



Improving thermal stability of organic photovoltaics via constructing interdiffused bilayer of polymer/fullerene



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ABSTRACT

The thermal stability of organic photovoltaics (OPVs) is greatly enhanced by using an interdiffused polymer/fullerene bilayer (ID-BL) as a photoactive layer. The solutions of poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) and phenyl-C₇₁-butyric-acid-methyl ester (PCBM) are sequentially deposited to form the ID-BL. For comparison, a single photoactive layer consisting of mixed domains of PCDTBT and PCBM (MX-SL) is prepared by depositing blended solution of PCDTBT and PCBM, which is the most widely used method for fabricating OPVs. After applying thermal stress at 80 °C for 10 days, the OPV utilizing the ID-BL photoactive layer maintained 97.2% of its initial efficiency, whereas the efficiency of the OPV utilizing the MX-SL photoactive layer decreased to 37.5% of its initial efficiency. The glazing angle X-ray diffraction (GIXRD) and Flory-Huggins interaction parameter analysis reveal that the ordered domain size of PCDTBT in ID-BL is greater than that of the MX-SL and the ordered domain is maintained after the thermal stress test. These findings imply that mixing of the PCDTBT and PCBM domains does not occur due to the enhanced ordering of PCDTBT in ID-BL during the thermal stress test. Meanwhile, the domain size of PCDTBT in MX-SL is reduced due to further mixing of the PCDTBT and PCBM domains during the thermal stress test, which deteriorates the optimized bulk heterojunction (BHJ) morphology. These results show that efficient and thermally stable OPVs can be realized by utilizing the ID-BL photoactive layer prepared by the sequential solution deposition.

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1. Introduction

Organic photovoltaic (OPV) devices mainly utilize a single layer consisting of mixed domains of polymer and fullerene (MX-SL) as a photoactive layer. The MX-SL is usually prepared via the deposition of conjugated polymer and fullerene blended solution (BSD). The bulk heterojunction (BHJ) is formed in the MX-SL. Phase separation (de-mixing) between polymer and PCBM domains is required to evolve the bulk heterojunction (BHJ) with a proper domain size for efficient exciton dissociation and charge transport. The morphologically optimized MX-SL shows high solar cell performance due to a large heterojunction area and improved exciton dissociation efficiency. So far, the performance of OPVs utilizing the MX-SL (MX-SL OPV) has been quickly developed, from ~1% to ~10% [1].

Construction of a bilayer-type photoactive layer via sequential

solution deposition (SqSD) of a polymer and a fullerene solution could be a promising alternative for the highly efficient OPVs. Because the thickness of each layer can be controlled independently, the SqSD process is more flexible when finding the optimum condition. Moreover, the ordering of polymer chain can be enhanced during the polymer bottom layer formation because it could be deposited without disturbing from the bulky fullerene. When fabricating a photovoltaic layer through the SqSD process (SqSD), it is essential to form an interdiffused bilayer (ID-BL) through the effective swelling and diffusion of fullerene into the polymer bottom layer.

Recently, several SqSD processed OPVs utilizing ID-BL photoactive layer (ID-BL OPV) have been reported for poly(3-hexylthiophene) (P3HT) and other small band gap polymers [2–11]. For the SqSD processed P3HT/PCBM bilayer, thermal annealing is the common process used to obtain ID-BL and to improve the crystallinity of the polymer [10,12]. Yang et al. proved that the ID-BL OPVs utilizing the P3HT/PCBM can potentially have better performance than MX-SL OPV due to significant reduction of

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bimolecular charge recombination [13]. It was reported that the morphology of ID-BL could be controlled by using tailored semi-orthogonal solvent blends [6,14]. More recently, several groups, including our group, reported highly efficient ID-BL OPVs utilizing a small band gap polymer/fullerene layer [3,6,15]. During the SqSD process, the PCBM solution swelled and penetrated into polymer bottom layer, which provided the formation of an efficient BHJ morphology without thermal annealing [6,15].

In addition to the facile process and efficiency, high morphological stability is expected from the ID-BL OPV because the PCBM will be deposited onto the highly ordered domains of the polymer bottom layer. In this study, the morphological stability of ID-BL OPV was investigated by applying thermal stress at 80 °C for 10 days, which to our knowledge has not yet been reported. After conducting a thermal stress test, the ID-BL OPV maintained its initial efficiency, whereas significant reduction of the efficiency was observed from the MX-SL OPV. Results of opto-electrical and morphological investigation revealed that the morphology of the ID-BL was very stable compared to that of MX-SL under thermal stress. This result is believed to provide a solution for realizing an OPV showing high thermal stability and efficiency, which is one of the important factors to be considered for the commercialization of OPVs.

2. Materials and methods

2.1. Photo-active layer fabrications

Glass substrates with a pre-patterned (20 Ω) tin-doped indium oxide (ITO) transparent electrode were cleaned via ultra-sonication with isopropyl alcohol (IPA), acetone, and IPA sequentially and dried in a convection oven (60 °C) for 30 min. Onto the prepared substrates, UV ozone treatment was conducted for 20 min. The mixed solvent of PEDOT:PSS (CleviosTMPVPAI 4083, Germany) and Methanol (MeOH), with a 1:1 vol percent ratio, was spin-coated onto the cleaned substrate at a speed of 4000 rpm for 35 s. Poly[[9-(1-octylonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) (1-Materials, Lot number: YY7092C, Canada) was used for the bottom top layer. The number-average molecular weight (M_n) and polydispersity index (PDI) of the PCDTBT determined by the gel permeation chromatography with polystyrene standard were 16.7 kDa and 2.4, respectively. Phenyl-C₇₁-butyric-acid-methyl ester (PC₇₀BM) (Nano-C, USA) was used for the top layer. The chemical structure of PCDTBT and PC₇₀BM is shown in Fig. 1. For the fabrication of ID-BL OPV (Fig. 1), PCDTBT (10 mg/ml) solution dissolved in chlorobenzene (CB):1,8-Diiodooctane (DIO) (TCI, Japan), with a 95:5 vol percent ratio, was spin-coated onto the PEDOT:PSS substrates at a speed of 2500 rpm for 30 s and dried in a 110 °C vacuum oven for 15 min, followed by 150 °C drying on a hotplate. A PC₇₀BM solution (6 mg/ml) was prepared in dichloromethane (DCM), with 1 vol% of Diiodomethane (DIM). The PCBM solution was deposited onto the PCDTBT bottom layer at a speed of 4000 rpm for 30 s and then dried in a 110 °C vacuum oven for 15 min. The thickness of the photoactive layer was around 80 nm. The DCM solvent can dissolve the PCDTBT if the film was prepared without additive. However, addition of additive (DIO) improved ordering of PCDTBT and the film was less destructive against the DCM [3]. In our previous paper, we have investigated the absorption intensity change of PCDTBT film before and after fabricating the interdiffused bilayer. It was found that 65.8% of the PCDTBT bottom-layer remained even after spin-coating with the PC₇₀BM solution. The amorphous part of the PCDTBT is thought to be removed during the spin coating process. For the formation of PCBM top layer, the addition of DIM into the PCBM solution enables conformal coating on the PCDTBT bottom

layer [3]. For comparison, BSD processed OPV was fabricated. PCDTBT (12 mg/ml) and PCBM were dissolved in 1,2-dichlorobenzene, with a 1:4 wt% ratio, spin-coated onto the top of the PEDOT:PSS layer at a speed of 5000 rpm for 30 s, and dried in a 110 °C vacuum oven for 15 min. Usually no additive has been utilized for fabricating the PCDTBT based OPV by the BSD process. For example, the PCDTBT based solar cell exhibiting internal quantum efficiency of ~100% was achieved without any processing additive [16–18]. Therefore, the optimum fabrication condition was different for the BSD and SqSD OPVs. Those prepared photoactive films were subjected to a thermal stress test. Since there are a lot of factors influencing on the stability of device, such as increased electrical resistance at the photoactive layer/metal electrode interface due to the oxidation of electrode, we annealed the active layer prior deposit electrode to investigate the thermal annealing effect on the morphological stability of photoactive layer. For the thermal stress test, the fabricated photoactive films were placed onto a hot plate at a temperature of 80 °C in a glove box for 4 and 10 days. Twenty SqD processed and twenty BSD processed OPVs were prepared for the thermal stress test. After the thermal stress test, titanium dioxide (TiO₂) nanoparticles dispersed in butanol (0.4 wt %) were deposited by spin-coating at 3000 rpm onto the ID-BL or MX-SL photoactive layer. After drying using 70 °C hot plates for 1 h, the Al electrode, with a thickness of 100 nm, was thermally evaporated under a pressure of 3.0×10^{-6} Torr. The device configuration of the MX-SL OPV and ID-BL OPV was Glass/ITO/PEDOT:PSS/Photoactive layer/TiO₂/Al.

2.2. Measurements

Current density-voltage characteristics were obtained by using a Keithley 2400 source meter under AM 1.5 G irradiation (100 mW/cm²) in a 150 W Xenon lamp-based solar simulator (McScience, Korea) at room temperature. The UV-vis absorbance spectrum was obtained using spectrophotometer UV-2450 (SHIMADZU, Japan). The photoluminescence (PL) spectra of the films were obtained using a LS 55 (Perkin Elmer, USA). The atomic force microscopy (AFM) images were obtained by using XE-70 (Park Systems Corp., Korea). Grazing incidence X-ray diffraction (GIXRD) measurements were performed at the PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory (Korea). The operating conditions were set at a wavelength of 1.12 Å and a sample-to-detector distance of 224 mm. The incidence angle (α_i) was set at 0.130° in this study. 2D GIXRD patterns were recorded using a 2D CCD detector (SX-165, Rayonix) with exposure time of 10–60 s. Depth profiles of the active layer were obtained via time of flight secondary ion mass spectrometry (TOF-SIMS). The primary ion beam was a 60 keV Bi³⁺ with a current of 0.488 pA; the secondary sputtering ion beam was a Cs at 1 keV with a current of 60.9 nA. All the samples were prepared on an Si wafer. The sample area sputtered was $300 \times 300 \mu\text{m}^2$, and the analytical area was $100 \times 100 \mu\text{m}^2$. Negative secondary ions were detected.

3. Results and discussions

To investigate the chemical degradation during the thermal stress, UV-vis. absorption and PL spectra were measured for the MX-SL and ID-BL films before and after the thermal stress. The active layer was annealed prior deposit electrode to investigate the thermal annealing effect on the morphological stability of photoactive layer. Based on the absorption and PL experiment, it seems that the optical and chemical properties of PCDTBT and PCBM were not changed during the 10-day thermal stress test. The intensity and overall shape of the absorption and PL spectra of MX-SL and ID-BL films were almost identical before and after the thermal stress

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