [25]. For further improving the PCE of large-area inverted PSC, we used polyethylenimine ethoxylated (PEIE) material to tailor the nanostructure of ETL and reduce the surface traps from ETLs (based on ZnO and AZO materials) using two approaches: (1) ZnO/PEIE bilayer [26,27] formed by sequential deposition of PEIE on top of ZnO layer, and (2) hybrid ZnO:PEIE composite [22] as ETLs. These approaches were incorporated to our R2R large-area slot-die process, respectively, in order for effectively reducing the surface traps on the metal oxide nanoparticles [22] or film layer [26,27], adjusting the work function and improving the interface morphology between layers [23]. Basically, each R2R large-area slot-die process for PSC fabrication has its optimum parameters due to the different machines, operation parameters and solvent evaporation (film formation) conditions. The present work would demonstrate how the performance of the R2R large-area slot-die coated PSC can be improved by modifying the ZnO- and AZO-based ETL structures (in the form of the bilayer and hybrid layer containing PEIE). We also performed the various measurements of photovoltaic properties and structural characterization to understand (1) the morphological control of active layer and ETL prepared by the R2R slot-die coating process and the subsequent annealing treatment, and (2) the influence of the various R2R slot-die coated ETLs on the improvement of performance of PSC. This is the first case applying the modification of ETL to the R2R slot-die coated PSC. These results provide the valuable information on optimization of large-area inverted PSC device fabrication.

2. Experiments

2.1. Materials

P3HT and PCBM were purchased from Rieke Metals. The P3HT:PCBM solution (12 mg/ml: 12 mg/ml in chlorobenzene) was prepared for active layer. PEIE solution was provided by Aldrich. The ITO-coated PET substrate is received from Optical Filters Ltd (EMI-ito 15, surface resistance of 15 Ω/square). To prepare ZnO precursor solution, we dissolved zinc acetate (1 g) and ethanolamine (0.28 g) in 10 ml of 2-methoxyethanol. The formed pristine ZnO was then diluted with IPA by the volume ratio of 1:10. To prepare the AZO solution, aluminum acetate (0.015 g), zinc acetate (1 g) and Zonyl FS-300 (0.06 g; surfactant) were dissolved in 10 g of deionized water (DIW). The formed pristine AZO was then diluted with DIW by the ratio of 1:1. Prior to the ETL deposition, the flexible ITO-coated PET substrate was ultrasonically cleaned in a series of organic solvents (methanol, acetone and isopropanol), and then treated with O_2 plasma for 3 min. PEIE was diluted in 2-methoxyethanol into 0.4 wt% of solution. For the bilayer case, PEIE solution was then diluted with IPA by the volume ratio of 1:18. For preparing the solution in the hybrid ETL case, ZnO or AZO was mixed with different volume ratio of PEIE (i.e., 5, 10, 20 and 40 vol % PEIE).

2.2. R2R slot-die coating process for PSC fabrication

The P3HT:PCBM active layer and various ETLs were slot-die-coated on the ITO-coated PET substrate under ambient conditions using Coatema R2R system (Fig. 1a), and the width of roller and our slot-die is 14.2 and 10 cm, respectively. The coating speed for active layer and ETLs (two types: bilayer and hybrid layer) is 1 m/min. The deposited ETLs were dried at 150 °C for 60 and 10 min for ZnO and AZO, respectively. The thickness of both ETLs is about 60 nm, and the diameter of ZnO and AZO nanoparticles is about 50–60 nm. After the desired deposition of P3HT:PCBM active layer, the thermal annealing at 130 °C for 10 min was conducted. It is worthy to note that our laboratory scale R2R machine is not suitable for full-R2R process; therefore, the PET/ITO foil was cut to 10×10 cm^2 and it was spliced in the machine, as shown in Fig. 1b. The dried ITO/ETL and ITO/ETL/photoactive layer foils were thermally treated or annealed in an ambient oven outside the machine. The picture of PET/ITO foil with ETL and P3HT:PCBM layer by slot-die coating process is shown in Fig. 1c. The corresponding PSC devices based on the above processes were fabricated with a structure PET/ITO/ETL/BHJ active layer/MoO_3/Ag.

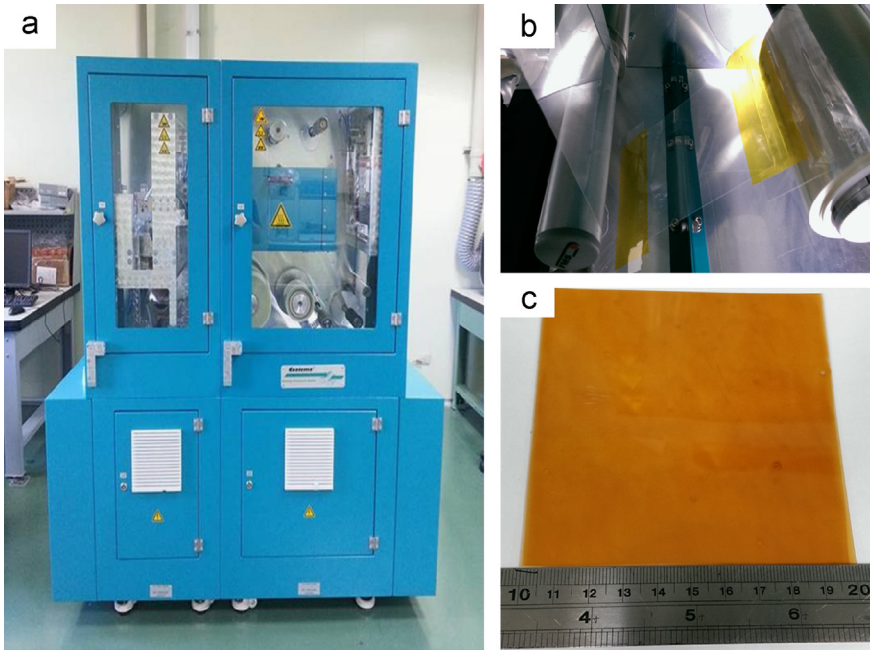

Fig. 1. Photograph of (a) Coatema R2R system, (b) PET/ITO foil stuck in the R2R machine and (c) the PET/ITO foil with ETL and P3HT:PCBM layer by slot-die coating process.