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Modification of a PEDOT:PSS hole transport layer for printed polymer solar cells

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ABSTRACT

Printed polymer solar cells (PSCs) were demonstrated by doctor-blade coating a zinc oxide (ZnO) material, slot-die coating photoactive and PEDOT:PSS materials, and screen-printing a silver (Ag) electrode. To make a PEDOT:PSS film on a hydrophobic photoactive layer, we tried to modify various types of commercial PEDOT:PSSs (Clevios P, N 1005, S 305, AI 4083) with the surfactants Zonyl FS-300 and FS-31 (Capstone® Dupont™). The addition of the FS-31 surfactant successfully reduced the contact angle of PEDOT:PSS on the hydrophobic photoactive layer, and the wetting property was sufficiently developed, even using a slot-die coating method. A relatively thick PEDOT:PSS layer, Clevios P modified by FS-31, prevents the penetration of the Ag ink solvent into the photoactive layer. Accordingly, a power conversion efficiency of 4.06% was attained in the printed PSCs.

1. Introduction

In recent decades, polymer solar cells (PSCs) based on bulk heterojunction (BHJ) blends comprising conjugated polymers and fullerene derivatives have become a popular area of study as a next-generation energy source due to their advantages of flexibility, low cost, and high-throughput production with easy printing processes [1–6]. Intensive research on PSC applications has given rise to outstanding progress in power conversion efficiency (PCE), and over 10% PCE has been reported in a lab-scale PSC device [7–11]. However, a high PCE for small-scale cells, which are usually fabricated using the spin-coating method and vacuum deposition, must be realized using an appropriate printing method for the ultimate goal of the industrial mass production of PSCs. Toward this goal, many researchers have tried to fabricate printed PSCs using various printing technologies, such as slot-die coating, screen printing, gravure printing, and flexographic printing [12–16]. The printing of metal electrodes has also been studied for the commercialization of PSCs [17–20].

Until now, most printed PSCs have been demonstrated in an inverted architecture (transparent electrode/electron transport layer/active layer/hole transport layer/top electrode), mainly due to the well-developed and commercialized Ag ink for top electrode deposition using a printing process. In the structure of PSCs, selective electron transport layers (ETLs) and hole transport layers (HTLs) are required for efficient charge collection to the outer electrodes. Zinc oxide (ZnO), titanium oxide (TiO_x), and n-type polyelectrolytes have been commonly used as ETLs due to their band structure for selective electron transport and work-function tuning properties [21–23]. WO_x, MoO_x, V_2O_x and PEDOT:PSS are well known selective hole transport layer materials and are used for lab-scale PSC cell fabrication using the evaporation technique or spin-coating method [24–27]. Among the HTL materials, PEDOT:PSS is the most promising candidate for printed PSC fabrication and large-area module production using printing methods, as various types of PEDOT:PSS are well commercialized, and their basic properties have been studied.

However, water-based PEDOT:PSS has a wettability problem on the hydrophobic photoactive layer, and several studies on the improvement of wettability have been reported by the modification of PEDOT:PSS through the addition of solvent or surfactant [28–31]. To use a PEDOT:PSS layer as an HTL in printed PSCs, more investigation is needed because early studies on modified PEDOT:PSS were designed for the spin-coating method, which is not suitable for mass production. There is a big difference between the spin-coating method and the printing method using the meniscus coating principle. In the spin-coating method, the film formation is

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instantaneous because the centrifugal force results in the fast evaporation of the solvent. In contrast, the meniscus coating method has no external force to make an even film except for surface tension, and only natural evaporation exists. Thus, it could be expected that the wetting property of PEDOT:PSS should be better in the printing process than in the spin-coating method to make a uniform film on a hydrophobic surface.

To create a well-coated PEDOT:PSS film using the meniscus coating method, we systematically added non-ionic fluorosurfactants (Zonyl FS-300, FS-31) to a variety of PEDOT:PSSs, such as Clevios P (Heraeus), neutral PEDOT:PSS N 1005 (Agfa), high-conductivity PEDOT:PSS S 305 (Agfa), and low-viscosity PEDOT:PSS AI 4083 (Heraeus). Then, the modified PEDOT:PSS was coated using the slot-die coating method, which is the most promising printing method due to its compatibility with roll-to-roll printing and one-dimensional direct patterning. Both surfactants FS-31 and Zonyl FS-300 reduced the surface tension between the PEDOT:PSS HTL and the photoactive layer, making it possible to deposit PEDOT:PSS using the meniscus coating method onto any photoactive layer with a contact angle below 25°.

The modified PEDOT:PSS layer was also used as a protective layer against the Ag ink solvent for efficient printed PSCs. To prevent the detrimental effect of the Ag ink solvent, the deposited PEDOT:PSS layer has to be thick. There is a limit to the film thickness that can be achieved using low-viscosity AI 4083 PEDOT:PSS, but the Clevios P and N 1005 PEDOT:PSSs were deposited with sufficient thickness to prevent Ag ink solvent penetration when using the slot-die coating method. The measured device performance showed no chemical damage to the photoactive layer after the screen printing of Ag ink onto each of the Clevios P and N 1005 PEDOT:PSS layers. As a result, the printed PSCs were demonstrated using the modified PEDOT:PSS solution. The best power conversion efficiency in printed PSCs is 4.06% under air mass (AM) 1.5 conditions.

2. Experimental

Fig. 1 shows the device structure and our printing machines for each layer of the deposition process. The inverted structure of the PSCs was fabricated by a printing method consisting of doctor-blade coating a zinc oxide (ZnO) material, slot-die coating a photoactive P3HT:ICBA and a PEDOT:PSS layer, and screen-printing a silver (Ag) electrode. Fig. 1(b) shows the three PSC devices fabricated using the printing method; each of them has the same active area of 1×1 cm^2.

2.1. ZnO layer

The ZnO precursor was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H2O$, Aldrich, 99.9%, 1 g) and ethanolamine ($NH_2CH_2CH_2OH$, Aldrich, 99.5%, 0.5 g) in isopropyl alcohol ($CH_3OCH_2CH_2OH$, Aldrich, 99.8%, 50 g) under stirring for 24 h. To fabricate printed PSCs in the air, ITO/glass substrates were cleaned with detergent and then sequentially washed using ultrasonic treatment in de-ionized water, acetone and IPA. The ZnO solution was coated onto the ITO/glass substrate using a doctor blade coater (Fig. 1(e)) at 40 °C and then annealed at 150 °C for 20 min in the air.

2.2. Active layer

P3HT (purchased from Rieke Metal) and ICBA (purchased from Nano-C) were dissolved in the DCB solvent at concentrations of 12 mg/mL and 10 mg/mL, respectively. The P3HT:ICBA composite solution was coated on top of the ZnO layer in air using the slot-die coating method at room temperature. The pumping rate was 10 mL/h when using a mask of 50 μm thickness and a coating speed of 2.0 m/min. Then, the P3HT:ICBA-coated samples were put into Petri dishes to undergo a solvent annealing process for 1.5–2 h. The thickness of the dried P3HT:ICBA film was 250 nm.

2.3. PEDOT:PSS layer

Various poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) solutions were purchased: Clevios P and AI 4083 from Heraeus and N 1005 and S 305 from Agfa. Clevios P and N 1005 were diluted with de-ionized water to reduce their viscosity to obtain thinner films. The surfactants Zonyl FS-300 and FS-31 (Capstone®Dupont™) were added into the PEDOT:PSS solutions in different ratios (1–4 wt%) 24 h prior to coating. The PEDOT:PSS solution was coated on top of the photoactive layer in air using the slot-die coating method at room temperature and then annealed at

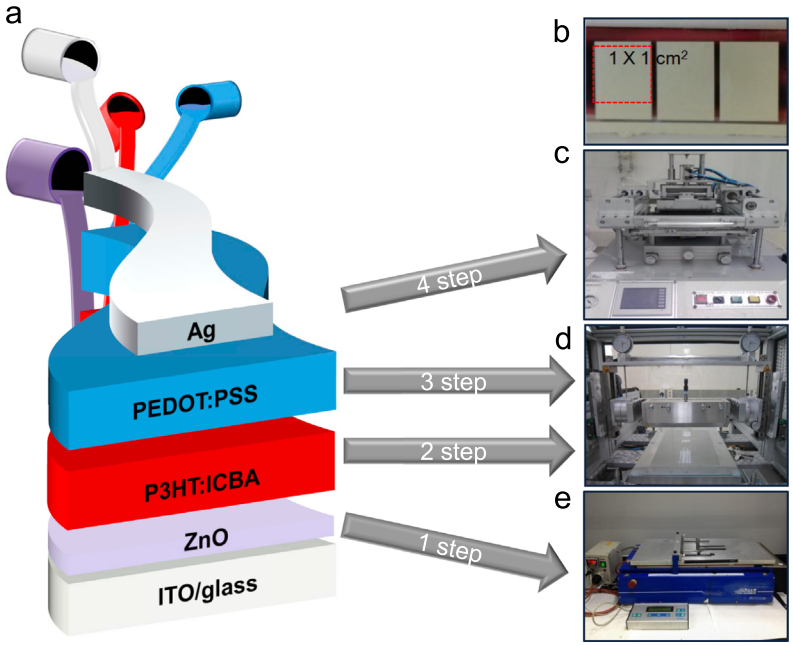

Fig. 1. (a) Inverted device structure of printed PSCs. Photographs of (b) fabricated PSC devices, (c) screen printer, (d) slot-die coater, (e) doctor blade.