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Effects of solvent-vapor annealing on bulk-heterojunction morphology of photoactive layers prepared by electrostatic spray deposition

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ABSTRACT

We studied the effects of solvent-vapor annealing (SVA) on the device performance of bulk-heterojunction organic photovoltaic solar cells. Electrostatic spray deposition (ESD) was used to prepare photoactive layers composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) blend. While the surface of the photoactive layer could be flattened by SVA, excessive treatment resulted in a decrease in open-circuit voltage. We attribute this to too large vertical phase separation within the P3HT:PCBM blend and accumulation of P3HT on the surface of the photoactive layer, which can induce recombination of photogenerated charges at the cathode/photoactive layer interface. A decrease in the open-circuit voltage could be prevented to some extent by depositing the photoactive layers using smaller droplets produced in the ESD process; this was probably due to the slower progress of vertical phase separation. Furthermore, introducing LiF as a hole-blocking layer between the cathode and the photoactive layer significantly reduced recombination-related leakage current, thereby preventing a decrease in open-circuit voltage.

1. Introduction

Organic photovoltaic solar cells (OPVs) have gained considerable attention as a promising candidate for ubiquitous power sources that are inexpensive, lightweight, and flexible [1–11]. Simple roll-to-roll or printing processes for mass production of these devices are expected to reduce fabrication costs significantly [12–16]. Bulk-heterojunction (BHJ) photoactive layers have been extensively studied since the BHJ concept dramatically increased the interfacial area between electron donor and acceptor for highly efficient dissociation of excitons into free charges [5,15–22].

In this study, photoactive layers composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) blend have been prepared by electrostatic spray deposition (ESD). ESD is a printing method that can tailor the morphology of photoactive layers by varying the process conditions [3,23]. Electrospraying is an electrohydrodynamic liquid atomizing technique that can generate monodisperse droplets with diameters ranging from 100 μm down to several tens of nanometers [24,25]. The solvent evaporation rate of droplets can be controlled to some extent by adjusting the solution condition and deposition parameters [10]. Post-drying treatments with high curing temperature or time-consuming evaporation of residual solvents can be omitted when the photoactive layers are prepared in dry conditions [26]. However, the surface of the photoactive layer prepared in a dry condition is relatively rough due to the existence of a number of droplet traces [5,27], and the presence of the inter-droplet boundaries limits the device performance due to large series resistance [15]. High-temperature thermal annealing (over 150 °C) is generally required for devices fabricated using ESD to improve the crystallinity or molecular orientation of the photoactive layers, thereby enhancing the power conversion efficiency (PCE). However, such high-temperature treatments are not applicable to roll-to-roll processes since flexible plastic substrates are not available [9].

Instead of high-temperature thermal annealing, we have performed solvent-vapor annealing (SVA) at temperatures below 100 °C for P3HT:PCBM BHJ photoactive layers. The inter-droplet boundaries on the surface of the photoactive layer can be eliminated by SVA, which leads to a decrease in series resistance [15]. A significant decrease in the surface roughness of the photoactive layer also provides a good contact with the cathode, resulting in increased shunt resistance [9,28]. The device performance of OPVs could be considerably enhanced by SVA treatment [4,22]. However, evolution of the vertical phase separation in the photoactive layer occurs during SVA because the P3HT surface energy is substantially less than that of PCBM, and consequently P3HT is preferentially concentrated on top of the photoactive layer [3,5,10,18]. Since SVA kinetically alters the vertical phase morphology of the photoactive layer, the device performance could deteriorate upon excessive treatment due to the larger degree of phase separation [3,9,22]. In the present work, the solar cell performances were compared under various SVA conditions, and the effects of SVA on the morphology of the photoactive layer were investigated by UV–vis absorption spectroscopy. We demonstrated that both controlling the morphology of the photoactive layer

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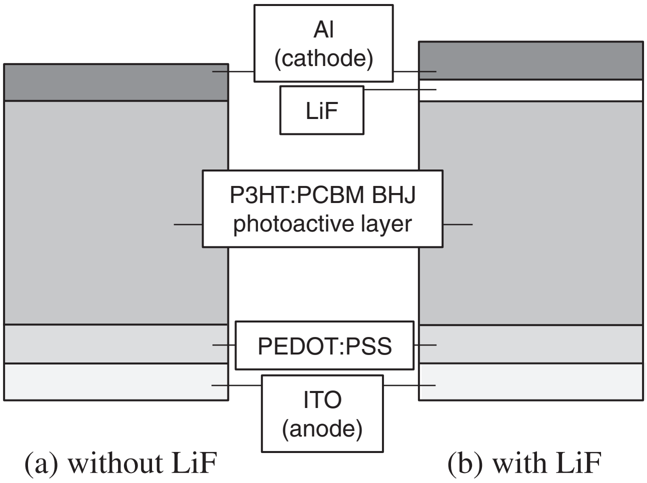

Fig. 1. Device architectures fabricated in this study: (a) without LiF, (b) with LiF.

and optimizing the device structure are critical to the device performance, especially the open-circuit voltage.

2. Experimental

The device architectures fabricated in this study, which are conventional cell structures with the cathode on top of the photoactive layer and the anode at the bottom, are schematically illustrated in Fig. 1. Indium tin oxide (ITO)-coated glass substrates (10 mm × 10 mm) with a sheet resistance of 10 Ω/sq. were cleaned by ultrasonication with conventional organic solvents (acetone, methanol, and ethanol) for 10 min at each step, followed by UV-ozone treatment. The ITO/glass substrates were spin-coated with a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrolsulfonate) (PEDOT:PSS) (ca. 50 nm), subsequently transferred into a nitrogen-filled glovebox, and annealed at 200 °C for 20 min. Photoactive layers composed of P3HT:PCBM blend (1:0.8 weight ratio) were prepared by ESD. P3HT and PCBM were purchased from Sigma-Aldrich and used without further purification. 2.0 mg of P3HT molecules was dissolved in 1.0 mL of chlorobenzene (CB), and 1.6 mg of PCBM molecules was dissolved in 1.0 mL of 1,2-dichlorobenzene (o-DCB). The P3HT and PCBM solutions were vigorously stirred (700 rpm) at 32 °C for 6 h in a nitrogen-filled glovebox and mixed with each other, and then the mixed solution was stirred for 1 h. Acetonitrile was added (10 or 20 vol%), and the mixed solution was stirred again for 30 min. To obtain a multijet mode of spraying (which is a mode suitable for large-area, uniform deposition) [24], it was necessary to mix the good solvents (CB and o-DCB) with an additional solvent that has a high relative dielectric constant such as acetonitrile ($\varepsilon = 37.5$) [29]. The P3HT:PCBM blend solution was electrosprayed onto the PEDOT:PSS-coated ITO anode electrodes in air at 50 °C. The schematic of our ESD system is depicted in Fig. 2(a). The solution feed rate of 10 or 5 μL/min was precisely controlled by a syringe pump. The nozzle diameter, nozzle-substrate distance, and voltage applied to the nozzle were 250 μm, 10 cm, and 9 kV, respectively. The thickness of the photoactive layers ranged from 100 to 150 nm, which could be easily controlled by adjusting the solution feed rate and deposition time [11]. The SVA treatment was performed on as-deposited photoactive layers under various conditions: the treatment temperature ranged from 65 to 90 °C and the treatment time ranged from 2 to 10 min. As schematically presented in Fig. 2(b), the samples were placed into a covered Petri dish filled with hot CB vapor during the SVA treatment. Finally, Al cathode electrodes (ca. 80 nm) were deposited on top of the SVA-treated photoactive layers through a shadow mask via thermal evaporation. The shadow mask was used to define the active device area of 7.85×10^{-1} mm^2 (circular electrode with a diameter of 1 mm). For some devices, an ultrathin LiF layer (ca. 1 nm) was thermally evaporated prior to Al deposition, which was introduced as a hole-blocking layer between the cathode and the photoactive layer (Fig. 1(b)).

The surface morphologies of the photoactive layers were characterized by atomic force microscopy (AFM, Keyence). Current density-voltage (*J*-*V*) curves were measured with a Keithley 2400 source meter under AM 1.5G illumination with the power of one sun (100 mW/cm^2) using a solar simulator (Ushio optical modulex). The light intensity was calibrated using a Si photodiode reference cell (BS-520, Bunko Keiki). The solar cell performances were characterized in air at ambient circumstance. The absorption spectra were acquired using an UV–vis spectrometer (Lambda 25, Perkin-Elmer).

3. Results and discussion

Fig. 3(a) and (b) exhibit the AFM images of as-deposited and SVA-treated P3HT:PCBM BHJ photoactive layers, respectively. The SVA treatment was performed at 65 °C for 2 min. While a number of droplet traces were seen on the surface of the photoactive layer prepared by ESD in a dry condition, a flattened surface without those marks could be successfully obtained due to SVA. This demonstrates that the SVA treatment eliminated the droplet traces because the hot CB vapor effectively penetrated the surface of the photoactive layer and reconstructed

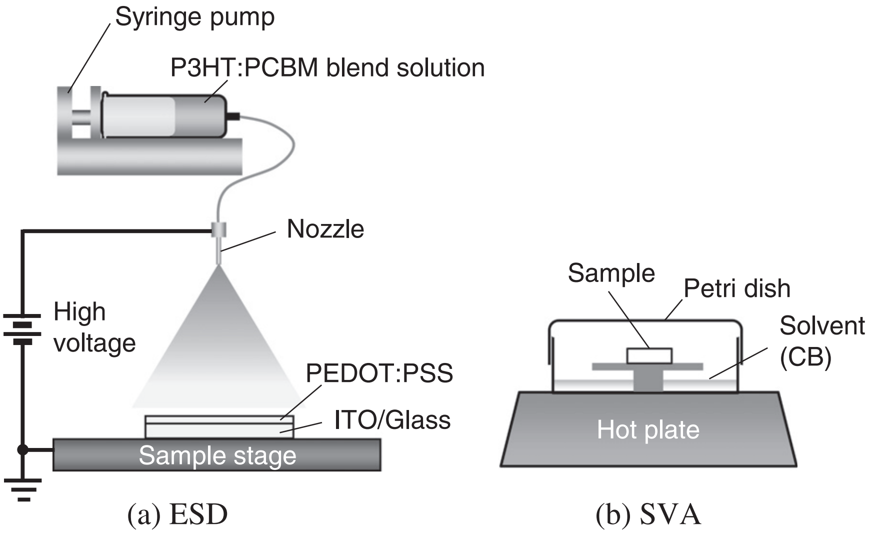

Fig. 2. Schematics of (a) our ESD system and (b) SVA treatment using hot CB vapor performed in this study.