Analyses of Charge Accumulation of PTzBT Ternary Polymer Solar Cells Using ESR Spectroscopy

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Ternary polymer solar cells based on a polymer PTzBT have attracted attention because its power conversion efficiency (PCE) and thermal stability have been greatly improved by adding a small amount of an oligomer ITIC. However, the charge accumulation states of the PTzBT ternary polymer solar cells have not yet been completely clarified. Here, we report electron spin resonance (ESR) spectroscopy of layered samples of ZnO/(blend or pristine film) using PTzBT, ITIC, and a fullerene derivative PC61BM to investigate the charge accumulation states of the PTzBT ternary solar cells at a molecular level. We have observed monotonic increases in the ESR intensity of the ZnO/(blend or pristine film) samples under simulated solar irradiation, where the increases in the ESR intensity of the PC61BM with ITIC component are smaller than those without ITIC component. The present results would be useful to develop further highly efficient and durable polymer solar cells.

Keywords: Charge accumulation, Electron spin resonance spectroscopy, Ternary polymer solar cells, ITIC

1. Introduction

Polymer solar cells have been extensively investigated as they have characteristics such as low manufacturing cost, enabling large-area, and flexibility that are difficult to be realized with silicon-based solar cells [1–3]. In recent years, the power conversion efficiency (PCE) of ternary polymer solar cells has been remarkably improved [4]. However, the internal deterioration mechanism has not yet been completely clarified. Ternary polymer solar cells with a wide-band gap polymer based on thiophene and thiazolothiazole (PTzBT) (Fig. 1a) have attracted attention because the maximum PCE of the solar cells with PTzBT and [6,6]-phenyl C61-butyric acid methyl ester (PC61BM) have been improved from 7.4% to 10.3% by adding a small amount of ITIC (Fig. 1b). This ternary polymer solar cells with ITIC have excellent thermal stability that the PCE has almost not changed even after the storage at 85°C for 1000 h in a nitrogen-filled glove box under dark conditions under open-circuit conditions. Thus, the PTzBT solar cells are expected as polymer solar cells with high PCE and stability, and ITIC are expected as an ideal additive [5].

Sealing solar cells can suppress the extrinsic irreversible degradations from oxygen and moisture [6–12]. However, there is still some internal deterioration factors that cannot be prevented such as charge accumulation. Electron spin resonance (ESR) spectroscopy is a useful method that can directly investigate the states of accumulated charges in polymer solar cells and organic solar-cell materials at a molecular level [13–23]. It is very interesting to investigate the charge accumulation in PTzBT ternary polymer solar cells with ITIC.

In this study, we have measured layered samples of the active layer and an electron transport layer (ETL) ZnO using light-induced ESR spectroscopy, and have found some differences of the ESR signals between the samples of ZnO/PTzBT:ITIC:PC61BM and ZnO/PTzBT:PC61BM. We conducted a further study by measuring layered samples of ZnO/ITIC:PC61BM and ZnO/PC61BM. We have
observed several signals and monotonic increases in the ESR intensities of all the ZnO layered samples. The ESR signal of PC$_{61}$BM electron (or radical anion), namely, the electron signal of PC$_{61}$BM, is observed and the signal increase in the ESR intensity of PC$_{61}$BM with ITIC component is smaller than that without ITIC. This deep understanding of the charge accumulation states would be important for optimizing the device structures and for improving the PCE and durability of ternary polymer solar cells.

2. Experimental
In the present work, the ternary polymer solar cells were fabricated with PTzBT, ITIC (Fig. 1b), and PC$_{61}$BM (Solenne BV, purity > 99.5%). A quartz substrate (20 mm × 3 mm) was cleaned with acetone and 2-propanol in ultrasonic treatment. A ZnO layer was prepared by a spin-coating method (at 1500 rpm) from a diluted solution of ZnO nanoparticles. PTzBT, ITIC, and PC$_{61}$BM (1:0.2:2 w/w/w) dissolved in chlorobenzene (CB) solvent was mixed at 100 °C for 30 min with a vibrational method. Active layers (PTzBT:ITIC:PC$_{61}$BM or PTzBT:PC$_{61}$BM) were fabricated by a spin-coating method (600 rpm, 20 s) on the quartz substrate in a nitrogen-filled glove box (O$_2$ < 0.2 ppm, H$_2$O < 0.5 ppm). The fabricated samples were measured under dark conditions or simulated solar irradiation with a solar simulator (AM1.5G, 100 mW cm$^{-2}$) (OTENTOSUN-150LX).

3. Results and discussion
3.1. ESR measurements
ESR is a magnetic resonance phenomenon occurring for unpaired electrons, which is a non-destructive and highly sensitive method that can evaluate materials at the molecular level by observing the microwave absorption at the magnetic resonance. We used a continuous-wave ESR method in the experiments which performs a lock-in detection with an external magnetic field ($H$) modulation of 100 kHz. Thus, photogenerated charges with a lifetime (<10 μs) cannot be observed, and it is possible to observe only long-lived (or accumulated) photogenerated charges with an unpaired spin with a long lifetime (>10 μs) in thin films and solar cells [19, 21–23].

We simultaneously measured the ESR signals of our sample and a same standard Mn$^{2+}$ marker sample in a same ESR cavity in all ESR measurements in order to compare these g factors directly. The calibration of the g factor was performed by using a software program of the ESR system considering high second-order correction of the effective resonance field. Its correctness was also confirmed by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as another standard sample. The present ESR system significantly reduces experimental errors because the fluctuation of experimental conditions such as microwave power etc. can be calibrated by using the signal of the marker sample [19, 21–23].

By using ESR measurements, it is possible to investigate accumulated charge states in the samples directly. The light-induced ESR spectrum is a difference spectrum between ESR spectra obtained from under dark condition and simulated solar irradiation. We can study the effect of the irradiation for the samples. In our study, the substrate plane was
parallel to the $H$ direction. All measured light-induced ESR spectra were averaged over 1 h irradiation [19, 21–23].

3.2. ESR spectra of layered samples

Investigating the effect of ITIC addition on charge accumulation is a very interesting issue to clarify the internal deterioration mechanism of the ternary polymer solar cells. For this purpose, layered samples of ZnO with PTzBT:ITIC:PC$_{61}$BM or PTzBT:PC$_{61}$BM have been fabricated and measured using ESR spectroscopy. Fig. 2 shows the ESR spectra of the layered samples after 14 h simulated solar irradiation. According to Fig. 2, whether or not ITIC has been used, apparent two signals have been observed. We define the signal on the left as Signal A, and the signal on the right as Signal B, respectively. The $g$ factors of the Signal A and Signal B are obtained as $g = 2.0026±0.0004$ and $g = 2.0001±0.0004$, respectively.

In order to find out the origins of ESR signals, layered samples of PTzBT:PC$_{61}$BM, ZnO/PC$_{61}$BM,
ZnO/ITIC:PC$_{61}$BM, and ZnO/ITIC were fabricated and measured using ESR spectroscopy. The observed ESR spectra are shown in Fig. 3a,b,c,d, respectively. As the duration of the light irradiation increased, the intensity of the ESR signals in Fig. 3a,b,c increased, while the ESR intensity in Fig. 3d was almost constant. The ESR signal of Fig. 3a is identified as a hole signal of PTzBT because the spin-lattice relaxation time of PC$_{61}$BM is so short that the ESR signal of PC$_{61}$BM cannot be observed at room temperature [21−23]. The $g$ factor of holes in PTzBT is identified as $g = 2.0024\pm 0.0004$. When measuring the ESR signals of ZnO/PC$_{61}$BM (Fig. 3b) and ZnO/ITIC:PC$_{61}$BM (Fig. 3c), we observed same signals of two components with their $g$ factors $g = 2.0027\pm 0.0004$ and $g = 2.0003\pm 0.0004$, respectively. The observed signals of ZnO/PC$_{61}$BM (Fig. 3b) and ZnO/ITIC:PC$_{61}$BM (Fig. 3c) are almost the same as those of ZnO/PTzBT:ITIC:PC$_{61}$BM and ZnO/PTzBT:PC$_{61}$BM (Fig. 2), whose $g$ factors are $g = 2.0026$ (Signal A) and $g = 2.0001$ (Signal B) as mentioned above. The ESR signal of $g = 2.0027$ has been reported as the signal of a singly positively charged oxygen vacancy ($V^+_O$) in ZnO [24,25]. The ESR signal of $g = 2.0003$ has been reported as the electron signal of PC$_{61}$BM.

In order to get more accurate component signal, we performed fitting analyses for the light-induced ESR signals of ZnO/PC$_{61}$BM (Fig. 3b) and ZnO/ITIC:PC$_{61}$BM (Fig. 3c) after 14 h light irradiation, and the calculated results are shown in Fig. 3f and 3e, respectively. In previous studies, the electron signal of PC$_{61}$BM with an anisotropic lineshape have been observed at low temperatures such as 30 K [26]. However, the molecular vibrations are large and the electron signal of PC$_{61}$BM is averaged at room temperature [24,27]. Thus, we have fitted the light-induced ESR signals of ZnO/ITIC:PC$_{61}$BM and ZnO/PC$_{61}$BM at room temperature using isotropic signals, and found that the best result can be described using the sum of two Lorentzian functions. The results of the fitting analyses are evaluated as follows: ESR parameters of Signal A are $g$ factor $g = 2.0027\pm 0.0004$, peak-to-peak ESR linewidth $\Delta H_{pp} = 0.23\pm 0.02$ mT, and ESR parameters of Signal B are $g = 2.0003\pm 0.0004$, $\Delta H_{pp} = 0.30\pm 0.02$ mT. Thus, the Signal A ($g = 2.0026$) is identified to be composed of both the hole signals of PTzBT ($g = 2.0024$) and ZnO ($g = 2.0027$), and the Signal B ($g = 2.0001$) is identified to be due to the electron signal of PC$_{61}$BM ($g = 2.0003$). It is worth noting that the electron signal of PC$_{61}$BM, which have not been observed with the active layer thin films at room temperature because of the short spin-lattice relaxation time due to the rotation of wave function of electrons on PC$_{61}$BM [21−23], has been observed when we have measured ZnO/PC$_{61}$BM (Fig. 3b) and ZnO/ITIC:PC$_{61}$BM (Fig. 3c). The observation of the Signal B indicates the interactions between ZnO and PC$_{61}$BM electrons with a strong spin-orbital interaction due to a heavy element Zn in the ZnO layer. Compared to the previous study, our observed $g$ factor of PC$_{61}$BM is slightly larger because the heavy element Zn is effective in shifting the $g$ factor [28].
3.3. Effect of ITIC addition.

Schematic energy level diagrams of ZnO, ITIC, and PC$_{61}$BM are shown in Fig. 4. The values of energy levels are taken from previous studies [29-33]. The energy levels of valence band (VB) top and conduction band (CB) bottom of ZnO have been reported as a range of $-7.4$ to $-7.7$ eV and $-4.0$ to $-4.3$ eV, respectively [29-31]. The energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PC$_{61}$BM have been reported as a range of $-6.0$ to $-6.2$ eV and $-3.8$ to $-4.2$ eV, respectively [30-33]. The energy level of the oxygen vacancy $V_{O}$ is $-0.05$ eV deeper than the CB bottom of ZnO [29]. Normally, the electrons are transferred from PC$_{61}$BM to ZnO. However, our present ESR results indicate that the electrons are transferred from ZnO to PC$_{61}$BM. In the case of ZnO/PC$_{61}$BM (Fig. 3b), the electron signal of PC$_{61}$BM and the hole signal of $V_{O}^{+}$ are observed. We infer that the LUMO of PC$_{61}$BM may be deeper than the energy level of the $V_{O}$, and thus electrons can transfer from the $V_{O}$ in ZnO to the LUMO of PC$_{61}$BM. The bandgap energy of ITIC calculated by the difference between HOMO and LUMO energy levels, which have been determined by photon yield spectroscopy and low-energy photoemission spectroscopy, respectively, is 2 eV [5]. This is actually different from the value determined by optical absorption onset of ITIC (1.59 eV) [5]. Such difference originates in the exciton binding energy and is typical to π-conjugated organic materials [34].

It is interesting to find out the effect of the ITIC addition by comparing the ESR spectra of ZnO/PC$_{61}$BM (Fig. 3b) and ZnO/ITIC:PC$_{61}$BM (Fig. 3c) after 14 h simulated solar irradiation. The compared ESR spectra are shown in Fig. 5. It is worth noting that the intensity of the Signal B with ITIC is weaker than that without ITIC (see Fig. 2 and 5). The reason may be that some of ITIC molecules prevent the contacts between the ZnO layer and PC$_{61}$BM molecules, and thus the electron signal of PC$_{61}$BM cannot be observed because of the short spin-lattice relaxation time of PC$_{61}$BM without contacting ZnO at room temperature as mentioned above [21-23,26]. From our ESR study, we suggest that PC$_{61}$BM and ITIC are mixed, and both are in contact with the ZnO layer. Our clarification of the charge accumulation at the interface between the ZnO and active layers would be important for improving the PCE and durability of ternary polymer solar cells.

4. Conclusion

The layered samples of ZnO/PTzBT:ITIC:PC$_{61}$BM and PTzBT:PC$_{61}$BM have been investigated with ESR spectroscopy under dark conditions and simulated solar irradiation. As the duration of the light irradiation increased, the intensities of the hole signal of PTzBT, the hole signal of ZnO, and the electron signal of PC$_{61}$BM increased. The observation of the electron signal of PC$_{61}$BM indicates the interactions between ZnO and PC$_{61}$BM with the strong spin-orbital interactions due to the heavy element Zn in the ZnO layer. The electron signal of PC$_{61}$BM with ITIC are smaller than that without ITIC under simulated solar irradiation. The reason may be that some of ITIC molecules prevent the contacts between the ZnO layer and PC$_{61}$BM molecules, and thus some electrons’ signal of PC$_{61}$BM cannot be observed. This deep understanding of the charge accumulation states at the interface between the ZnO and active layers of ternary polymer solar cells will be useful for optimizing the device structures and for improving the PCE and durability.

Acknowledgement

This work was partially supported by JSPS KAKENHI Grant Number JP19K21955, by JST PRESTO, by The Hitachi Global Foundation, by The MIKIYA Science And Technology Foundation, by Iketani Science and Technology Foundation, and by JST ALCA Grant Number JPMJAL1603, Japan.

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