Polymer Bulk Heterojunction Photovoltaic Devices with Multilayer Structures Prepared by Thermal Lamination

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ABSTRACT Multilayer structures consisting of two blend layers of poly(3-hexylthiophene) (P3HT):(6,6)-phenyl C_{61} butyric acid methyl ester (PCBM) and poly{N-[1-(2'-ethylhexyl)-3-ethylheptanyl]-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl-alt-4,7-di(2-thie-nyl)-2,1,3-benzothiadiazole-5', 5''-diyl} (PDTPDTBT):PCBM were prepared by a simple thermal lamination technique. Both of the layers contributed to the photocurrent generation simultaneously, as shown by external quantum efficiency spectra. The recombination rate at the interfaces was largely affected by the stacking order of the layers, resulting in the difference of the fill factors. The broadened light absorption range of the multilayer devices compared to that of single-layer P3HT:PCBM devices improved the short-circuit current from 8.83 to 9.41 mA cm^{-2} because of the absorption of the PDTPDTBT:PCBM layer, resulting in a power conversion efficiency of 3.0 % with an open circuit voltage of 0.58 V and a fill factor of 54 %.

KEYWORDS: polymer photovoltaic devices • thermal lamination • multilayer • low band gap

P olymer photovoltaic devices have recently drawn considerable attention as alternative inexpensive solar cells (1 −4). After the development of the so-called bulk heterojunction (BHJ) structure (5), in which electron-donating and electron-accepting materials are blended together to form a single active layer, the power conversion efficiency (PCE) of polymer solar cells has improved drastically. Several groups have achieved PCE of over 5 % by optimizing the combination of the donor/acceptor materials and the preparation methods for the BHJ structures (6, 7). However, further improvement of PCE is necessary for practical use of polymer photovoltaic devices.

An effective way of improving the efficiency is to use low-band gap polymers (LBPs) to absorb a larger fraction of the sunlight (8, 9). The theoretical upper limit of the short-circuit current (I_{SC}) of the solar cells can be almost doubled by narrowing the band gap of active materials from 1.9 to 1.4 eV (9). In the case of the polymer solar cells, however, this calculation is not always applicable, because the absorption spectra of the conjugated polymers show narrow and discontinuous peaks unlike the inorganic semiconductors. Although the absorption offset can be shifted to longer wavelength in LBPs, absorption in the shorter wavelength region tends to decrease, which limits further improvement of the absorption matching the solar spectrum.

An interesting approach to overcome this problem is stacking two kinds of polymer layers with different absorption ranges. Polymer layer combinations of poly(3-hexylthiophene) (P3HT):(6,6)-phenyl C_{61} butyric acid methyl ester (PCBM) with vacuum deposited (10, 11) or solution-processed bulk heterojunctions (12−14) have been demonstrated in so-called "tandem" structures (15).) In the tandem devices, two polymer blend layers are separated by a (semi)transparent metal or semiconducting layer, which works as charge recombination center; therefore, the two cells are considered to be connected in series. As a result, the tandem device has an open circuit voltage (V_{OC}) that is the sum of the values for the two devices, whereas the I_{SC} of the device is restricted to the smaller value of the two. In contrast, a "multilayer device" in which the two active layers are stacked directly (i.e., without any interfacial layer) has an I_{SC} value that is the sum of the values for the two cells. Although high efficiency of the tandem device can be expected, there have been few reports on polymer multilayer devices (16, 17). To the best of our knowledge, only one example of a multilayer device with two different polymer BHJ layers has been reported (18). This is likely the result of preparation difficulties. Although interesting approaches have been reported to insolubilize the polymer layers by thermocleavage (19, 20) or cross-linking (21), because the polymers are generally soluble in the same solvents, it is difficult to cast the second polymer layer from solution without dissolving the first layer.

In this paper, we report the first demonstration of solution-processed multilayer photovoltaic devices prepared by lamination of two different polymer BHJ layers. The thermal
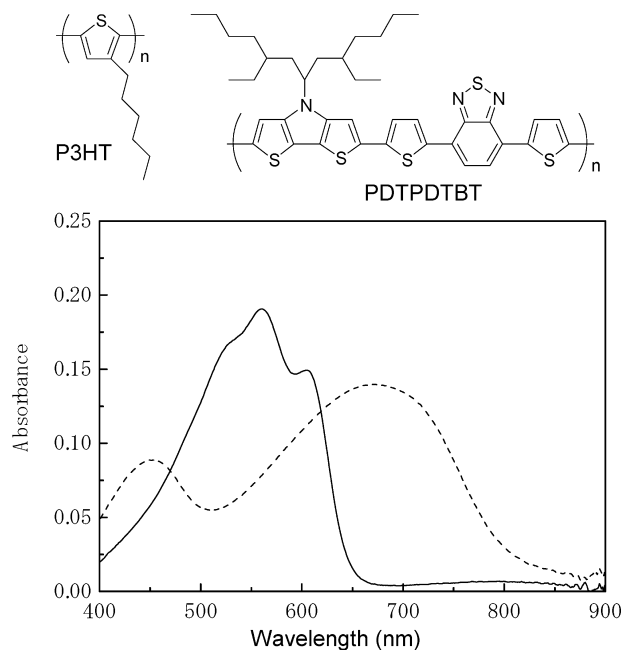
FIGURE 1. Molecular structures and absorption spectra of P3HT (solid line) and PDTPDTBT (dashed line) in thin films.

lamination technique that we have established recently enables the fabrication of multilayer structures in simple and easy processes regardless of the solvents (22). P3HT:PCBM and poly{N-[1-(2′-ethylhexyl)-3-ethylheptanyl]-dithieno[3,2-b:2′,3′-d]pyrrole-2,6-diyl-alt-4,7-di(2-thienyl)-2,1,3-benzothi-adiazole-5′,5″-diyl} (PDTPDTBT):PCBM BHJ layers were selected as the two active layers, because they have some-what complementary absorption spectra (Figure 1). PDTP-DTBT is an LBP that we have developed recently, with which PCE of more than 2% has been achieved by mixing with PCBM in conventional BHJ devices (23).

Experimental Section. The fabrication procedure of the multilayer devices is as follows. Diluted TiO_2 precursor solution (NDH-510C, Nippon Soda, Japan) was spin-coated on a cleaned ITO substrate followed by drying at 140 °C for 60 min and calcination at 500 °C for 30 min to form a hole-blocking layer. The PDTPDTBT:PCBM BHJ layer was depos-ited on the ITO/TiO_2 substrates by spin-coating a chloroben-zene solution containing 10 g L^{-1} of PDTPDTBT and 10 g L^{-1} of PCBM. Au electrode was thermally deposited on a cleaned glass substrate precovered with 0.5 nm of Cr adhe-sion layer. The PEDOT:PSS hole-transporting layer was coated on the glass/Au substrate by spin coating followed by drying at 150 °C for 15 min in a N_2 atmosphere. The P3HT:PCBM BHJ layer was then deposited on the glass/Au/PEDOT:PSS substrates by spin-coating a 1,2-dichloroben-zene solution containing 30 g L^{-1} P3HT and 24 g L^{-1} PCBM at a spinning rate of 700 rpm according to the procedure reported by Yang (24).) The thickness of the layer was 250 nm with these conditions. Finally, this glass/Au/PEDOT:PSS/P3HT:PCBM substrate was placed on top of the ITO/TiO_2/PDTPDTBT:PCBM substrate and laminated together under a pressure of 2 MPa at 150 °C by using a hydrostatic pressurizer with hot plates (AH-1TC, AS ONE, Japan). Sche-matic images of the device structure and the energy diagram

of the ITO/TiO_2/PDTPDTBT:PCBM//P3HT:PCBM/PEDOT:PSS/Au device are shown in Figure 2a, where // denotes the laminated interface. PCE under AM1.5 irradiation of 100 mW cm^{-2} was measured using a xenon-lamp-based solar simulator (PCE-L11, Peccell Technologies, Inc., Japan). The light intensity was calibrated with a standard silicon solar cell with an optical filter (BS-520, Bunkoh-Keiki, Japan). The external quantum efficiency (EQE) of the devices was mea-sured with a Hypermonolight System SM-250F (Bunkoh-Keiki, Japan). The active area of the device irradiated by the light was defined as 0.03 cm^2 by using a metal photo mask. All electrical measurements were performed in air.

Results and Discussion. The EQE spectra of the P3HT:PCBM (1:0.8 wt, 250 nm) single-layer device and the multilayer device with P3HT:PCBM (1:0.8 wt, 250 nm) and PDTPDTBT:PCBM (1:1 wt, 25 nm) layers are compared in Figure 3. The data were the best of a series of the devices. While the single-layer device generates almost no photocur-rent at wavelengths longer than 650 nm, the multilayer device responds up to the wavelength of 850 nm, which corresponds to the absorption edge of PDTPDTBT. This result indicates that the multilayer photovoltaic device fab-ricated by this simple lamination process successfully ab-sorbs light and generates photocurrent in a broader range of the spectrum.

The $I-V$ characteristics of the best devices are compared in Figure 4. Under the irradiation of simulated sunlight, the multilayer device has higher PCE than the single-layer device. Namely, the P3HT:PCBM single-layer device has I_{SC} of 8.83 mA cm^{-2}, V_{OC} of 0.58 V, and fill factor (FF) of 53%, resulting in PCE of 2.7% (25). On the other hand, the multilayer device has higher I_{SC} of 9.41 mA cm^{-2}, V_{OC} of 0.58 V, and FF of 54%, leading to improved PCE of 3.0%. Because the V_{OC} and FF values of the multilayer device are almost the same as those of the single-layer device, it can be concluded that this improvement in device performance is the result of the better collection of photons by the PDTPDTBT:PCBM layers as expected from the EQE spec-trum in Figure 3. The I_{SC} under AM1.5 irradiation was calculated by integrating EQE and the solar spectrum from 400 to 900 nm. The calculated values were 8.74 and 9.51 mA cm^{-2} for the single-layer and multilayer devices, respec-tively, which coincides with the observed improvement in I_{SC} within experimental error. As long as the thickness of the PDTPDTBT:PCBM layer was not too thick (less than ca. 25 nm), the same tendency (i.e., the improvement of I_{SC} and the larger EQE response up to 850 nm) was repeatedly observed in the multilayer devices compared with the refer-ence single-layer ones. The EQE response in the long wavelength further increased with a thicker PDTPDTBT:PCBM layer, however, the I_{SC} decreased because of the decrease in the EQE response from P3HT:PCBM, resulting in the deteriorated device performance of the multilayer devices.

The similar FF of the two devices also suggests that the laminated interface of two organic layers does not have a large barrier for charge transport. This can be understood
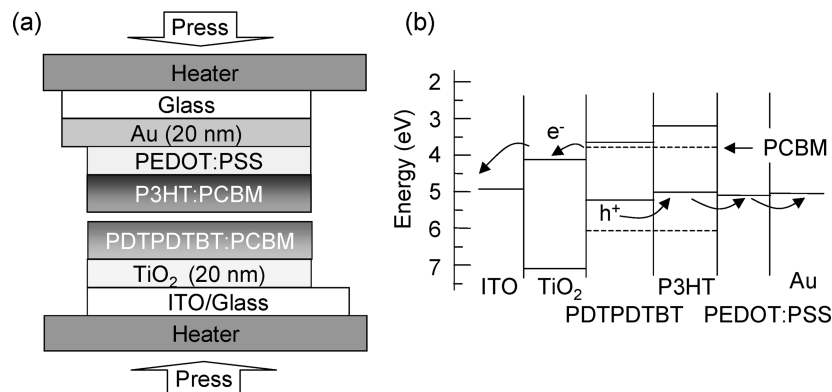
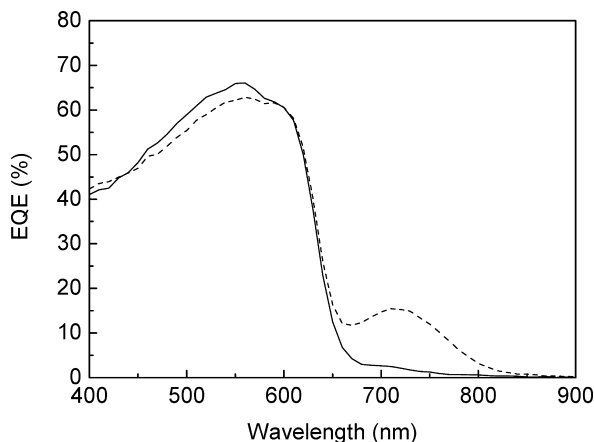FIGURE 2. (a) Schematic representation of lamination of the device and (b) energy diagram of the materials.

FIGURE 3. External quantum efficiency (EQE) spectra of P3HT:PCBM single-layer (solid line) and multilayer (dashed line) devices.
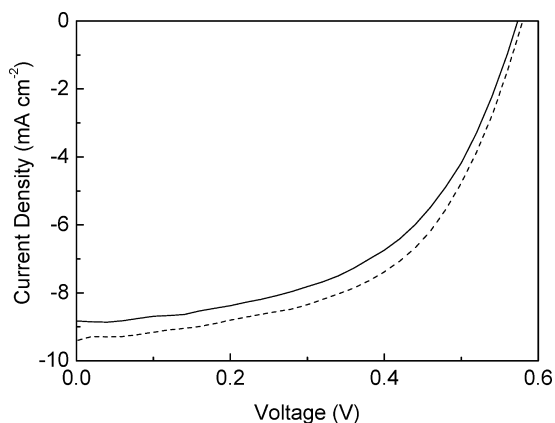

FIGURE 4. $I-V$ curves of P3HT:PCBM single-layer (solid line) and multilayer (dashed line) devices under irradiation of AM 1.5 simulated sunlight (100 mW cm^{-2}).

by referring to the energy diagram of the multilayer device shown in Figure 2b. The ionization potential of the PDTP-DTBT film was 0.2 eV higher than that of the P3HT film as measured by photoelectron yield spectroscopy (PYS). Therefore, the stacking order of the BHJ layers is advantageous for the transport of both electrons and holes from the viewpoint of energy level matching at the laminated interface. Indeed, when the other stacking order of the layers (ITO/TiO$_2$/P3HT:PCBM//PDTPDTBT:PCBM/PEDOT:PSS/Au) was used, the multilayer device showed a convex $I-V$ curve around the operation voltage, resulting in a much lower FF

and PCE (26).) This result suggests the presence of large internal resistance at the laminated interface because of the unfavorable HOMO level alignment for hole transport in this configuration.

Unfortunately, because the absorption ranges of P3HT and PDTPDTBT are not totally complementary to each other and the internal quantum efficiency of the PDTPDTBT:PCBM layer is lower than that of the P3HT:PCBM layer, introduction of PDTPDTBT:PCBM layers thicker than 25 nm caused a decrease in EQE in the shorter wavelength region, resulting in smaller I_{SC} under AM1.5 irradiation. Further improvement of the performance is expected by combining the P3HT:PCBM layer with a BHJ layer composed of an LBP having complementary absorption to P3HT as well as higher hole mobility and better charge separation ability.

Conclusions. We demonstrated the first successful fabrication of multilayer polymer photovoltaic devices by a simple thermal lamination technique. A wider range of photons can be utilized in multilayer devices, leading to improved I_{SC} and PCE. In combination with the recent rapid development of various LBPs, multilayer photovoltaic devices can be a general approach for improving the device performance of polymer solar cells. From the viewpoint of manufacturing process, although there would be many technical challenges such as electrode alignment, the thermal lamination of the polymer layers could be compatible to roll-to-roll processes (27, 28) in principle and have a potential to contribute to the low cost fabrication of the flexible polymer solar cells.

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(25) This performance of the reference device (2.7%) is lower than the highest value previously achieved by thermal lamination (3.3%) with the same device configuration (see ref 22.). This can be attributed to the difference in the lamination interfaces. In the previous report, the lamination interface was ITO/TiO$_2$/P3HT:PCBM//PEDOT:PSS/Au, whereas in the current work it was ITO/TiO$_2$//P3HT:PCBM/PEDOT:PSS/Au (// denotes the laminated interface). This change was necessary because we need to use exactly the same P3HT:PCBM layers deposited on PEDOT:PSS/Au for the accurate comparison with ITO/TiO$_2$/PDTPDTBT:PCBM//P3HT:PCBM/PEDOT:PSS/Au devices.

(26) When the same mixing ratio and layer thickness (1:1 wt, 60 nm for PDTPDTBT:C$_{70}$PCBM layer and 1:0.8 wt, 250 nm for P3HT:C$_{70}$PCBM layer) were used as the two BHJ layers, the device with ITO/TiO$_2$/PDTPDTBT:PCBM//P3HT:PCBM/PEDOT:PSS/Au configuration had I_{SC} of 8.67 mA cm^{-2}, V_{OC} of 0.56 V, FF of 46%, and PCE of 2.2%. The device with ITO/TiO$_2$/P3HT:PCBM//PDTPDTBT:PCBM/PEDOT:PSS/Au had I_{SC} of 7.36 mA cm^{-2}, V_{OC} of 0.52 V, FF of 28%, and PCE of 1.1%.

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