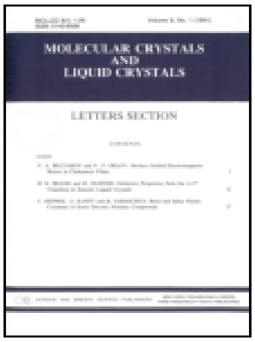
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Direct observation of UV-induced accumulated charges in inverted-type polymer solar cells with TiO_x layer by electron spin resonance

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ABSTRACT
We present an electron spin resonance (ESR) study of inverted-type polymer solar cells with the structure of indium tin oxide (ITO)/amorphous titanium oxide (TiO_x)/regioregular poly(3-hexylthiophene) (P3HT):phenyl-C_{61}-butyric acid methyl ester (PCBM)/Au. Two light-induced ESR signals with narrow and broad linewidth were observed by light irradiation. We found a strong correlation between typical light-soaking effects and the ESR signal with the broad linewidth under UV light irradiation. From the fact that the light-soaking effect requires UV irradiation, the ESR signal with the broad linewidth is found to be related with the light-soaking effect.

KEYWORDS
inverted-type polymer solar cell; electron spin resonance; titanium oxide; light-soaking effect

Introduction

Organic thin film solar cells are attracting much attention because of its potential of low-cost production and flexible nature [1–3]. One of the major problems in commercializing these devices is durability. Among these devices, inverted-type polymer solar cells show excellent stability compared to other organic solar cells even in ambient air condition [4]. Performance of the inverted-type devices employing amorphous titanium oxide (TiO_x) as electron collection layer is often affected by the duration of light irradiation, which is called as light-soaking effect [5–10]. The devices suffering from this phenomenon require adequate amount of UV irradiation to generate electricity. This behavior is relatively well-known; however, its microscopic origin is not yet clarified.

We have been utilizing electron spin resonance (ESR) spectroscopy to investigate the internal states of organic solar cells during device operation, and we were able to observe direct evidence that charge-accumulation in the cells is one of the main causes of device deterioration in normal-type polymer solar cells [11,12]. Because charge carriers in most organic semiconductors accompany spins, one can directly observe charge carriers that are accumulated during device operation with ESR by using spins as probes.

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In this paper, we report on an interesting charge-accumulation phenomenon which is observed during the irradiation of UV light on the inverted-type polymer solar cells using TiO_x as electron collection layer.

Experimental

Indium tin oxide (ITO) substrate was cleaned in an ultrasonic bath filled with isopropyl alcohol (IPA). The substrate is then treated with boiling IPA, and subsequently dried in air. Deposition of TiO_x layer was carried out using chemical bath deposition (CBD) method. A titanium(IV) oxysulfate ($TiOSO_4$) solution was mixed with hydrogen peroxide aqueous solution, and diluted with ultrapure water down to 0.03 M with respect to both components. Cleaned substrate was immersed in the precursor solution at 80 °C for 10 min. As-deposited film was additionally ultrasonicated in water for 10 min, and finally annealed at 150°C for 1 h. Thickness of the resulting TiO_x film was approximately 30 nm. A more detailed description of CBD procedure can be found out elsewhere [4]. Regioregular poly(3-hexylthiophene) (P3HT):phenyl-C_{61}-butryic acid methyl ester (PCBM) (5:4 w/w) chlorobenzene (CB) solution was spin-coated on top of the TiO_x film. Thickness of the active layer was about 250 nm. 150 nm Au back electrode was deposited using thermal evaporation, and finally annealed at 150 °C for 5 min on a hot plate. Active area of the device is 0.16 cm^2. Two lead wires were connected to each ITO and Au electrode using Ag paste for electrical measurement, and then the device was sealed in an ESR sample tube under nitrogen atmosphere.

ESR measurement was performed using JEOL RESONANCE JES-FA200 X-band spectrometer at room temperature. A standard Mn^{2+} marker sample was used to calibrate the g value, the ESR linewidth, and the number of spins. Absolute value of the number of spins in Mn^{2+} marker was calculated using a 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) solution. The calibration of g value with respect to Mn^{2+} marker was performed using data processing software from JEOL RESONANCE. Electrical measurements were carried out using Keithley 2612A source meter under AM 1.5G 100 mW cm^{-2} simulated solar irradiation (white light) or simulated solar irradiation in the presence of UV-cutoff filter which blocks out light whose wavelength is less than 420 nm (UV-cut light). Bunkoukeiki OTENTOSUN-150BXM solar simulator was used as the light source.

Results and discussion

Current density (J)-voltage (V) characteristics of the device from its initial state are shown in Fig. 1. Note that “White” in the figure legend stands for the condition under simulated solar irradiation including UV light, while “UV-cut” denotes the condition under simulated solar irradiation without UV wavelength region. The initial-state device irradiated by UV-cut light showed S-shape J-V characteristic and the performance was very poor. By irradiating UV-cut light for several hours, the performance somewhat improved, but the curve still maintained its S-shape, indicating that the cell is not working properly. Once the cell is irradiated with white light, both short-circuit current and open-circuit voltage greatly increased and the curvature changed to J-shape. This improvement is typical behavior of light-soaking phenomena [7-10]. The performance of the device was gradually improved during continual irradiation of white light. When the device was light-soaked with UV light, it worked well even without UV region light.

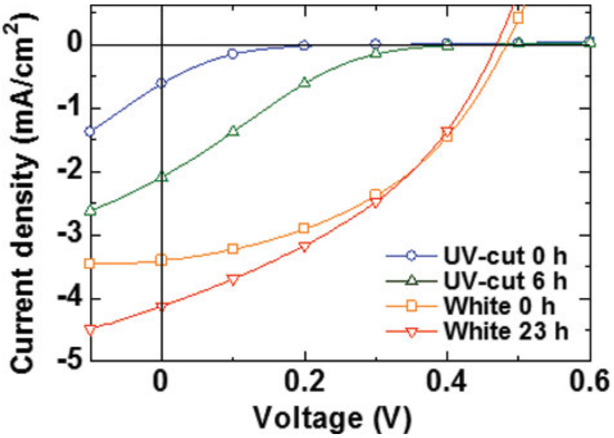

Figure 1. *J-V* characteristics of ITO/TiO_x/P3HT:PCBM/Au device irradiated with UV-cut light (blue and green lines) and with white light after being irradiated by UV-cut light (orange and red lines). Measurements were performed at room temperature.

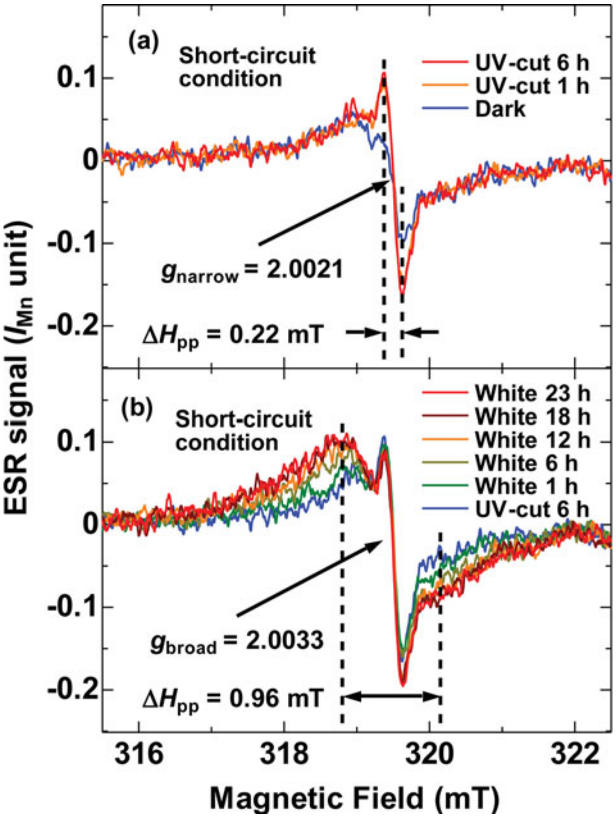

Figure 2. ESR signals of ITO/TiO_x/P3HT:PCBM/Au device irradiated with (a) UV-cut light and (b) white light after 6 h of UV-cut light irradiation. Measurements were performed at room temperature under short-circuit condition. External magnetic field was kept parallel to the substrate. Intensity of the ESR signals was calibrated by the peak-to-peak intensity of the ESR signal of the Mn^{2+} standard marker (I_{Mn}).

Figure 2 shows the dependence of the ESR signals of the operating device under short-circuit condition on light irradiation. It is apparent that the ESR signal consists of two components each having narrow and broad linewidth. Respective ESR parameters of two components are $g_{\mathrm{narrow}} = 2.0021$, $\Delta H_{\mathrm{pp}} = 0.22$ mT and $g_{\mathrm{broad}} = 2.0033$, $\Delta H_{\mathrm{pp}} = 0.96$ mT. Fig. 2a demonstrates the change in the ESR spectrum upon device operation by UV-cut irradiation. UV-cut irradiation clearly and immediately increases the ESR signal with the sharp linewidth, although the response time cannot be determined from this data because it shows an averaged spectrum over an hour. Once the ESR signal with the narrow linewidth increased, there was almost no change in the ESR spectrum during UV-cut irradiation up to 6 h. Fig. 2b represents the ESR spectrum obtained under white light irradiation right after UV-cut light irradiation. As it can be seen from Fig. 2b, the ESR signal with the broad linewidth gradually and monotonically increases with white light irradiation, and the increase in the signal did not saturate up to 23 h. It is remarkable that only the ESR signal with the broad linewidth changes by white light irradiation, implying that the increase in the ESR signal of the device has a strong correlation with UV light.

Figure 3 shows the transient response of the number of spins, N_{spin}, due to the accumulation of photogenerated charges in the device under UV-cut and white light irradiation. N_{spin} is obtained by double-integrating the light-induced ESR signal and comparing this value with that of the standard Mn^{2+} marker sample. Because N_{spin} is proportional to the square of the linewidth of an ESR spectrum, the signal with the narrow linewidth does not significantly contribute to the value of N_{spin}. Fig. 3 clearly shows the response of the ESR signal on UV light irradiation, corresponding to the above discussions. The ESR signal with the narrow linewidth is identified to be due to P3HT radical cations (positive polarons) from its ESR parameters, which are basically holes generated by light absorption in the P3HT:PCBM active layer [11]. P3HT:PCBM layer can absorb light in non-UV region. Therefore, the response of the signal with the narrow linewidth can be seen from UV-cut light irradiation. Its fast response to the irradiation implies that the origin of this signal is stationary $\mathrm{P3HT}^{+}$ species created by the charge separation between P3HT and PCBM. Note that photogenerated PCBM radical

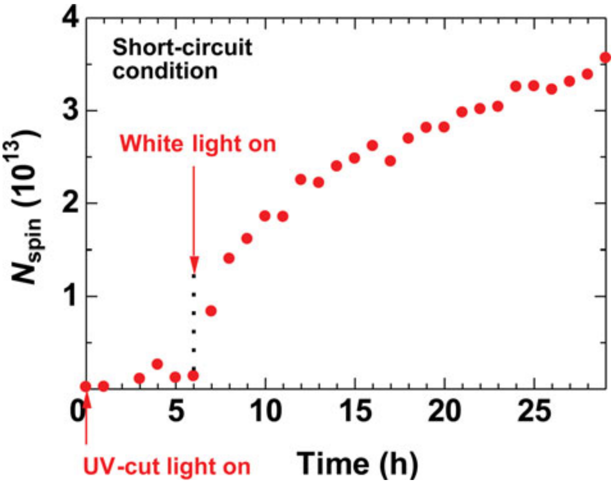

Figure 3. The dependence of N_{spin} on the duration of UV-cut light and white light irradiation. N_{spin} denotes the number of spins due to the accumulation of photogenerated charges in the device.

anions cannot be detected at room temperature because of the fast spin-lattice relaxation time [11,13].

The origin of the ESR signal with the broad linewidth can be related with P3HT because of the absence of the ESR signal of PCBM radical anions and TiO_x at room temperature, as explained below [11, 14]. It seems that there is an influence of the signal on the device characteristics in terms of the light soaking. Reminding that the ESR signal with the broad linewidth only increases with UV light, the device exhibits good performance in the case when it shows the broad signal. As shown in Fig. 3, in addition to the gradual increase in N_{spin}, we can also find the rapid increase in N_{spin} just after 1 h white light irradiation. Thus, there are at least two components for time response; one is a fast-responding component and the other is a slow-responding component. The plotted data is an average over an hour, so we cannot obtain the response time of the fast component. The fast component is considered to be related to the light-soaking effect just after white light irradiation. The slow component is considered to be related to further light-soaking effect after light irradiation for long time because the short-circuit current increased as the duration of white light irradiation increased as shown in Fig. 1.

It has been reported that anatase TiO_2 has electron traps, mainly Ti^{4+} centers, and when Ti^{4+} become Ti^{3+} by electron trappings, Ti^{3+} can be detected as ESR signal with the g value of approximately 1.99 [14]. Because the present ESR spectra did not show any signals around $g = 1.99$, the observed signal with the broad linewidth is not likely due to Ti^{3+} in this case. Furthermore, it is known that ESR signal of Ti^{3+} is only observable at low temperatures because of its fast relaxation time at the temperature higher than that of liquid nitrogen (77 K) [14].

We performed several additional experiments to further clarify the origin of the broad signal. When we turn off UV light irradiation by either turning off the light source or using UV-cutoff filter, N_{spin} of the broad signal decreases gradually. After the decrease in the broad signal, we observed the gradual increase in the broad signal again by UV light irradiation. This increase and decrease process is reversible. In addition, we reproduced the broad signal using quartz/P3HT:PCBM sample by irradiating white light, and no signal was observed for quartz/TiO_x sample by irradiating white light even at low temperature (4.5 K). These results support that the broad signal is originated from P3HT, not from radical species created by the decomposition of organic materials or defects in P3HT due to TiO_x. Although some hole injection into P3HT layer possibly occurs by photocatalytic reaction, such as oxygen release from TiO_x layer by UV light irradiation, hole accumulation in P3HT is definitely supported by the results mentioned above.

Therefore, we assign the origin of the signal with the broad linewidth to holes that are electrostatically attracted with trapped electrons in TiO_x layer. These holes exist in P3HT of the active layer, because holes will recombine if they stay inside of TiO_x layer. However, as we can judge from its ESR parameters, they are different from $P3HT^+$ species due to $P3HT^+$-$PCBM^-$ charge transfer created by light absorption in the active layer. For the reason for the observed larger g value than those of typical π electrons, we consider the effect of bromine remained at the chain ends of P3HT where holes accumulate because bromine is known to be remained at the chain ends of P3HT during polymer synthesis [15,16]. In this case, the g value of accumulated holes near bromine is shifted by large spin orbit coupling constant of bromine, which explains the experimental results. Thus, these holes probably exist in disordered P3HT chains such as chain ends at TiO_x/polymer interfaces. Once electron traps of TiO_x are filled, especially ones near TiO_x/polymer interfaces, the device can generate electricity without being hindered by electron traps. Thus, UV-excited electrons in TiO_x trapping sites and holes residing in polymer side form quasi-stable electron-hole pairs at TiO_x/polymer interface, and as a result, electron traps of TiO_x layer no longer act as recombination centers.

Summary

We have investigated charge accumulating phenomenon for ITO/TiO_x/P3HT:PCBM/Au during light irradiation. Our device showed the typical light-soaking phenomenon in terms of *J-V* characteristics of the device and simultaneously, the ESR signal showed the strong correlation with UV light. The light-induced ESR signal can be described as the sum of the signals with the narrow and broad linewidth. The signal with the broad linewidth only increased by UV light irradiation, which implies that the increase in the signal has strong correlation with the light-soaking phenomenon. The origin of the signal with the broad linewidth can be ascribed to holes in P3HT that are electrostatically attracted with trapped electrons in TiO_x layer. In this case, the UV induced electron-trap filling in TiO_x layer is the main cause of the light-soaking phenomenon.

Acknowledgments

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