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Patternable brush painting process for fabrication of flexible polymer solar cells

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ABSTRACT

The brushing painting method is one of the typical solution processes, which makes it possible to fabricate electronic devices by simply using polymers. For the fabrication of modules and large-area devices, however, a patterning process is required for each layer. Due to the problems associated with the conventional patterning, many studies have been conducted to develop new patterning . In this study, we successfully fabricated bulk heterojunction (BHJ) structured polymer solar cells (PSCs) on a plastic substrate with an active layer through the brushing painting process. In particular, flexible PSCs with hole transporting and photo-active layers formed by the repositionable adhesive-based patterning method were fabricated to produce large-area solar cells. The fabricated PSCs exhibited Jsc, Voc, FF and power conversion efficiency (PCE) values of 8.5 mA/cm^2, 0.636 V, 48.8% and 2.6%, respectively. In other words, they were more efficient than those fabricated by the spin coating method. In particular, an increase in the Jsc and FF values was observed when the series resistance (Rs) decreased to 29 Ω cm^2 while the shunt resistance (Rsh) increased to 2018 Ω cm^2.

1. Introduction

The fabrication of devices such as polymer solar cells (PSCs) [1–7], polymer light-emitting diodes (PLEDs) and organic thin-film transistors (OTFTs) as next-generation devices has attracted a great deal of attention. In fact, there have been numerous studies on this topic. The π-conjugated polymers, which are used in the active layer of these devices have good stability, good mechanical properties and excellent electro-optical properties. As they enable the solution process to be used, it is possible to fabricate low-cost and large-area devices by a simple method such as spin coating instead of vacuum deposition. For the fabrication of modules and large-area devices, however, a patterning process is required for each layer. Various patterning methods can be used, including plasma etching, plasma patterning [8,9] and laser ablation [10]. To apply the plasma patterning method, however, etching should be carried out by a plasma after forming a photoresist layer (e.g.: water soluble resist, protective parylene, etc.) as an etch mask. In addition, the application of a flexible substrate can cause the dimensional distortion of the substrate and degradation of the inherent properties [8]. Hence, various methods, which enable the polymer solution to be directly patterned have been investigated, such as ink-jet printing, slot-die coating and the roll-to-roll process [11–16].

Recently, low cost and flexible solar cells have become a reality in PSCs thanks to the increase in efficiency that was obtained following studies on their material and device structure. In particular, numerous studies have been performed on the optimization of the polymer: PCBM blend conditions, thermal treatment and related coating processes. In the studies by Li et al. [17] and Yang et al. [18], the PCE reached 4% due to the improvement in the crystallinity of P3HT after the pre/post-thermal treatment of the device that was fabricated using the spin-coating method by blending poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}butyric acid methyl ester (PCBM). Aernouts et al. [19] fabricated PSCs, which had a pinhole free film, with PCE of 1.4% through the optimization of the polymer: PCBM blend concentration by using the ink-jet printing method. Huang et al. [20] fabricated PSCs to which the stamping method was applied with a PDMS stamp and reported a PCE of 3.2%. Wang et al. [21] reported inverted PSCs with a PCE of 3.19% by applying the stamping method that used a UV curable resin coated polycarbonate film. However, it was difficult to use them in the roll-to-roll process, because of the additional need for a complicated patterning process.

In addition, Kim et al. [22] reported an improvement in the efficiency of polymer solar cells as a result of the improved organization of P3HT afforded by a simple brush painting method. This highly ordered active layer, which was spun off from the P3HT and PCBM interfaces, exhibited improved charge transport. As a result, the PCE was increased up to 5.4% through the increase in fill factor. Also, the brush painting method makes it possible to fabricate annealing free PSCs efficiently for the mass production

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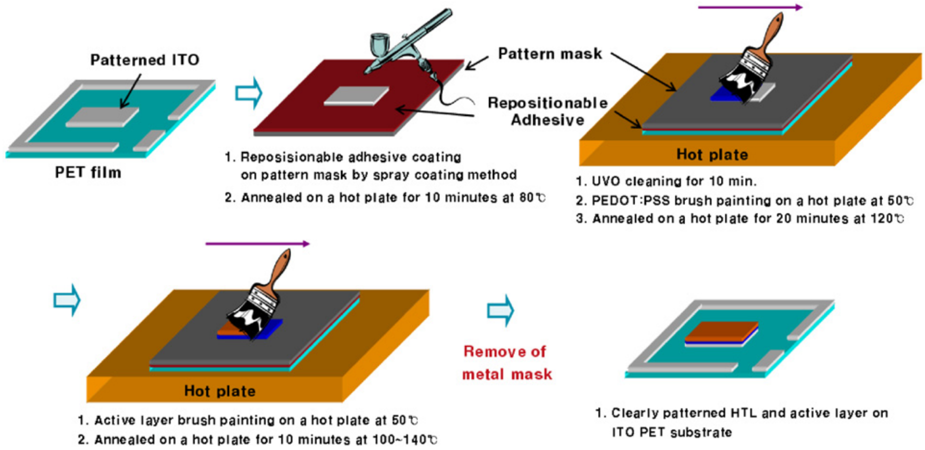

Scheme 1. Manufacturing process of flexible PSCs by patternable brush painting method.

of organic devices based on high-speed roll to roll systems [23]. In previous research, however, the brush painting method was used to fabricate a simple unit solar cell. Furthermore, there have been no studies in which sub-modules or large area cells were fabricated by applying the bush painting method to a plastic substrate. In order to make large area devices or modules, a patterning process is necessary. However, in the case where a patterned mask was used, as in the screen printing method, capillary phenomena were generated between the mask and substrate because of the low viscosity of the polymer ink. Therefore, a clean pattern could not be obtained by the conventional brush painting method. As shown in Scheme 1, a simple process, which makes it possible to pattern hole transporting and photo active layers using a repositionable adhesive was developed. Furthermore the traditional shortcomings of plastic substrates, viz. the dimensional distortion of the substrate and degradation of its inherent properties [8] were not found in this process. Moreover, this new method makes it possible to obtain very clear pattern images and to fabricate large-area PSCs. In addition, in this paper, we compared the properties of the devices fabricated using the spin-coating method, including their J–V and IPCE characteristics, and observed their surface morphology by AFM.

2. Experimental

2.1. Materials

The ITO PET film, which is used as the transparent electrode is an SKC product (PET: 125 μm, ITO:170 nm, 100 Ω/sq). As the repositionable adhesive, used in the patterning hole transporting and photo-active layers, a 3M (Model: #75 repositionable adhesive) product was used. In addition PEDOT: PSS (AI 4083) was purchased from Clevios and poly(3-hexylthiophene, P3HT), which was used as a donor material in the photo-active layer was purchased from Rieke metal. $PC_{61}BM$, an acceptor material was purchased from Nano C.

2.2. Measurements

All of the thin films were fabricated using a GMC2 spin coater (Gensys, Korea), and their thickness was measured using an alpha step 500 surface profiler (KLA-Tencor). In addition, the electro-optical properties of the fabricated device were characterized with a Keithley 2400 source meter unit (Keithley) and solar simulator (Newport). The thin film morphology of the fabricated device was measured by atomic force microscopy (PSIA XE-150).

2.3. Cleaning of PET film

To clean the PET film, sonication was performed using a detergent (Alconox® in deionized water, 10%), acetone, IPA (isopropyl alcohol) and deionized water in the order listed, for 20 min each. The moisture was removed by blowing thoroughly with N_2 gas. In order to ensure the complete removal of all of the remaining water, the ITO was baked on a hot plate for 10 min at 100 °C. For the hydrophilic treatment of the PET surface, it was cleaned for 10 min in a UVO cleaner.

2.4. Preparation of pattern mask

As shown in Fig. 2a, a square-patterned (15 mm × 15 mm) mask made of SUS 304 was prepared. After cleaning the pattern mask in the same manner as that of ITO PET, the 3M repositionable adhesive was evenly sprayed on it using the spray-coating method. After the coating process, the residual solvent was removed from the repositionable adhesive. Additionally, to increase the strength of the adhesion to the pattern mask, it was annealed at 80 °C on a hot plate for 10 min.

2.5. Fabrication of flexible PSCs by patternable brush painting method

After attaching the repositionable adhesive-coated pattern mask onto the patterned ITO PET, UVO cleaning was performed for 10 min to make the ITO PET surface hydrophilic. To form the hole transporting layer, the masked ITO PET substrate was placed on a hot plate preheated at 50 °C and PEDOT: PSS was brush painted at a speed of 1 cm/s. As a result, a film with a thickness of about 40 nm was obtained. To eliminate the residual solvent, it was annealed on a hot plate at 120 °C for about 20 min. It was possible to regulate the thickness of the PEDOT: PSS and photo-active layers by adjusting the brushing speed. Fig. 1 shows the structure of the flexible PSCs and the chemical structure of the material used in the photo-active layer. As shown in this figure, the photo active ink was blended in ortho-dichlorobenzene (ODCB) at a ratio of 1:0.6 between the donor material, P3HT, and the acceptor material, $PC_{61}BM$, at a concentration of 3.0 wt% and annealed at 90 °C for about 30 min.

After placing the PEDOT: PSS-coated ITO PET substrate onto the hot plate preheated at 50 °C, the photo-active ink was brush painted at 1 cm/s. As a result, a film with a thickness of about 130 nm was obtained. To remove the residual solvent and determine the optimum annealing temperature, it was annealed at temperatures ranging from 100 to 140 °C for about 10 min.