Systematic optimization of low bandgap polymer/[6,6]-phenyl C_{70} butyric acid methyl ester blend photodiode via structural engineering

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ARTICLE INFO

ABSTRACT

Synthetic approaches for optimizing polymer-based organic photodiodes (OPDs) by systematically analyzing the effects of the hole-blocking layer, the electron-blocking layer, and the thickness and morphology of the active layer with respect to the dark current and detectivity have been reported. PBDTT-DPP with a repeating alkylthienylbenzodithiophene (BDTT) and diketopyrrolopyrrole (DPP) units is used as a p-type polymer for achieving both broadband absorption and a high absorption coefficient in conjunction with n-type [6,6]-phenyl C_{70} butyric acid methyl ester ($PC_{70}BM$) for constructing photoactive layers. Through systematic investigations of various interfacial layers, we found that the thickness of the active layer and the energy level of the hole/electron blocking layer were critical for minimizing the dark current of OPDs. By changing the deposition method of the PBDTT-DPP/$PC_{70}BM$ blend and using post treatment, we discovered that the morphology of the active layer was directly related to the photocurrent of OPDs. Furthermore, we conducted a comparative study between a bulk heterojunction and a planar heterojunction (PHJ) to demonstrate the effectiveness of the PHJ for suppressing the dark current. Consequently, we realized a high detectivity of 5.3×10^{12} Jones with an optimized device architecture and morphology. This work shows the importance of a synthetic approach for optimizing OPDs that requires both a high photocurrent and a low dark current in the reverse saturation regime.

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1. Introduction

Recently, organic photodiodes (OPDs) have attracted considerable attention as a promising alternative to Si-based photodetectors [1–5]. Generally, for optoelectronic applications such as organic field-effect transistors (FETs) and organic photovoltaic cells (OPV), organic semiconductors have major merits compared with their inorganic counterparts, mostly owing to their low-cost processability and mechanical flexibility [3]. For OPD applications, organic semiconductors not only guarantee the aforementioned merits but also offer unique characteristics. Because organic semiconductors have a higher absorption coefficient for visible/near-infrared light compared with Si, the active layers in OPDs can be far thinner, which can significantly enhance the range of the incident angle with a higher reliability [6]. This provides greater flexibility to the lens design, facilitating the reduction of the overall camera size. Therefore, there have recently been tremendous research efforts to fabricate high performance OPDs by developing new

semiconductor materials or optimizing the diode structure.

The figure of merit for photodiodes is the specific detectivity, D^*, which is given as $D^* = R/(2qJ_d)^{1/2}$ ($cmHz^{1/2}/W$), where R is the responsivity, q is the absolute value of the electron charge, and J_d is the dark current density [5]. In an OPD structure, a high responsivity is related to a high photocurrent under a given light power, and a low dark current is related to a low charge injection under a given reverse bias. Similar to the case of OPVs, a high photocurrent can be obtained by providing a large interfacial area between the donor and acceptor interfaces and by constructing efficient charge transport pathways for the hole and electron charge carriers [7]. Unlike the case of OPVs, in OPDs, the dark current in the reverse saturation regime should be minimized without sacrificing the high photocurrent. To satisfy these complicated requirements, various research methods have been implemented. For example, a variety of hole/electron blocking layers have been introduced to suppress the dark current density, yielding high detectivity OPDs [8,9]. A morphology-driven high photocurrent, which is typical for OPVs, has also been found to be beneficial for obtaining high detectivity OPDs [10,11]. In addition, the influence of the device architecture, such as an inverse diode structure, on the performance of OPDs has

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been examined [12]. Nonetheless, attempts to realize high performance OPD via comprehensive and versatile approaches in terms of the morphology and crystalline structure of the organic semiconductor, the device structure, the interfacial layer, and the thickness of each layer have been very limited.

In this study, we attempted to optimize polymer-based OPDs by a systematic approach considering the hole blocking layer, electron blocking layer, and the thickness and morphology of the active layer. Although there have been efforts to optimize one of these device parameters to fabricate high performance OPDs, synthetic approaches for optimizing all the device parameters are difficult to find. As a target p-type semiconductor, we selected poly{2,6′-4,8-di(5-*ethylhexylthienyl*)benzo[1,2-b,3,4-b]dithiophene-alt-5-dibutyloctyl-3,6-bis(5-*bromothiophen*-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (PBDTT-DPP), which has a backbone consisting of repeating alkylthienylbenzodithiophene (BDTT) and diketopyrrolopyrrole (DPP) units [13]. BDTT is one of the most widely used donor units, and DPP is a highly light-absorbing/electron withdrawing unit [13]. The resulting low bandgap PBDTT-DPP is known to be a promising p-type material for OPV applications [14]. Considering its high optical/electronic properties, we attempted to fabricate high performance OPDs in conjunction with [6,6]-phenyl C_{70} butyric acid methyl ester (PC$_{70}$BM) as an n-type semiconductor. Through systematic investigations of various interfacial layers, we found that the thickness of the active layer and the energy level of the hole/electron blocking layer were critical for minimizing the dark current of the OPDs. By changing the deposition method of the PBDTT-DPP/PC$_{70}$BM blend and using post treatment, we also discovered that the morphology of the active layer was directly related to the photocurrent of the OPDs.

2. Experimental

2.1. Materials

PBDTT-DPP and PC$_{70}$BM were purchased from Solarmer and Ossila, respectively and used without further purification.

2.2. Device fabrication

The ITO-patterned glass substrates were mechanically cleaned with cotton buds and aqueous hydrochloric acid solution, followed by sequential sonication in Mucasol, distilled water, acetone and 2-propanol (IPA). Then the substrates were dried under nitrogen flow. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was spin-coated at 4000 r.p.m. to form a thin film with a nominal thickness of 30 nm, followed by baking at 150 °C for 30 min in ambient condition. MoO$_3$ thin films were fabricated by thermal evaporation under a vacuum of ~5 × 10^{-6} Torr. Solutions of PBDTT-DPP and PC$_{70}$BM with various total concentrations of 10–60 mg/mL were prepared in 1,2-dichlorobenzene by overnight-stirring in N$_2$-filled glove box. Active layers with an area of 0.09 cm^2 were formed by spin-coating on substrates for over 240 s and pre-baked at 80 °C for 5 min. Sol-gel based TiO$_x$ solution was synthesized as described previously [15] and used as diluted solution in IPA. The solution was spin-coated on the active layer at 6000 r.p.m. and annealed at 150 °C for 10 min. The Al or Ag electrodes were deposited by thermal evaporation through shadow mask with a nominal thickness of 100 nm.

2.3. Device characterization

J-V characteristics, including space-charge limited current measurements and detectivity plots were measured with the combination of LabView-controlled Keithley 2400 sourcemeter and Oriel Cornerstone 130 1/8 m Monochromator. AFM images were taken by using an XE-100 instrument from PISA. Two dimensional grazing incidence x-ray diffraction images were collected at the 9A beam line at the Pohang Accelerator Laboratory (PAL). For the measurements, the sample-to-detector distance was 224.0 mm and the incident beam energy was 11.02 keV.

3. Results and discussions

Fig. 1(a) shows the chemical structures of PBDTT-DPP and PC$_{70}$BM, which were selected as the target p-type and n-type semiconductors, respectively. These can form well-defined type-II junctions, as shown in Fig. 1(b). When they are blended to form a thin bulk heterojunction (BHJ), the resulting thin film can respond to the entire visible light spectrum, which is a prerequisite of alternatives to Si for photodetector applications (Fig. 1(c)). The absorption coefficient obtained from a thin film is directly related to the penetration depth (α^{-1}) at each wavelength of incident light by the following equation: $I = I_0 e^{-\alpha t}$, where I and I_0 are the incident and transmitted light intensities, respectively; α is the absorption coefficient; and t is the film thickness [16]. The obtained penetration depth of the BHJ film comprising PBDTT-DPP and PC$_{70}$BM was 400 nm at an incident wavelength of 600 nm, which corresponds to the minimum absorbance of the film. This is far thinner than the active layer of the conventional Si photodiode, guaranteeing a far broader incident angle in the fabrication of the image pixel of a digital camera [6].

Photodiodes with a p-n junction structure operated under a reverse bias are basically free from high dark currents because the ideal energy diagram does not allow charge injection. For example, as shown in Fig. 1(b), even without any hole/electron blocking layers, both the electron injection from indium tin oxide (ITO) into the active layer and the hole injection from Al into the active layer were blocked by the large energy barrier of ~0.9 eV. The charge injection through such a Schottky junction was practically inhibited because it followed the diffusion-limited thermionic emission model: $J \propto \exp(-\phi_B)$, where ϕ_B is the injection barrier [17]. Therefore, in ideal cases, the dark current of an OPD is not important. However, in the case of OPDs comprising conjugated organic semiconductors, the presence of chemical impurities or voids often results in diagonal disorders (energetic disorders) via the formation of locally different highest occupied molecular orbital (HOMO)/lowest occupied molecular orbital (LUMO) energy levels. In particular, organic semiconductor/electrode interfaces formed via solution processes often suffer from local polarization effects, causing the fluctuation of the local HOMO/LUMO energy levels, which considered as a source of dark current [20]. In such cases, there may exist local points with a low ϕ_B where charge injection occurs, resulting in a high dark current. In many cases, OPDs have rendered a relatively high dark current density despite having a high energy level offset in the reverse saturation mode [8,18]. Therefore, the easiest method for controlling the dark current issue is increasing the thickness of the active layer so that the influence of the interface is negligible. As shown in Fig. 2(a), when we systematically varied the thickness of the active layer among 30, 120, 530, and 1600 nm, the dark current density significantly decreased as the thickness increased. This may indicate that the increased bulk resistance achieved by the higher thicknesses led to a decrease in the dark current. However, we need to note that the increased thickness of the active layer is inferior to the charge extraction because of the longer charge carrier pathways as well as the higher probability of the recombination loss of excitons. The photocurrent was reduced by increasing the thickness, decreasing by almost two orders of magnitude between OPDs with active layers 30 and 1600 nm thick. Thus, we consider that the thickness of ~500 nm is