Analyses of PTzNTz Polymer Solar Cells Using ESR Spectroscopy

Dong Xue¹, Shinpei Kamiya¹, Masahiko Saito², Itaru Osaka², and Kazuhiro Marumoto¹,³*

¹Division of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
²Graduate School of Engineering, Hiroshima University, Higashihiroshima, Hiroshima 739-8527, Japan
³Tsukuba Research Center for Energy Materials Science (TREMS), University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan
*marumoto@ims.tsukuba.ac.jp

Inverted-type polymer solar cells with semiconducting polymers based on PTzNTz have attracted attention because of its high power conversion efficiency (PCE) and thermal stability. In recent years, the PCE of the polymer solar cells has been remarkably improved. However, the effect of these hole transport layers (HTLs) on PTzNTz solar cells have not yet been completely clarified. Here, we report operand electron spin resonance (ESR) spectroscopy of the PTzNTz layered samples to investigate the deterioration mechanism of the PTzNTz solar cells at a molecular level. We have observed monotonic increases in the ESR intensity of the PTzNTz layered samples, where the increases in the ESR intensity of PTzNTz active layers with WOₓ HTL are smaller than those with MoOₓ HTL. The present results would be useful to develop further highly efficient and durable polymer solar cells.

Keywords: Polymer solar cells, Electron spin resonance spectroscopy, Charge accumulation

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 polymer solar cells has been remarkably improved [4]; however, the internal deterioration mechanism has not yet been completely clarified. Inverted-type polymer solar cells with semiconducting polymers based on PTzNTz (Fig. 1) have attracted attention because they have both high PCE and thermal stability [5]. PTzNTz has a narrow band gap (1.57-1.58 eV), and the maximum PCE of 9.0% has been reported for inverted-type polymer solar cells with PTzNTz and [6,6]-phenyl C71-butyric acid methyl ester (PC71BM) [5]. These solar cells have excellent thermal stability that the PCE has almost not changed even after the storage at 85 °C for 500 h in a nitrogen-filled glove box under dark conditions under open-circuit conditions, and thus are expected as high PCE and stability polymer solar cells [5].

Oxygen and moisture have been reported as external degradation factors for polymer solar cells [6–8]. Sealing the solar cells can suppress the extrinsic irreversible degradations [9–15]. However, the sealing of the cells cannot prevent the internal deterioration factors such as charge accumulation. Electron spin resonance (ESR) spectroscopy is a useful method that can investigate the states of accumulated charges in polymer solar cells directly at a molecular level [16–19]. Several groups have studied organic solar-cell materials using the ESR technique [20–22]. It is very interesting to investigate the charge accumulation in PTzNTz polymer solar cells. In our previous studies, the signals of PTzNTz solar cells have been identified as a hole signal of PTzNTz and an electron signal of PC71BM under simulated solar irradiation [23]. We also have found that the ESR intensity of the PTzNTz cell with a hole transport layer (HTL) of
WO\textsubscript{x} is smaller than that with MoO\textsubscript{x} HTL. However, the effect of these HTLs on PTzNTz solar cells have not yet been completely clarified.

In this study, we have measured PTzNTz layered samples using light-induced ESR spectroscopy and have found a difference of the ESR signals between the samples of PTzNTz:PCBM/MoO\textsubscript{x} and PTzNTz:PCBM/WO\textsubscript{x}. We have observed monotonic increases in the ESR intensity of the PTzNTz layered samples, where the increases in the ESR intensity of PTzNTz active layer with WO\textsubscript{x} HTL are smaller than those with MoO\textsubscript{x} HTL. This deep understanding of the internal deterioration mechanism would be important for optimizing the device structures and for improving the PCE and durability of polymer solar cells.

2. Experimental

In the present work, the polymer solar cells were fabricated with PTzNTz-BOBO (Fig. 1), which is PTzNTz with two 2-butyloctyl group, and PC\textsubscript{71}BM (Solenne BV, purity > 99%). A quartz substrate (20 mm \times 3 mm) was cleaned with acetone and 2-propanol in ultrasonic treatment. PTzNTz and PC\textsubscript{71}BM (1:1.5 w/w) dissolved in chlorobenzene (CB) solvent was mixed at 100 °C for 30 min with a vibrational method. Then, 2 vol% 1,8-diiodooctane (DIO) was added in the mixed solution. An active layer (PTzNTz:PC\textsubscript{71}BM or PTzNTz:PC\textsubscript{61}BM) were fabricated by a spin-coating method (600 rpm, 20 s) on the quartz substrate in a nitrogen-filled glove box (O\textsubscript{2} < 0.2 ppm, H\textsubscript{2}O < 0.5 ppm). Then the HTL MoO\textsubscript{x} (7.5 nm) or WO\textsubscript{x} (15 nm) and Ag (hole collecting electrode, 100 nm) were fabricated by a vacuum-deposition method below 4.0×10\textsuperscript{-5} Pa. The fabricated samples were measured under dark or simulated solar irradiation conditions using AM1.5G, 100 mW/cm\textsuperscript{2} solar simulator (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 resonance. We used the continuous-wave ESR method in the experiments which performs a lock-in detection with an external magnetic field (\textit{H}) modulation of 100 kHz. Thus, photogenerated charges with a lifetime (<10 \mu s) 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 \mu s) in thin films and solar cells [23–26].

We simultaneously measured the ESR signals of our sample and a same standard Mn\textsuperscript{2+} marker sample in the same ESR cavity in all ESR measurements in order to compare these \textit{g} factors directly. The calibration of the \textit{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 [23,26].

By using ESR measurements, it is possible to investigate accumulated charge states in the samples directly. The light-induced ESR spectra are difference spectra between ESR spectra obtained from under dark and simulated solar irradiation conditions. We can study the effect of the irradiation for the samples. In our study, the substrate plane was parallel to the \textit{H} direction. All measured light-induced spectra were averaged under 1 h irradiation [23,26].

3.2. Light-induced ESR spectra of PTzNTz:PCBM with MoO\textsubscript{x} or WO\textsubscript{x} HTL layered samples

Investigating the effect of these two HTLs are a very interesting issue to clarify the internal deterioration mechanism of the cells. For this purpose, PTzNTz:PC\textsubscript{71}BM or PC\textsubscript{61}BM with WO\textsubscript{x} or MoO\textsubscript{x} HTL layered samples have been fabricated and measured using ESR spectroscopy. Figure 2 shows the light-induced ESR signals. As the duration of the light irradiation increased, the intensity of the light-induced ESR signals of all the samples increased, which indicate that charges with spins are accumulated.

The ESR parameters of PTzNTz:PC\textsubscript{71}BM with
WO_x and MoO_x HTL layered samples for 20 h irradiation are $g$ factor $g = 2.0025(\pm 0.0002)$, and peak-to-peak ESR linewidth $\Delta H_{pp} = 0.26(\pm 0.02)$ mT; the ESR parameters of the PTzNTz:PC_{61}BM with WO_x and MoO_x HTL sample for 20 h irradiation are $g = 2.0023(\pm 0.0002)$, and $\Delta H_{pp} = 0.24(\pm 0.02)$ mT. The $g$ factor can be evaluated from the resonant magnetic field [25]. All the ESR parameters have been calibrated using a standard sample Mn^{2+} marker. Since we didn’t find any anisotropy of ESR signals of the PTzNTz cells by changing the $H$ direction with respective to the substrate plane in the ESR measurements, the location of accumulated charges has been confirmed as amorphous.

According to Figs. 2(a,c) and 2(b,d), no matter which HTL has been used, the obtained ESR signals of the layered samples with PC_{71}BM are larger than those with PC_{61}BM. In the previous study, the ESR parameters of PTzNTz:PC_{71}BM thin-films are $g = 2.0024$ and $\Delta H_{pp} = 0.24$ mT [23], which accord with the results of the present layered samples with PC_{71}BM. In the case with PC_{61}BM, the spin-lattice relaxation time of PC_{61}BM is so short that the signal cannot be observed at room temperature [23-24,26]. Thus, the difference of the ESR signals between the layered samples with PC_{71}BM and PC_{61}BM are due to the electron signal of PC_{71}BM.

The $g$ factor of PTzNTz:PC_{71}BM/MoO_x ESR signal for 1 h irradiation is smaller than that for 20 h irradiation (Fig. 2(b)). To clarify the reason, we fabricated PTzNTz:PC_{71}BM/MoO_x/Ag samples and measured using ESR spectroscopy. Figure 3 shows the ESR signals of PTzNTz:PC_{71}BM/MoO_x/Ag. The shift of $g$ factor was prohibited by the Ag deposition. Moreover, the ESR parameters of PTzNTz:PC_{71}BM/MoO_x/Ag are same as those of PTzNTz:PC_{71}BM/WO_x. From these results, we can infer that the MoO_x has some defects worked as
electron trappings, and that defects are disappeared by the annealing effect from the Ag deposition. Under simulated solar irradiation, the electrons of PTzNTz transfer to the defects in MoO$_x$, and holes of PTzNTz mainly contribute to the observed ESR signals for 1 h irradiation. If the sample has been irradiated for a long time, the defects of MoO$_x$ have been filled up, and electrons has started to be accumulated on PCBM. The ESR linewidth of PTzNTz:PC$_{61}$BM for 1 h irradiation is narrower than that for the long-time irradiation because holes in PTzNTz are easily mobile due to the long distance between the electrons in MoO$_x$ and the holes in PTzNTz.

3.3. Numbers of accumulated charges in the PTzNTz:PCBM with MoO$_x$ or WO$_x$ samples

It is interesting to find out the difference between the two HTLs. Thus, we have compared the number of accumulated charges ($N_{\text{spin}}$) of those layered samples. The ESR signals were doubly integrated and compared with the signal of the standard sample Mn$^{2+}$ marker to evaluate the $N_{\text{spin}}$ corresponding to the charge’s accumulation. Figures 4(a, b) show the light-induced ESR signals of the layered samples with PC$_{71}$BM and with PC$_{61}$BM after 20 h simulated solar irradiation, respectively. Figures 4(c, d) show the transient responses of the $N_{\text{spin}}$ for the layered samples with PC$_{71}$BM and PC$_{61}$BM, respectively. Interestingly, not only the $N_{\text{spin}}$ of PTzNTz:PC$_{71}$BM with WO$_x$ is less than that with MoO$_x$, but also the $N_{\text{spin}}$ of PTzNTz:PC$_{61}$BM with WO$_x$ is less than that with MoO$_x$. This result indicates that less charges are accumulated in the active layer when we use
WO$_x$ as the HTL.

It is interesting to clarify the reason why the charges of the samples with WO$_x$ are less accumulated in the active layer. We can explain the reason by considering the energy levels of the sample materials. Figures 5(a, b) show the energy diagrams of PTzNTz:PCBM/WO$_x$ and PTzNTz:PCBM/MoO$_x$, respectively. The valence-band level of MoO$_x$ has been reported approximately $-5.6$ eV [27], which is deeper than highest occupied molecular orbital (HOMO) of PTzNTz ($-5.4$ eV) [5], and holes tend to be accumulated in the active layer. In contrast, for the case with WO$_x$, holes transfer in the conduction band of WO$_x$ ($-5.3$ eV) [27], and thus the holes can transfer smoothly from PTzNTz to Ag. At the surface of polymer blends, PTzNTz is likely to be highly crystalline because of free space. Thus, the crystalline phases would be contact with the HTL materials. The HOMO level of PTzNTz crystalline phases (Fig. 5), which is shallower than $-5.40$ eV, would match with the conduction band of WO$_x$ but not with the valence band of MoO$_x$. This is the reason why less charges are accumulated in the samples with WO$_x$. However, WO$_x$ cannot prevent the reverse electron transfer from PTzNTz to Ag. This is the reason why the open-circuit voltage ($V_{oc}$) of the PTzNTz cell with WO$_x$ ($-0.78$ V) is smaller than that of the cell with MoO$_x$ ($-0.84$ V) [5]. Therefore, although the PTzNTz polymer solar cells with WO$_x$ HTL have a high durability because of less charge accumulation, the non-negligible decrease in the $V_{oc}$ due to the reverse electron transfer is still a subject. In the case with MoO$_x$, the charge accumulation should be decreased to improve the durability and PCE.

4. Conclusion

PTzNTz:PCBM with MoO$_x$ or WO$_x$ HTL layered samples have been investigated with ESR spectroscopy. As the duration of the light irradiation increased, the intensity of the light-induced ESR signals of all the samples increased. Less charges are accumulated in the samples with WO$_x$ HTL because the holes smoothly transfer from PTzNTz to Ag. The $V_{oc}$ of PTzNTz cell with WO$_x$ is smaller than that with MoO$_x$ because of the reverse electron transfer from PTzNTz to Ag. Thus, further decrease in the number of accumulated charges in the active layer and the prevention of the reverse electron transfer from PTzNTz to Ag would be necessary for developing solar cells with higher PCE and durability.

Acknowledgements

This work has been partially supported by JSPS KAKENHI Grant Number JP15K13329, by JST PRESTO, by The Hitachi Global Foundation, by The MIKIYA Science and Technology Foundation, by The Futaba Foundation, and by JST ALCA Grant Number JPMJAL1603, Japan.

References

1. S. Günes, H. Neugebauer, and N. S. Sariciftci, *Chem. Rev.*, **107** (2007) 1324.
2. T. M. Clarke and J. R. Durrant, *Chem. Rev.*, **110** (2010) 6736.
3. R. Søndergaard, M. Hösel, D. Angmo, T. T. Larsen-Olsen, and F. C. Krebs, *Mater. Today*, **15** (2012) 36.
4. Y. Chang, T. K. Lau, M. A. Pan, X. Lu, H. Yan, and C. Zhan, *Mater. Horizons*, **6** (2019) 2094.
5. M. Saito, I. Osaka, Y. Suzuki, K. Takimiya, T. Okabe, S. Ikeda, and T. Asano, *Sci. Rep.*, **5** (2015) 14202.
6. A. Seemann, T. Sauermann, C. Lungenschmied, O. Armbruster, S. Bauer, H. J. Egelhaaf, and J. Hauch, *Sol. Energy*, **85** (2011) 1238.
7. M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, and F. C. Krebs, *Adv. Mater.*, **24** (2012) 580.
8. Y. W. Soon, H. Cho, J. Low, H. Bronstein, I. McCulloch, and J. R. Durrant, *Chem. Commun.*, **49** (2013) 1291.
9. C. Y. Chang, C. T. Chou, Y. J. Lee, M. J. Chen, and F. Y. Tsai, *Org. Electron.*, **10** (2009) 1300.
10. S. Sarkar, J. H. Whyland, M. Garvan, and V. Misra, *Org. Electron.*, **11** (2010) 1896.
11. M. Hermenau, S. Schubert, H. Klumbies, J. Fahlteich, and L. Müller-Meskamp, *Sol. Energy Mater. Sol. Cells*, **97** (2012) 102.
12. H. J. Lee, H. P. Kim, H. M. Kim, J. H. Youn, D. H. Nam, Y. G. Lee, J. G. Lee, A. R. Bin Mohd Yusoff, and J. Jang, *Sol. Energy Mater. Sol. Cells*, **111** (2013) 97.
13. M. D. Clark, M. L. Jespersen, R. J. Patel, and B. J. Leever, *Org. Electron.*, **15** (2014) 1.
14. T. M. Abdel-Fattah, E. M. Younes, G. Namkoong, E. M. El-Maghraby, A. H. Elsayed, and A. H. Abo Elazm, *Synth. Met.*, **209** (2015) 348.
15. A. Singh, A. Dey, D. Das, and P. K. Iyer, *ACS Appl. Mater. Interfaces*, **8** (2016) 10904.
16. K. Marumoto, S. I. Kuroda, T. Takenobu, and Y. Iwasa, *Phys. Rev. Lett.*, **97** (2006) 256603.
17. K. Marumoto, N. Arai, H. Goto, M. Kijima, K.

101
Murakami, Y. Tominari, J. Takeya, Y. Shimoi, H. Tanaka, S. Kuroda, T. Kaji, T. Nishikawa, T. Takenobu, and Y. Iwasa, Phys. Rev. B., 83 (2011) 075302.
18. D. Son, T. Kuwabara, K. Takahashi, and K. Marumoto, Appl. Phys. Lett., 109 (2016) 4963285.
19. G. Sato, D. Son, T. Ito, F. Osawa, Y. Cho, and K. Marumoto, Phys. Status Solidi A, 215 (2018) 1700731.
20. T. Biskup, M. Sommer, S. Rein, D.L. Meyer, M. Kohlstädt, U. Würfel, and S. Weber, Angew. Chem. Int. Ed., 210 (2015) 148.
21. V. I. Krinichnyi and E. I. Yudanova, Synth. Met., 54 (2015) 7707.
22. Y. Kobori, T. Ako, S. Oyama, T. Tachikawa, and K. Marumoto, J. Phys. Chem. C, 123 (2019) 13472.
23. D. Xue, S. Kamiya, M. Saito, I. Osaka, and K. Marumoto, ACS Appl. Energy Mater., 3 (2020) 2028.
24. T. Nagamori and K. Marumoto, Adv. Mater., 25 (2013) 2362.
25. T. Kubodera, M. Yabusaki, V. A. S. A. Rachmat, Y. Cho, T. Yamanari, Y. Yoshida, N. Kobayashi, and K. Marumoto, ACS Appl. Mater. Interfaces, 10 (2018) 26434.
26. V. A. S. A. Rachmat, T. Kubodera, D. Son, Y. Cho, and K. Marumoto, ACS Appl. Mater. Interfaces, 11 (2019) 31129.
27. Z. Yin, J. Wei, and Q. Zheng, Adv. Sci., 3 (2016) 1500362.