Solution-processable polymer solar cells from a poly(3-hexylthiophene)/[6,6]-phenyl C$_{61}$-butyric acidmethyl ester concentration graded bilayers

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Polymer photovoltaic (PV) device prepared with a vertical phase separation has intensified the research on the effectiveness of the concentration graded active layer. In this paper, a polymer PV device with a poly(3-hexylthiophene)/[6,6]-phenyl C$_{61}$-butyric acidmethyl ester (P3HT/PCBM) bilayers active film with a concentration gradient has been fabricated via solution process. The concentration variation has been confirmed by the Auger spectroscopy. The devices showed an enhanced photocurrent density and power conversion efficiency compared to those of the bulk heterojunction PV prepared under the same fabrication condition. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3192360]

In recent years, photovoltaic (PV) devices based on polymer-fullerene thin films have been widely investigated throughout the world due to the possibility of solution processing, capability of the large area device, and the PV devices' the flexibility.[1–3] As C. W. Tang reported in 1987, when the device is composed of an electron donor and acceptor in a single, active layer, the cell performance showed the efficiency of 1% range.[4] Since the short diffusion length of the exciton is typically limited to 1–10 nm scale,[5,6] most of the generated charge carriers may be trapped or recombined in the active layer before the charge separation and transport to the electrodes. Therefore, bulk heterojunction (BHJ) concept has been introduced to overcome this low charge carrier mobility and to increase the photocurrent density of polymer based PVs.

From the charge separation's point of view, a *p*-type polymer [poly(3-hexylthiophene) (P3HT)] and an *n*-type material ([6,6]-phenyl C$_{61}$-butyric acidmethyl ester or PCBM) in BHJ interact well in polymer solar cells due to its high interfacial contact area between the donor and acceptor.[7,8] In the device of the bilayers structure, effective charge separation will occur only at the interface of two layers with a different electron affinity resulting in low power conversion efficiency. However, the bilayers structure could be more favorable compared to the BHJ from the charge transporting's point of view since the separated electrons and holes can easily transport to each electrode with a lower possibility of recombination. Yang *et al.*[9] reported on enhanced cell performance of solar cell by making the active layer richer in donors and acceptors near the anode and cathode respectively. Generally, it is very difficult to prepare a well-organized bilayer structure with P3HT and PCBM from solution process because most solvent for the PCBM can

dissolve and destroy the bottom P3HT layer. Yang *et al.*[9] also used the thermal evaporation method for the composition gradient in the active layer.

In this study, solution processed P3HT/PCBM bilayers polymer PV cell with a concentration gradient has been fabricated by choosing the proper solvent system for each layer. The cell performance of the solution processed P3HT/PCBM bilayers polymer PVs has been also investigated. Since the solvent for the upper PCBM layer can partially swell the bottom P3HT layer, an intermixed zone with a concentration gradient of P3HT and PCBM is created between two layers. This concentration graded bilayer structure will induce not only an increase in charge generation and separation similar to BHJ, but it may also impact effective charge transporting and harvesting similar to bilayer structure in the active layer.

Polymer solar cells having a P3HT/PCBM bilayers with a concentration gradient were prepared by using the following method of which the layer structure is shown in Fig. 1(a). Indium tin oxide (ITO) glass was cleaned by chloroform, acetone, and isopropanol to remove residual organic materials. It was then treated with oxygen plasma in order to reform the surface. A conducting polymer that is well known for hole transporting material, poly(3,4-ethylene dioxythiophene: poly(styrene sulfonate) (PEDOT:PSS, Baytron P), was spin-coated to a thickness of ~35 nm. The device was prebaked using a digitally controlled hotplate at 200 °C for 5 min. The active layer of controlled device was composed of 4 wt % of P3HT from chlorobenzene (~110 nm) and 5 wt % of PCBM from dichloromethane (~110 nm). As reference to the BHJ device, a device consisting of P3HT and PCBM at a ratio of 1:0.6 was spin coated at 900 rpm for 5 s in a glove box made of chlorobenzene solvent. The thickness of the active layer was 220 nm. Subsequently, an Al metal electrode with a thickness of 150 nm was thermally deposited under a pressure of 2.3×10^{-6} torr. Thermal annealing was then carried out in the glove box by directly

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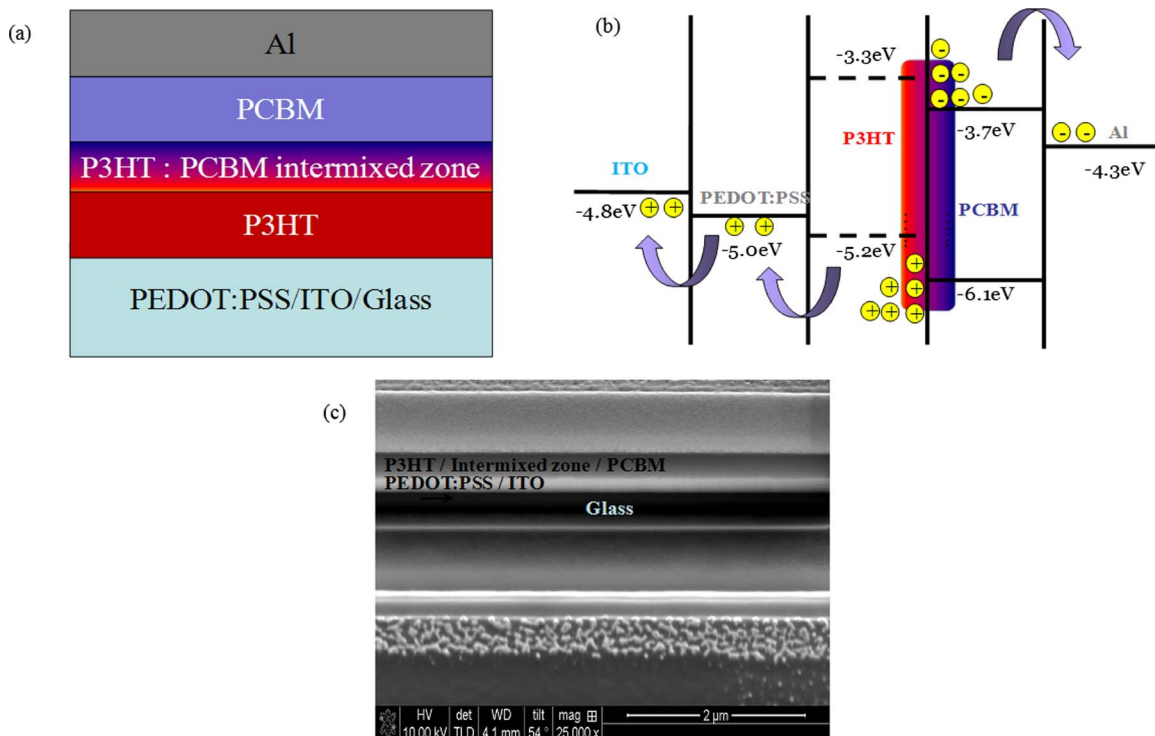[b]Electronic mail: ookpark@kaist.ac.kr.

FIG. 1. (Color online) (a) Schematic diagram of the proposed device structure with P3HT/PCBM bilayer structure. (b) Band gap diagram of the bilayer device. (c) FIB 54° tilted images of the device's inner structure of P3HT/PCBM bilayer with PEDOT:PSS on the ITO glass.

placing the fabricated devices on a digitally controlled hotplate at 150 °C for 30 min. The area of active device with the deposited Al electrode was confirmed in the range of 4–6 mm². The *J-V* curves were measured at an illumination rating of AM 1.5 by using a Keithley 2400 source measure unit. Oriel 91193, which is a 1000 W xenon lamp, served as the light source to the device and its intensity was calibrated using a silicon reference cell (Fraunhofer ISE, Certificate No. C-ISE269).

Figure 1(b) illustrates the band gap diagram of the bilayer device with the expected concentration gradient of the generated hole and electron charges. Due to the P3HT/PCBM intermixed interfacial area, the charges were efficiently generated similar to the active layer of BHJ. Accordingly, the P3HT/PCBM intermixed zone had the highest concentration of hole and electron charges. Then, the generated charges were separated and transported to each electrode, respectively, following the pathway of P3HT or PCBM regions by the driving force of its chemical potential.[8]

Figure 1(c) shows the focused ion beam (FIB) 54° tilted images of the device's inner structure with a P3HT/PCBM bilayer that has PEDOT:PSS on the ITO glass. From this image, we can easily confirm the whole device's sequential structures. It was found out that the controlled cell of the bilayers has a color gradient ranging from a dark region (PCBM) to a light region (P3HT).

In order to confirm whether the intermixed zone shows a concentration gradient of the donor (P3HT) and acceptor (PCBM) in the active layer, depth profiles of the active films were analyzed by recording the –S– (sulfur) concentration of the PCBM layer to P3HT layer in combination with ion-beam milling of the Auger spectroscopy. P3HT is composed of sulfur elements, which can be detected by Auger spectroscopy while PCBM has no sulfur contents which cannot be

detected accordingly (see the inset of Fig. 2). Figure 2 shows the peak-to-peak Auger signal of the two different donor (P3HT)/acceptor (PCBM) bilayer films as a function of the depth of the active layer. The sulfur signal was zero at the surface of the PCBM layer, whereas a sharp increased signal was observed from the 60 nm region of the top point. This result suggests that the intermixed zone of P3HT/PCBM bilayer was generated during the spin coating process. Therefore, the concentration gradient regions of the intermixed zone were created with two layers of P3HT and PCBM from different solvents.

Figure 3(a) shows the photocurrent (*J*)-potential (*V*) curves of devices with the BHJ and the bilayer film. The BHJ cell exhibits 2.59% as overall performance while the controlled bilayer cell fabricated here does higher performance of the increased up to 2.64%. The critical factor that in-
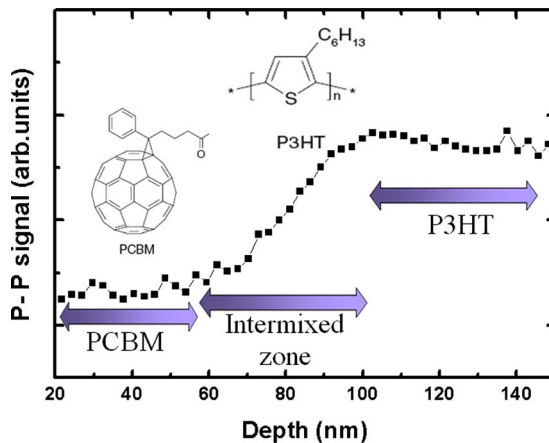

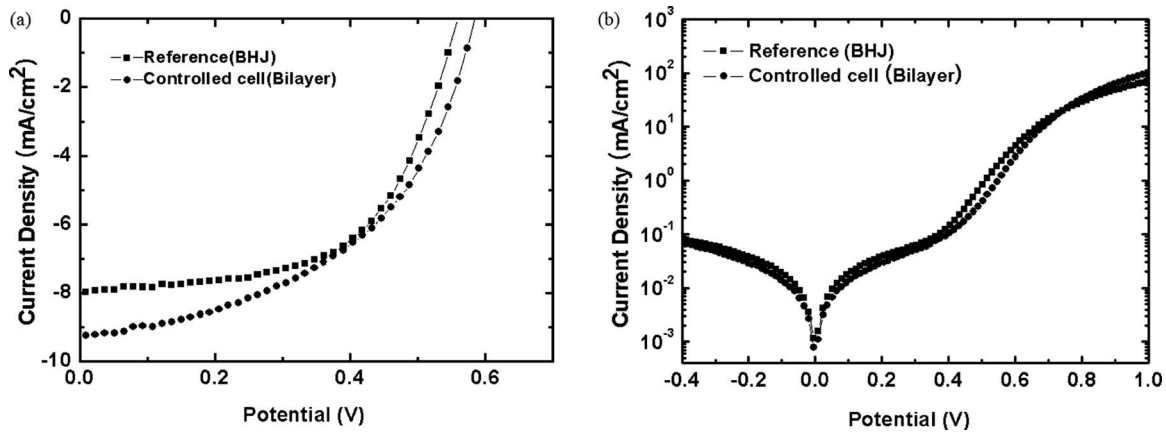FIG. 2. (Color online) Depth profile of P3HT/PCBM bilayers (the Auger spectroscopy).

FIG. 3. (a) $J-V$ curves of devices with BHJ-heterojunction or bilayer. (b) $J-V$ curves of devices with BHJ or bilayer in the dark. (-■- BHJ, -●- P3HT/PCBM bilayer).

creased the efficiency of the devices was J_{sc}. As Fig. 3(a) shows, the photocurrent values of the reference device with BHJ is 7.98 mA/cm^2 while the controlled cell with a bilayer active film shows 9.35 mA/cm^2 value. It suggests improved charge carrier harvesting since the P3HT rich bottom region and PCBM rich top region will collect the electrons and holes more efficiently. From these results, it can be concluded that the P3HT/PCBM intermixed zone plays an important role in the bilayer active layer in the PV. Thus, the bilayer device with a concentration gradient could be another alternative for more efficient device structure along with the single BHJ device. Moreover, as can be seen in the dark current of the devices [Fig. 3(b)], the controlled cell with a bilayer has a low leakage current and series resistance than the BHJ device.[9] Generally speaking, the V_{oc} value is strongly affected by not only the energy difference between the highest occupied molecular orbital level of the donor and the lowest unoccupied molecular orbital level of the acceptor materials, but also by electrode work functions.[10] So, the V_{oc} of the devices was not significantly changed (from 0.56 of reference to 0.58 of bilayer cell) since the same electron donor, acceptor components and ITO, Al electrode are employed. However, the fill factor decreases from 0.58 to 0.48. Dyakonov *et al.*[11] reported that the fill factor of P3HT/PCBM blended solar cells is strongly related with the PCBM concentration. The fill factor showed a maximum around 1:0.66 (weight ratio of P3HT:PCBM). From Fig. 2, the intermixed zone consists of more PCBM weight ratio than the reference device with optimum PCBM content (1:0.6). That is the reason why the bilayer device showed lower fill factor.

In conclusion, it has been demonstrated that the P3HT/PCBM bilayer structured polymer solar cells with a concentration gradient can be fabricated. By spin coating PCBM from dichloromethane on the P3HT, an intermixed zone was created with an interfacial region between the P3HT layer and the PCBM layer. Polymer PVs with concentration gradient showed better J_{sc} and the performances were compared to the device with a single BHJ. The easy solution-processable method introduced in this study would initiate more in-depth research on the multilayer polymer based PVs.

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