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Continuous-wave photoinduced absorption study on trapped carriers in bulk-heterojunction solar cells connected to load

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ABSTRACT

By using continuous-wave photoinduced absorption spectroscopy, we investigate hole-transport processes in polymer-based bulk-heterojunction solar cells at various operating points between the open- and short-circuit conditions. The results reveal that the detrapping time constant of holes decreases as the short-circuit condition is approached. This decrease may be explained by an acceleration of detrapping that is caused by an internal electric field. This interpretation is supported by a numerical simulation based on rate equations, considering a low density of a single trap level. Since the detrapping signal disappears at short-circuit, we estimate the associated trap levels to be relatively shallow.

1. Introduction

Bulk-heterojunction (BHJ) solar cells based on blends of conjugated polymers and fullerenes have attracted considerable attention because of their strong potential to reduce the cost of solar energy. A semiconducting layer of a BHJ solar cell can be fabricated by an inexpensive solution process, e.g., by spin coating from a solution containing both polymer and fullerene [1]. The spontaneous phase separation results in the formation of an interpenetrating network of polymer and fullerene aggregates, which absorbs a large fraction of the incident photons and converts them with good efficiency to charged-carrier pairs [2,3]. However, the carrier mobility of organic semiconductors is much lower than that of inorganic crystalline semiconductors. Thus, some portion of the generated carriers is lost by recombination with oppositely charged carriers before the carriers can be collected at the electrodes. This carrier-collection efficiency depends on the carrier lifetime as well as the carrier mobility. Therefore, an experimental technique to measure the carrier lifetime in a working BHJ solar cell has been needed.

Recently, we reported that the hole lifetime in a working BHJ solar cell can be determined by modulation spectroscopy, i.e., continuous-wave photoinduced absorption (cw-PIA) spectroscopy. This spectroscopy is a kind of pump-probe measurement in which a modulated continuous wave beam is used as an excitation source instead of a femtosecond or nanosecond laser [4], which is a key component of better-known transient PIA spectroscopy. An advantage of cw-PIA spectroscopy is its good sensitivity for detecting signals due to excited species with lifetimes ranging from microseconds to milliseconds, which is the time scale on which carriers in a working BHJ solar cell recombine or are swept out [5]. Although PIA spectroscopy has been applied to transparent samples, we demonstrated that cw-PIA spectroscopy is applicable to hole lifetime determination of real BHJ solar cells composed of an opaque electrode [6]. The applicability to real BHJ solar cells is very important for organic semiconductors because their physical constants, including hole lifetime, are affected by even slight changes in fabrication conditions [7,8].

Previously [6], we used cw-PIA spectroscopy to determine the lifetimes of trapped and free holes in a working BHJ solar cell comprised of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). Under open-circuit (OC) conditions, the lifetimes of trapped and free holes are several tens of microseconds and a few microseconds, respectively. Under short-circuit (SC) conditions, the apparent lifetime of free holes decreases because an additional recombination channel through the external circuit is provided, and a signal that we attribute to trapped holes is largely suppressed. However, the mechanism behind the suppression of the signal is still an open question, and the recombination mechanism of trapped holes is also unclear. Since trapped carriers may reduce power conversion efficiency and may be associated with device degradation, it is essential to understand the nature of trapped carriers in a BHJ solar cell to improve the device performance. Therefore, in this study, we use cw-PIA spectroscopy to investigate hole-transport processes, focusing on the process of hole detrapping, in a working BHJ solar cell at several operating points between the OC and the SC conditions.

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2. Experimental

We used P3HT and PCBM as received. A semiconducting layer was spin-coated from a solution of P3HT and PCBM dissolved in chlorobenzene onto an indium-tin-oxide (ITO) substrate coated with poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate). The thickness of the semiconducting layer was about 80 nm. After depositing the Al electrode, the sample was annealed at 150 °C for 30 min. All processing were done in a glove box filled with nitrogen gas. After encapsulation, the devices were brought into an ambient atmosphere and tested. Power conversion efficiency under stimulated AM 1.5G irradiation (100 mW/cm^2) was about 3%. A typical current–voltage curve and the solar-cell characteristics are shown in Fig. 1.

For cw-PIA spectroscopy, we used a 488-nm square-wave pump beam, a cw probe beam, and a lock-in amplifier. The probe beam was incident on the ITO side of the BHJ solar cell and was reflected by the Al electrode. Then, after passing through a monochromator, it was detected with a photodiode. We monitored the probe beam at 680 nm to focus on the free holes created in crystalline regions of P3HT [9,10]. Small changes in the probe transmission ($-\Delta T/T$) due to the pump were detected by a lock-in amplifier. The modulation frequency of the pump was varied from 100 Hz to 1 MHz. We recorded, as a function of modulation frequency, the magnitude of the out-of-phase component of the signal, which is phase delayed by 90° with respect to the pump. As demonstrated previously [6], the carrier lifetime τ can be determined from the peak frequency f of the out-of-phase component with $\tau = (2\pi f)^{-1}$. In this study, we measured the dependence of the PIA signal on the modulation frequency at the operating points shown in Fig. 1. An operating point was selected by connecting a metal-film resistor of appropriate resistance to the BHJ solar cell.

3. Results and discussion

Fig. 2(a) shows the dependence on modulation frequency of the out-of-phase component of the PIA signal measured with a pump intensity of 100 mW/cm^2 under OC and SC conditions. From the peak frequencies, the lifetime of free holes under OC conditions is determined to be 2.5 μs and the apparent lifetime under SC conditions to be 1.3 μs. An additional PIA band (shoulder) appears near 3 kHz under OC conditions. Because the magnitude of this PIA band is independent of pump intensity, it has been concluded that it is associated with trapped holes [6,11]. This independence of pump intensity occurs because of the saturation of the signal intensity due to a much lower density of trap states than free hole states [12,13]. In fact, the magnitude of this PIA band is saturated even at the much weaker pump intensity of 5 mW/cm^2, whereas the higher-frequency PIA band grows with pump

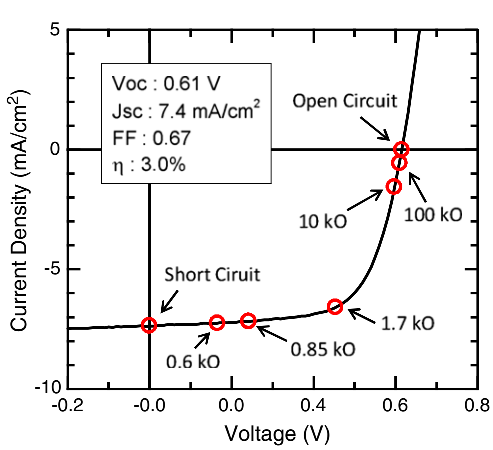

Fig. 1. (Color online) Current–voltage curve and solar-cell characteristics of a BHJ solar cell. Red circles on the curve show operating points where cw-PIA measurements were performed.

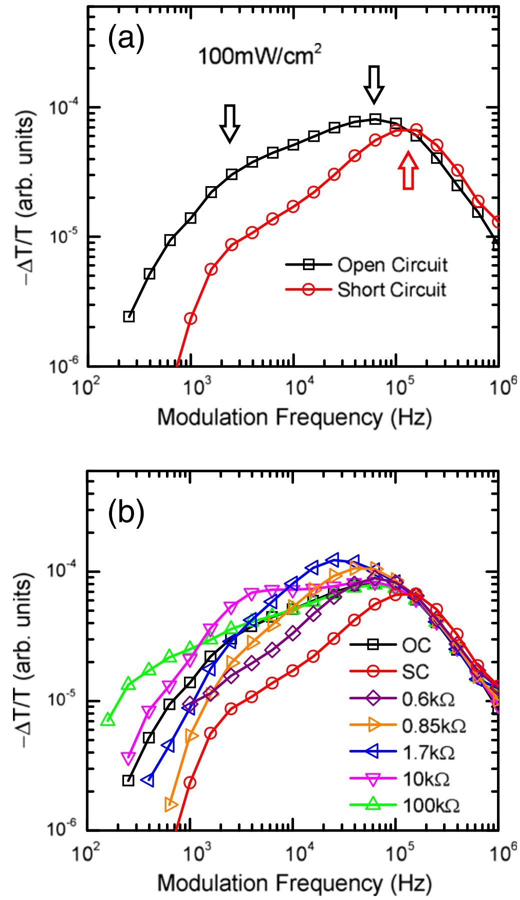

Fig. 2. (Color online) (a) Out-of-phase component of PIA signals as a function of modulation frequency for a BHJ solar cell, measured under OC and SC conditions. Arrows indicate the bands corresponding to the free-hole recombination (around 100 kHz) and free-hole generation by detrapping (around 3 kHz). (b) Out-of-phase component of PIA signals as a function of modulation frequency for a BHJ solar cell, measured at the operating points indicated in Fig. 1. The data for OC and SC conditions are the same as in panel (a).

intensity from 5 to over 100 mW/cm^2 (not shown here). Thus, we hereafter refer to the PIA bands at low and high frequencies as the trap-related and free-carrier bands, respectively. Note that the lifetimes determined in the present study are slightly different from those reported previously [6]. In particular, the apparent lifetime of free holes under SC conditions is shorter because the BHJ solar cells used in this study have higher collection and power conversion efficiencies. However, these values are in the same order as the lifetimes estimated with different methods [14–16], and more importantly, the trap-related band at lower frequency is suppressed under SC conditions, as previously found.

The dependence of the signal magnitude on modulation frequency at different operating points is shown in Fig. 2(b). These data indicate that the trap-related band is not simply suppressed as the operating point moves from OC to SC, but it also depends on modulation frequency in a complicated manner. When a 100 kΩ resistor is connected to a BHJ solar cell, an additional band appears around 300 Hz. Upon decreasing this resistance, the additional band shifts to a higher frequency and then seems to merge with the free-carrier band at 100 kHz. The band, which shifts depending on the operating point, is also attributed to the trapped holes because its magnitude is independent of the pump intensity (not shown here). We find that, as the trap-related band shifts from

Table 1
Measured detrapping time constants.

Load resistance (kΩ)	∞ (OC)	100	10	1.7	0.85
Time constant (μs)	53	160	32	6.3	3.1