

Improving NIR sensor detectivity of BODIPY/C₆₀ bulk heterojunction photodiode

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Abstract

The electrical characteristics of near infrared organic photodiodes (NIR-OPDs), fabricated by co-depositing with a BODIPY derivative (PhBODIPY) and fullerene (C₆₀), have been investigated. The NIR-OPD with PhBODIPY:C₆₀ = 1:1 demonstrated a maximum detectivity (D^*) of 1.70×10^{12} Jones at -1.5 V bias under the illumination of 820 nm that was higher value compared with PhBODIPY single-layered OPD (7.42×10^{11} Jones). It is considered that the improvement of D^* originates from the efficient charge separation at the PhBODIPY/C₆₀ interfaces and the increase of the electron diffusion efficiency through the C₆₀ in the bulk heterojunction (BHJ) structure.

1. Introduction

Photodiodes (PDs) are one of the important non-contact sensors. They are used in various types of applications such as image sensing, environmental monitoring, and chemical/biological sensing [1-2]. Especially, NIR-PDs are often used for vital sensing and monitoring systems of blood conditions [3-4], because NIR light passes through the living body. Silicon based NIR-PDs are the most popular NIR sensors and widely used. However, they are unsuitable for continuous monitoring of bio-information, because they are inherently hard and do not deform along the shape of the human body. This provides a feeling of discomfort to users who wear sensor devices.

Organic NIR dyes have increased interest of organic optoelectronic materials, because NIR-organic photodiode (OPDs) can apply to flexible and wearable photosensors. These dyes also show a high absorption coefficient with 10^4 – 10^5 cm⁻¹ [5], and can be prepared on flexible plastic substrate using lower-temperature deposition processes. Researchers have reported various types of organic NIR dyes, for example, phthalocyanine derivatives, porphyrins, and polymers, for OPDs [6-7]. However, there are only limited reports of NIR dyes so far.

We focus on a 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) molecular frame because its photo-absorption spectra significantly change with various substituents [8-9]. Also, some of its derivatives exhibit drastic absorption spectra changes depending on molecular aggregation and photoelectric conversion properties under white light illumination [10-11]. In this study, we have investigated the PhBODIPY/C₆₀ BHJ-type NIR-OPDs to improve the device

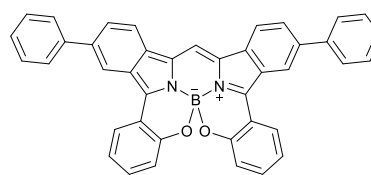


Fig. 1 A chemical structure of PhBODIPY.

performances by the optimization of the blend ratio of PhBODIPY(p-type) and C₆₀(n-type).

2. Experimental methods

The train-sublimated PhBODIPY dye was supplied from Nippon Kayaku Co., Ltd.

Samples for optical measurements were prepared by vacuum-deposition on quartz substrates at $\sim 10^{-4}$ Pa using a deposition apparatus (VPE-101, VIC International Co., Ltd., Japan). The optical absorption spectra of PhBODIPY neat and co-deposited films were measured with an ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectrophotometer (V-600, JASCO Corporation, Japan).

NIR-OPDs were fabricated as follows: PhBODIPY neat and PhBODIPY:C₆₀ co-deposited films were prepared on indium-tin-oxide (ITO) coated substrates by the same procedure as preparing samples for optical measurements. Then, an aluminum cathode was vacuum-deposited with active area of 4 mm². The device configurations of NIR-OPD were ITO / PhBODIPY:C₆₀ (device A: 1:0, device B: 4:1, device C: 1:1, device D: 1:4) / Al. Detectivity (D^*) of NIR-OPDs was measured by a NIR light-emitting diode with a wavelength of 820 nm (15.3 mW cm⁻²). The D^* calculated by $D^* = (J_{ph}/L_{light}) / (2qJ_d)^{1/2}$, where J_{ph} is the photocurrent under illumination, L_{light} is incident light intensity to the OPD, q is the absolute value of electron charge, and J_d is the dark current.

3. Results and discussion

PhBODIPY can be vacuum-deposited on substrates without decomposition. Figure 2 shows the absorption spectra of PhBODIPY neat, C₆₀ neat, and co-deposited films (the mixture ratios of PhBODIPY:C₆₀ are 4:1, 1:1, and 1:4). As shown in Fig. 2(a), two absorption peaks in the PhBODIPY neat film exist at 694 and 767 nm, corresponding to H aggregate and J aggregate, respectively. The spectra of co-deposited film with the mixture ratio of 4:1 and 1:1 shown in Fig. 2(b) are similar with PhBODIPY neat film. For the co-deposited film of 1:1

ratio, the increasing optical absorption around 460 nm originates from optical absorption of C_{60} molecules (see Fig. 2(a)). The relative intensity of absorption peak at 694 nm, corresponding to H aggregated state, tends to decrease with increasing the mixture ratio of C_{60} molecules. The spectral change is considered to be caused that C_{60} molecules were intercalated between BODIPY molecules, that is, the component of H aggregated state decreases. The spectrum of PhBODIPY neat film does not overlap with that of C_{60} neat film in NIR region. Thus, it is expected that the NIR light response in NIR-OPDs under NIR light of 820 nm are mainly occurred at PhBODIPY molecules.

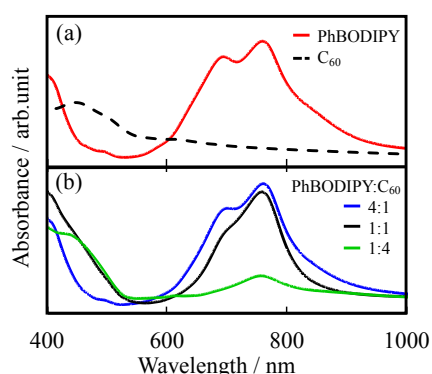


Fig. 2 The absorption spectra of (a) PhBODIPY and C_{60} neat, and (b) PhBODIPY: C_{60} co-deposited films

Figure 3 shows the results of current density-voltage (J - V) characteristics for NIR-OPDs with PhBODIPY neat and PhBODIPY: C_{60} co-deposited films. Device A shows clear diode characteristic with a threshold voltage (V_{Th}) of ~ 0.5 V in the dark condition. Photocurrent was observed under NIR light illumination at 820 nm. The photocurrent density (J_{ph}) of the device A at the reverse bias of 1.5 V were 2.32×10^{-1} mA cm $^{-2}$. The calculated D^* , which represents the performance of the photodiode, was 7.42×10^{11} Jones at -1.5 V. Whereas, the J_{ph} of the device B (4:1 w/w), C (1:1 w/w), and D (1:4 w/w) that consist of the PhBODIPY: C_{60} co-evaporated film, at the reverse bias of 1.5 V were 1.58, 2.18, and 2.07 mA cm $^{-2}$. The V_{Th} shifted to lower voltage and reached to approximately zero voltage for the co-deposited films. This is because electron injection and transport through C_{60} rich domain occurred in the co-deposited film. The NIR-OPD with PhBODIPY: C_{60} 1:1 w/w co-deposited film showed the highest J_{ph} , which is approximately 4.42×10^4 times higher than that in the dark current, 4.93×10^{-5} mA cm $^{-2}$ at -1.5 V. The calculated D^* s of Device B, C, and D were 7.80×10^{10} , 1.70×10^{12} , and 2.80×10^{11} Jones at the voltage, respectively. The dark current increases at reverse bias. This reason is probably because the diffusion current increases due to the existences of PhBODIPY: C_{60} interface and percolation path. As the results, the calculated D^* s decrease even though J_{ph} s increase owing to the PhBODIPY: C_{60} interface. Maximum D^* at the mixture ratio of PhBODIPY: C_{60} 1:1 w/w is equivalent to or or approximately one digit lower than in previous reports including Si-based photodiodes [12].

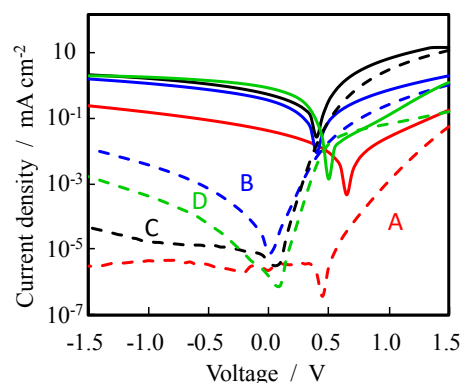


Fig. 3 J - V curves of NIR-OPDs in the dark and under NIR illumination at 820 nm.

3. Conclusions

We characterized PhBODIPY neat and PhBODIPY: C_{60} co-deposited films, and fabricated NIR-OPDs with the films. The films showed broad light absorption spectra in visible to NIR region with the absorption peak of 767 nm. Under NIR illumination of 820 nm, PhBODIPY-based NIR-OPDs with PhBODIPY: C_{60} 1:1 w/w co-deposited film exhibited photocurrent with the maximum D^* of 1.70×10^{12} Jones. This results suggest that PhBODIPY has potential applications in bio-sensing devices.

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