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Improved characteristics of P3HT:PCBM photodetectors with indium-tin-oxide electrodes modified by self-assembled monolayers

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Abstract

The mixed self-assembled monolayers (SAMs) serve to tune the work function of ITO by varying the blend ratio. P3HT:PCBM device with indium-tin-oxide modified by short treatment time of 1H,1H,2H,2H -perfluorooctanephosphonic acid exhibits the incident-photon -to-current conversion efficiency of 55 % at -2V., high on/off ratio and improved durability.

1. Introduction

Organic photodetectors (OPDs) have been the subject of extensive research owing to several advantages as follows: lightweight, flexibility, and low cost fabrication. The printable photodetectors have huge potential in fields of large area photosensor array, scanner and so on. Organic devices utilizing conjugated polymers have attracted considerable interest because of their advantages in large-area device fabrication. Fullerene derivatives doped in several conducting polymers act as an effective quencher and electron accepter. Its photophysics is known as ultrafast photoinduced charge transfer. Poly(3-alkylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) blend have been studied for organic bulk heterojunction photovoltaic cells because of high hole mobility and broad absorption spectrum, and achieved high photoelectric conversion efficiency.

Surface treatment of electrodes using self-assembled monolayers (SAMs) could be an effective means of improving the performance of organic devices. In general, the surface treatment time required to form the SAM is relatively long for several hours. A short treatment time is important for a high tact-time and production yield in industrial applications. This paper aims to improve the performance of PDs by introducing a SAM on indium-tin-oxide (ITO) under reverse voltages.

In this study, we investigated the properties of P3HT:PCBM photodetectors with ITO electrodes modified by short treatment time of SAMs.

2. Experimental Procedure

Poly(3-hexylthiophene)(P3HT, Mw=193K) purchased from Merch Co., Ltd. was used as the host material without further purification. Devices were fabricated on an ITO-coated glass substrate. The 2-propanol solution including SAMs first covered the whole set for a minute before spin coating. The solution was spun off at 4000 rpm for 60 sec. This step was then followed by thorough rinsing with 2-propanol and drying. 1H,1H,2H,2H-Perfluoro octanephosphonic acid (FOPA) and benzonylphosphonic acid (BPA) purchased from Sigma-Aldrich Co. were used as typical SAMs. These molecular structures are shown in Figure 1. Figure 2 shows the device structure and schematic energy level diagram of a P3HT. Next, organic layer was fabricated by spin-coating onto an ITO-coated glass substrate. The active layer was a blend of a donor, P3HT, and an acceptor, fullerene derivative PCBM, both dissolved in 1,2-dichlorobenzene with a ratio of 1:1. P3HT:PCBM layer was annealed at 150 ^{o}C in a dry nitrogen glove box. The Al/Ag electrode was vacuum-deposited. The typical active area of the device was 0.3 mm^2. Current density–voltage (J–V) and incident-photon -to-current conversion efficiency (IPCE) characteristics were measured using an electrometer (Keithley 6514) and a DC power supply (Advantest R6145) under dark and DC light irradiation from Xe lamp through the ITO electrode side for the devices. Work function of ITO substrates modified by SAM was measured using AC-2 (RIKEN KEIKI).

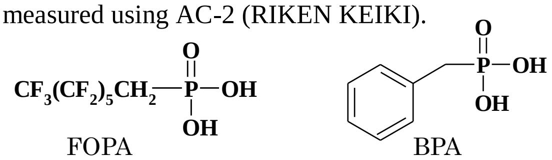
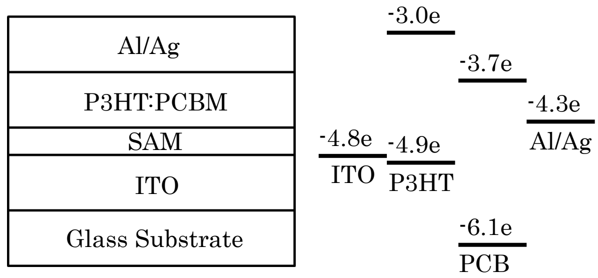


Fig. 1. Molecular structures of SAMs



(a) (b)

Fig. 2. (a) Device structure and (b) energy diagram

3. Results and Discussion

In order to examine SAM effect of hole transport, we investigated the electrical properties of P3HT hole-only device, of which the device structures consist of (+)ITO/SAMs/P3HT/MoOx/Au /Ag(-). Figure 3 shows J-V characteristics of the devices. In this experiment, FOPA was mixed with BPA in various blend ratios (FOPA:BPA = 1:0, 3:1, 1:1, 1:3). These work functions are also shown in Fig. 3. The values of work function of SAM treated electrodes increased with FOPA ratio. It is noted that the lowering of the interfacial barrier at ITO/P3HT interface results in the improved hole injection. The value of FOPA-treated ITO increased to about 5.3 eV. From the impedance spectroscopy measurement of hole only devices, the decreased contact resistance at ITO/P3HT interface also leads to the improved hole injection.

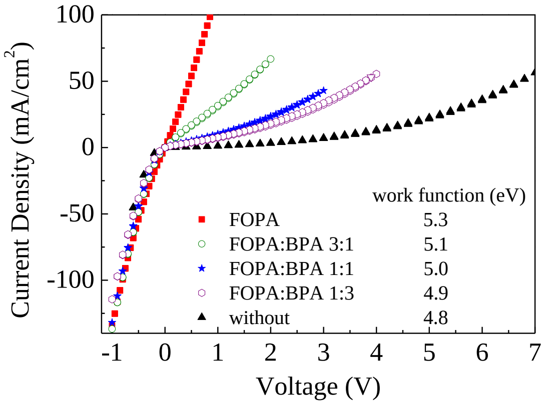


Fig. 3. J-V characteristics of the hole-only devices without and with various blend ratios of FOPA and BPA(FOPA:BPA = 1:0, 3:1, 1:1, 1:3)

J-V characteristics of the P3HT:PCBM devices without and with FOPA treatment under dark condition and blue light irradiation(460nm) are shown in Fig. 4. Under reverse bias voltage, the dark current was slightly decreased. As a result, on/off ratio was improved. The photocurrent increased with applied reverse voltage, which indicates that the dissociation of photogenerated excitons at the P3HT:PCBM bulk hetero-junctions is accelerated with increasing external electric field.

IPCE spectra of the devices of without and with FOPA at 0V and -2V are shown in Fig. 5. The device with FOPA treatment had higher IPCE than those without FOPA treatment. P3HT:PCBM device exhibited the IPCE of approximately 50 and 55 % at -2 V under blue light irradiation (460 nm).

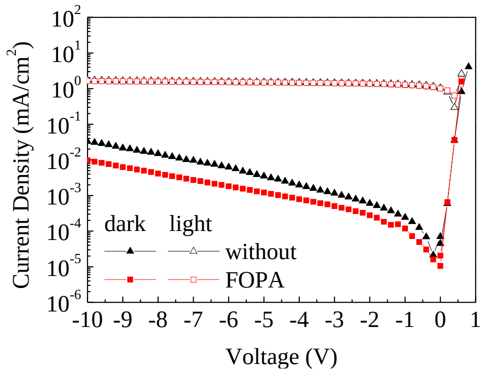


Fig. 4. J-V characteristics of the devices under dark condition and irradiation

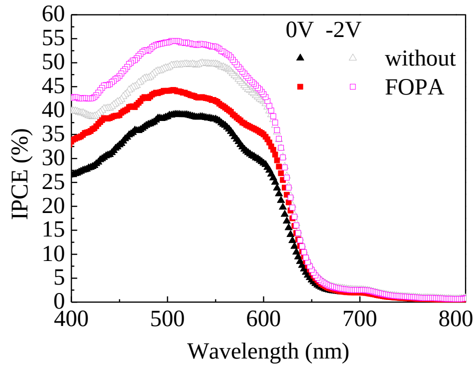


Fig. 5. IPCE spectra of the P3HT:PCBM devices at 0, -2 V.

The comparison of the normalized photocurrent against irradiation time for P3HT:PCBM devices without and with FOPA treatment are shown in Fig. 6. The photocurrent at the time of 0h irradiation time is defined as 100%. Irradiated light is blue light(460nm) and the power is 10.3mW/cm^2. For the device without FOPA treatment, the photocurrent decreased down to 81% after light irradiation for 4h. In contrast, the photocurrent for the FOPA treated device was decreased down to 97% after light irradiation for 4h. Thus, improved durability of FOPA treated device was demonstrated. This result suggests that ITO/P3HT interface was damaged under light irradiation, and FOPA treatment improve it.

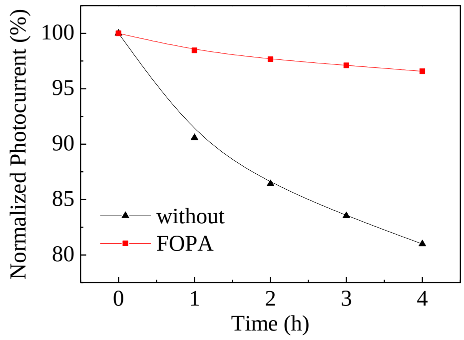


Fig. 6. Irradiation time dependence of the normalized photocurrents for the P3HT:PCBM devices without and with FOPA treatment

4. Conclusions

We investigated the characteristics of P3HT:PCBM devices with SAMs treated on ITO electrode. For the FOPA-treated device, the dark current was decreased, and the IPCE was increased to 55% at -2V. FOPA treated device showed improved durability after continuous irradiation of blue light (460nm, 10.3mW/cm^2).

Acknowledgements

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