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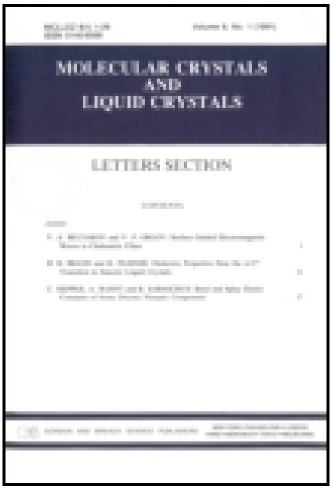

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Correlation between Hole Accumulation and Deterioration of Device Performance in Polymer Solar Cells as Investigated by Light-Induced Electron Spin Resonance

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Light-induced electron spin resonance (LESR) study of polymer solar cells has been performed to investigate accumulated hole carriers in these devices under device operation. We analyzed clear correlation between the number of accumulated holes in regioregular poly(3-hexylthiophene) (P3HT) evaluated by LESR and the deterioration of device performance (V_{oc}, J_{sc}) observed using the same device under simulated solar irradiation. The effects of hole accumulation with deep trapping levels formed in P3HT at the organic interfaces on the performance are examined by considering interfacial electric dipole layers and charge-carrier scattering by accumulated holes.

Keywords polymer solar cells; electron spin resonance; hole accumulation; performance deterioration; organic interfaces

Introduction

Organic thin-film solar cells are a promising alternative source of electrical energy because of their printable and flexible device structure, light weight, and low-cost production [1–3]. There has been a significant amount of interest in the high power conversion efficiency (PCE) of more than 10% due to their potential practical applications [4]. The durability of solar cells is another important parameter for the practical use of solar cells. The reversible initial deterioration of device performance has been reported for an organic thin-film solar cell with blend films of regioregular poly(3-hexylthiophene) (P3HT) and [6, 6]-phenyl C_{61}-butyric acid methyl ester (PCBM) [5, 6]. The deterioration has been ascribed to an accumulation of photogenerated charge carriers during device operation rather than to the degradation of organic materials and/or device structures; the accumulation sites were found to be located at interfaces between active layers and electrodes with various trapping levels [5, 6]. A more detailed study clarifying molecules and these sites where charge carriers are accumulated (trapped) is important for further improvements of device performance and durability.

Electron spin resonance (ESR) is one promising method for such a microscopic characterization of charge-accumulation sites because it is a highly sensitive and powerful

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approach that is capable of investigating organic devices at the molecular level [7, 8]. The ESR method has also been applied to organic thin-film solar cells with oligomers [9] and polymers [10]. For polymer solar cells, the accumulation sites with deep trapping levels for photogenerated hole carriers under device operation were identified as being formed in P3HT at the interfaces between poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) and P3HT:PCBM layers [10]. A clear correlation between the increase in the number of accumulated holes and the deterioration of the device performance was also observed [10].

In this paper, we investigate the above correlation in further detail. We analyze the effects of hole accumulation in P3HT at the PEDOT:PSS/P3HT:PCBM interfaces on the performance by considering interfacial electric dipole layers and charge-carrier scattering by accumulated holes. The analyses demonstrate that the hole accumulation in P3HT causes the initial deterioration of the device performance mentioned above.

Experimental

The device structure of ITO/PEDOT:PSS (~40 nm)/P3HT:PCBM (~160 nm)/Pd (1.2 nm)/LiF (0.6 nm)/Al (100 nm) was fabricated by spin coating PEDOT:PSS and P3HT:PCBM (1:0.8 w/w) solutions on an ITO substrate, followed by vacuum deposition of Pd, LiF, and Al on the organic layers to form an anode. Simultaneous measurements of light-induced ESR (LESR) and the device performance (open-circuit voltage V_{oc} and short-circuit current J_{sc}) were performed using a JEOL JES-FA200 X-band spectrometer and a Keithley 2612A source meter under simulated solar irradiation (AM 1.5G) with a 100 mW cm^{-2} intensity with a Bunkoukeiki OTENTOSUN-150BXM solar simulator under vacuum conditions at 290 K. The details for experimental conditions are described in Ref. [10].

Results and Discussion

First, we present the results of simultaneous measurements of LESR and device performance using the same device. To present the LESR results, we use the number of spins, N_{spin}, due to the accumulation of photogenerated hole carriers in P3HT varied from that before irradiation at each experiment, which was obtained by integrating the LESR signal twice [10]. Figures 1(a) and 1(b) illustrate the dependences of N_{spin} and the device performance V_{oc} and J_{sc} on the duration of the simulated solar irradiation, respectively. These results indicate that an increase in N_{spin} clearly correlates with the deterioration of the device performance. That is, N_{spin} monotonically increases and V_{oc} and J_{sc} concomitantly decrease as the duration of the irradiation increases. As discussed in the previous work, hole carriers are accumulated at the PEDOT:PSS/P3HT:PCBM interface [10]. Such hole accumulation causes a decrease in the V_{oc} because accumulated positive charges generate additional potential at the ITO/PEDOT:PSS cathode and then decrease the effective V_{oc} between the anode and cathode in the cells. This hole accumulation also causes a decrease in the J_{sc} because accumulated holes with positive charges prevent hole transport around hole-accumulated sites at the interface in the cells owing to the Coulomb repulsion between accumulated holes and flowing holes. We comment that sharp increase component of N_{spin} just after irradiation is due to bulk hole accumulation [10].

Next, we discuss the above correlation in detail. First, we explain the decrease in V_{oc} using interfacial electric dipole layers due to accumulated holes at the PEDOT: PSS/P3HT:PCBM interfaces. When interfacial electric dipole layers due to accumulated

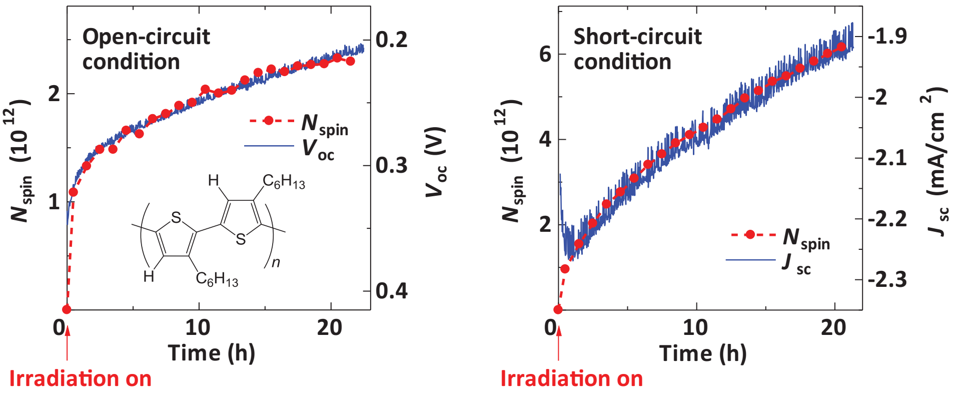

Figure 1. The dependences of $N_{\rm spin}$ and the device performance (a) $V_{\rm oc}$ and (b) $J_{\rm sc}$ on the duration of simulated solar irradiation at 290 K, respectively. The $N_{\rm spin}$ is obtained from the averaged LESR signal of P3HT under irradiation during 1 hour, and is plotted at each averaged time during 1 hour. In the inset of Fig. 1(a), chemical structure of regioregular poly(3-hexylthiophene) (P3HT) is shown.

charges are formed, vacuum-level shift occurs at the interface [11]. Such vacuum-level shift decreases the $V_{\rm oc}$ of solar cells because of the energy-level shift of molecules at the interface [12]. Here, we evaluate the interfacial electric dipole length (d) due to hole accumulation at PEDOT:PSS/P3HT:PCBM interface using capacitance formula $Q = CV$. Let S be the area at the interfaces, $\Delta N_{\rm spin}$ and $\Delta V_{\rm oc}$ be the increase in $N_{\rm spin}$ and the decrease in $V_{\rm oc}$ due to the hole accumulation at the interfaces, respectively, e be the elemental charge, ε_0 be the permittivity in vacuum, ε_r be the dielectric constants of P3HT:PCBM materials [13], then, d may be express as follows:

$$d = \varepsilon_0 \varepsilon_r \frac{S}{e \Delta N_{spin}} \Delta V_{oc} \tag{1}$$

Using the values of $S = 0.4$ cm^2, $\Delta N_{\rm spin} = 1.2 \times 10^{12}$, and $\Delta V_{\rm oc} = 0.11$ V, d is evaluated to be approximately 1 nm. This length probably corresponds to the length of alkyl-side chains in P3HT [14]; the alkyl-side chains are insulators without π electrons. It should be noted that the $\Delta V_{\rm oc}$ is proportional to the $\Delta N_{\rm spin}$ as shown in Fig. 1(a) and Eq. (1).

Finally, we explain the decrease in $J_{\rm sc}$ using charge-carrier scattering due to hole accumulation. Such scattering is considered to be independent of other charge-carrier scattering mechanisms in solar cells, and then we may use the Matthiessen's rule for the mobility μ in the cells as follows [15]:

$$\frac{1}{\mu} = \frac{1}{\mu_{\rm SC}} + \frac{1}{\left(c/N_{\rm spin}\right)\mu_{\rm HA}} \tag{2}$$

Here, we use two mobility constituents, $\mu_{\rm SC}$ and $\mu_{\rm HA}$, related to the charge-carrier scattering in solar cells without and with hole accumulation, respectively. The latter depends on $N_{\rm spin}$ with a proportionality constant c. Using Eq. (2), we may express the current density j in solar cells using charge density n and internal electric filed E in the cells as follows:

$$j = ne\mu E = ne \frac{\mu_{\rm SC}\mu_{\rm HA}}{\mu_{\rm HA} + \left(\mu_{\rm SC}/c\right) N_{\rm spin}} E \tag{3}$$

Eq. (3) shows that j decreases as N_{spin} increases. This behavior well explains the experimental result shown in Fig. 1(b). Therefore, the charge-carrier scattering induced by accumulated holes in the cells decreases J_{sc} during device operation under simulated solar irradiation.

Summary

We have investigated the clear correlation between the increase in the number of accumulated holes, N_{spin}, and the deterioration of the device performance in detail. The formation of the interfacial electric dipole layers due to hole accumulation at the organic interfaces decreases V_{oc}. The decrease in V_{oc} is proportional to the increase in N_{spin} due to hole accumulation at the interfaces. The interfacial electric dipole length d is evaluated to be approximately 1 nm. The charge-carrier scattering due to hole accumulation decreases J_{sc}, which is explained by the Matthiessen's rule. Thus, we demonstrates that the hole accumulation in P3HT in polymer solar cells causes the initial deterioration of the device performance without the degradation of organic materials and/or device structures.

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