Light illumination effects in ambipolar FETs based on poly(3-hexylthiophene) and fullerene derivative composite films

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Abstract

The effects of light illumination on field effect transistors based on Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric methyl ester (PCBM) composite films have been studied. It is found that the light illumination on pure P3HT and PCBM generally resulted in decrease of the threshold voltages and increase of the mobilities by a little. In the composite film at the PCBM contents of x = [P3HT]/([P3HT]+[PCBM]) = 0.67~0.9, an ambipolar field transport appeared. The light illumination effect was observed remarkably in the shift of threshold voltage for the hole generation at x = 0.75. Variations of Hole and electron mobilities and threshold voltage of electron generation upon light illumination were basically similar to those of the pure materials. The results were discussed in terms of the light assisted carrier generation in

field effects.

Key words: poly(3-hexylthiophene), PCBM, FET, ambipolar transport, light illumination effect, mobility, threshold voltage.

1. Introduction

Organic electroluminescence [1], solar cell [2-5] and field effect transistor (FET) [6-9] have been intensively studied, because of their low cost fabrication, light weight and mechanical flexibility. For these electronic devices, electrical transport materials by positive charge (p-type or hole) and negative charge (n-type or electron) are essential to functionalize electronic devices. The p- and n- channel FETs are basic components [9] to fabricate a complementary metal oxide FET (CMOS-FET).

Poly(3-hexylthiophene) [3-6] (P3HT) shown by Fig.1 (a) is one of conjugate polymers prospective as p-type transport polymers for solar cell and FET, because of the large hole mobilities[8] due to the self assembled crystallinity [10]. Fullerene and the derivatives are known to be an n-type material with high electron mobility [6,7,11]. Fullerene is hardly soluble in ordinary solvents, however, the derivatives like [6,6]-phenyl-C_{61}-butyric methyl ester (PCBM) (Fig.1(b)) and etc. are soluble in organic solvents such as chloroform [6,7]. The solution processes have many advantages in terms of low cost, large area and mass production.

P3HT and PCBM composite films have been studied intensively from the view point of organic solar cells with the bulk hetero structure [2-7]. It is suggested that photo excitons generated at P3HT site are efficiently dissociated by trapping electron at fullerene derivatives and holes appear at P3HT main chains [4]. The facts have been confirmed from facts of quenching of photoluminescence and enhancement of photo carrier generation by blending fullerene in P3HT. There have been a few papers which reported the carrier mobility in composite films of P3HT and PCBM from measurements of field effects [6,7,11,12]. In the composite films [6,12,13], ambipolar transports were observed due to the p-type and n-type natures of P3HT of PCBM, respectively. However, light illumination effects on the ambipolar transport have not been reported so far. In this paper, the preliminary results on the light illumination effects in field effects of P3HT, PCBM and their composite films are mentioned and the results are discussed.

2. Experimental procedures

P3HT and PCBM were purchased from Aldrich and Frontier Carbon Cooperation, respectively. P3HT was purified with tetrahydrofuran [14]. The purification procedure of P3HT was similar to previous reports [13,16]. PCBM was used as obtained. Chloroform solutions of P3HT and PCBM both at 0.75 Wt% were separately stirred with magnetic stirrer for one hour at 45℃, followed by mixing them at various ratios. The content of

PCBM was defined by [PCBM]/([P3HT]+[PCBM]) = x, where [PCBM] and [P3HT] are volume of the solutions. The mixed solution was further stirred by 250 rpm with magnetic stirrer for one hour at 65℃.

A silicon wafer with the n-type conductivity of 100 S/cm was used as the substrate. Gate insulator of SiO_2 with the thickness of approximately 300 nm was formed by thermal oxidation of the Si substrate [8]. The gate capacitance was approximately 10 nF/cm^2. The surface of Si/SiO_2 substrate was treated to make hydrophilic by exposure to a vapor of HMDS (hexamethyldisilazane) [15]. The films were prepared on Si/SiO_2 substrate by spin coating of solutions at 1,000 rpm for 20 s, followed by 2,000 rpm for 10 s. The thickness of films was measured by DEKTAK 6M and was typically 50 - 80 nm. Au electrodes with the thickness of 30 nm were deposited on the films by thermal evaporation to form source and drain electrodes (top contact). Generally, it is accepted that a contact with low work function metals like Al and Ca is preferable to n-type materials, however, it was shown that Au could be used for PCBM in FET [15,16]. The dimension of FET, namely, the channel length and width were 50 μm and 2 mm, respectively. The FET devices were thermally treated in dry N_2 at 100℃ for 30 min in order to anneal films[12].

Measurements of FET characteristics were carried out in vacuum chamber at pressure of approximately 1×10^{-3} Pa with a Keithley 6517A electrometer. A light source of a green laser with the wavelength of 532 nm and the approximate power of 20 mW/cm^2 was used to measure effect of the light illumination to FETs.

3. Results and Discussion

Figure 2 shows absorption spectra of PCBM, P3HT and their composite film at x = 0.75. In the composite film, absorptions peaking at 266 and 334 nm were sifted from the peaks at 270 and 338 in pure PCBM by 4 nm. The slight blue shift of absorption peaks is conjectured from the insertion of P3HT between PCBM molecules. The absorption peak at 470 nm in the composite film was pronounced and the 520 nm peaks associated with P3HT was not observed clearly. The results of blue shift indicate that weakened self-interaction and the hybridization between the lowest bands of P3HT and PCBM may occur, although the detail is not known and to be studied.

The ambipolar transport was observed at x = 0.67~0.91, namely, PCBM rich condition as described in our previous paper [13]. The on/off ratios of the FETs were between several and 10^4, and it was found that the values for composite films were relatively small [16]. Curves in Fig.3 (a) and (b) show the transfer characteristics, namely, $(I_D)^{1/2}$ vs. V_G, of pure P3HT and PCBM films, respectively, in dark and under light illumination. Mobilities (μ) and threshold voltages (V_{th}) were evaluated [6-12] from the gradient and the intercept of horizontal axis of the curves, respectively. All numerical data are summarized in Table1.

It is found that electron and hole mobilities were nearly constant or somewhat increased and both threshold voltages (V_{th}) decreased by light illumination as shown in

Fig.3. The results indicate that the generation of carriers was assisted by the light illumination. However, the heating effect of sample by light illumination can not be role out for the explanation to this result including the increase of carrier mobility. It should be noted that in the transfer characteristic of PCBM under light illumination, the I_D increased significantly at lower V_G as shown in Fig.3 (b). This tendency was not observed in dark. The result indicates that the hole generation was enhanced by light illumination. The p-type transport in PCBM under illumination has to be examined further by the future study.

Figure 4 shows the transfer characteristic of the P3HT and PCBM composite film at x = 0.75. In the composite film the hole and electron mobilities, which may originated from P3HT and PCBM, respectively, decreased significantly from their pure materials by more than one order of magnitude. The results were explained by a model [13] that the blending of P3HT and PCBM resulted in the introduction of impurities each other and distortion of crystallinity, which should be better in the pure materials. It is interesting to note that the effect of light illumination was remarkably found in the shifting of threshold voltage for hole generation (V_{th-p}) and slight increase of electron mobility. On the other hand, the hole mobility and the threshold voltage for electron (V_{th-n}) were basically unchanged or decreased slightly upon light illumination.

The effect of light illumination in the composite FET is conjectured as follows. The green light illumination results in the generation of excitons probably in the P3HT site and the excitons dissociate into electrons and hole in some probability. In the composite films [4], the dissociation is pronounced significantly as stated previously, namely, electrons are captured by PCBM and hole remains in P3HT chains, resulting in the decreases of V_{th} for holes as well as electrons. The explanation should support the large conversion efficiency in the bulk hetero solar cells.

4. Summary

The effect of light illumination in the FET based on P3HT and PCBM composite films, which are materials same to a bulk hetero interfacial solar cell, has been investigated. It is found that the light illumination of the FET, in which ambipolar transport was observed, significantly reduced the threshold voltage in the hole transport, whereas the hole and electron mobilities were not changed much. The mechanism was explained in terms of the enhanced exciton dissociation by blending of P3HT and PCBM. The results were expected in the bulk hetero solar cells, however, the present study could be the first report for the confirmation of the light effect so far. Further experiments are under study to elucidate the detailed mechanism of the transport in bulk hetero structure for solar cells.

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Figure captions

Fig.1. Molecular structures of (a) P3HT and (b) PCBM.

Fig.2 Absorption spectra of P3HT (approximate thickness: 110 nm), PCBM (70 nm) and composite film (70 nm) at x = 0.75.

Fig.3 Effects of light illumination on the transfer characteristics of (a) P3HT and (b) PCBM FETs.

Fig.4 Transfer characteristics of the P3HT and PCBM composite film for dark and light illumination.

Table 1 Mobilities and threshold voltages in P3HT, PCBM and their composite films for dark and light illumination.