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Determination of Carrier Lifetime in Bulk-heterojunction Solar Cells by Continuous-wave Photoinduced Absorption Spectroscopy

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1. Introduction

Bulk-heterojunction (BHJ) solar cells based on blends of poly(3-hekylthiotphene) (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM) have been extensively studied as potential low-cost, light-weight, and flexible solar cells [1]. In this type of BHJ solar cells, efficient charge separation of singlet exciton occurs at the distributed large-area interface between donor and accepter materials. Thus, solar conversion efficiency is largely dependent on how efficiently the resultant photocarriers can be extracted to the external circuit without being lost by the recombination process. To achieve high extraction efficiency, carrier lifetime must be much longer than transit time, which is the time required by photocarriers to travel from the interface to the electrodes. The typical transit time is estimated to be a few μs assuming that an internal electric field (built-in potential) of 0.6 V is uniformly applied to a 100-nm-thick blend layer and that the drift mobility of the carriers is about 1×10^{-5} $cm^2V^{-1}s^{-1}$ [2]. Thus, for the studies of development of new materials and optimization of the fabrication process, an experimental technique for determining carrier lifetime in a time range longer than μs must be established.

Transient photocurrent and transient absorption measurements have been employed as such techniques [2,3]. Although these techniques are excellent in terms of time resolution, they are unsuitable for the determination of carrier lifetime because of a poor signal-to-noise ratio in the time range beyond μs. In addition, the coexistence of trapped carriers with much longer lifetime makes data analysis more complicated. Thus, instead of time-domain techniques (transient measurements), we applied a frequency-domain technique, i.e., continuous-wave photoinduced absorption (cw-PIA) spectroscopy, to BHJ solar cells [4,5] and found that the lifetimes of trapped and free carriers can indeed be determined separately and precisely with this technique [5].

2. Experiments

BHJ solar cells were fabricated as follows: A hole transport layer of poly(3,4-ethylenedioxythiophene):poly (styrenesulphonate) (PEDOT:PSS) was spin-coated on indium tin oxide (ITO)-coated substrates. A 1:0.8 blend of P3HT and PCBM was spin-coated from a mixed solution over the PEDOT:PSS layer. Then, aluminum (Al) electrodes were evaporated on the top. After thermal annealing at 150 °C for 30 min, the devices were encapsulated. The entire procedure was carried out in a globe box filled with nitrogen gas. The solar conversion efficiency (SCE) of the devices under simulated AM1.5 irradiation was 2.3 %.

The setup for cw-PIA spectroscopy is illustrated in Fig. 1. A rectangular pump beam from a solid-state blue laser diode (405 nm) was used to create charged P3HTs (positive carriers), which exhibit additional absorption bands in the originally transparent infrared region. An additional absorption band was monitored by a probe beam; the probe beam reflected from the cell was monochromated and then received by a Si diode. The change in the probe beam ($-\Delta T/T$) synchronized with the pump beam was detected using a lock-in amplifier.

Since carriers have a finite lifetime, τ, their generation and decay cannot follow the modulation of the pump beam faster than a particular modulation frequency. This delay can be monitored sensitively by a lock-in amplifier as the out-of-phase component with a 90° phase shift relative to the modulated pump beam. As the modulation frequency f increases, the out-of-phase component increases and then starts decreasing around a modulation frequency of $f = (2\pi\tau)^{-1}$, while the in-phase component monotonically decreases. Using this feature, lifetime can be determined from the peak frequency of the out-of-phase curve [5]. More precise determination can be performed using the Cole-Cole function [5]. In this study, the modulation frequency was varied from 100 Hz to 1 MHz. All cw-PIA measurements were performed at room temperature.

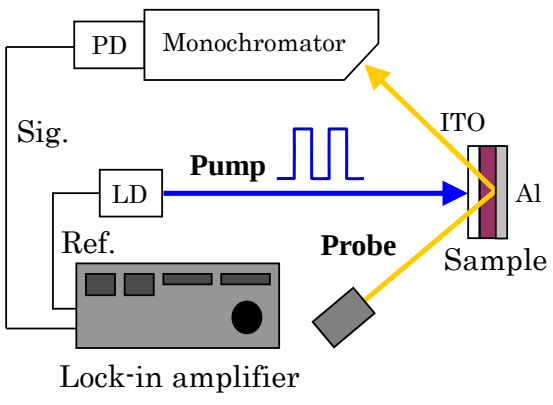

Fig. 1: Experimental setup of cw-PIA.

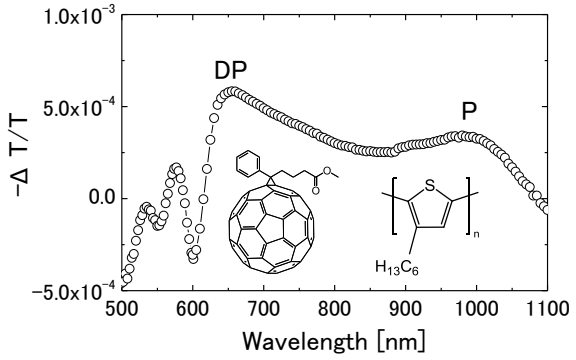

Fig. 2: Cw-PIA spectrum of a P3HT:PCBM BHJ solar cell. Inset: Chemical structures of P3HT and PCBM.

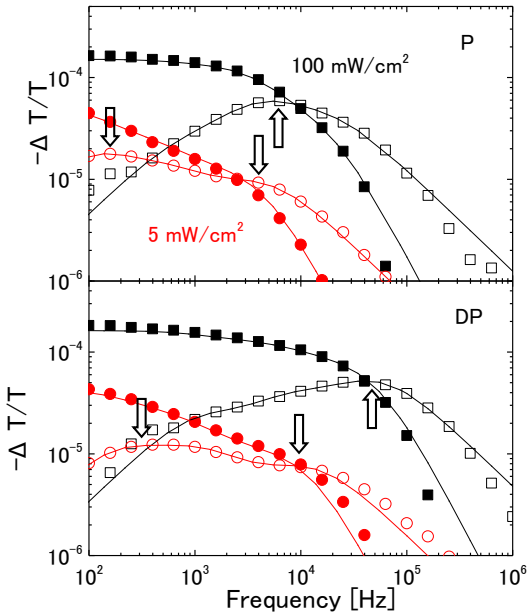

Fig. 3: Modulation-frequency dependence of cw-PIA signals of (upper) P and (lower) DP measured at pump intensities of 100 and 5 mW/cm^2. Filled and open symbols represent experimental in-phase and out-of-phase components, respectively, whereas the solid lines represent best fits with a sum of Cole-Cole functions.

3. Results and Discussion

The cw-PIA spectrum is shown in Fig. 2, which shows two absorption peaks at 980 nm and 680 nm. They correspond to (positive) carriers formed in amorphous and crystalline regions of P3HT and are called polaron (P) and delocalized polaron (DP), respectively [6]. At each wavelength, we measured modulation-frequency dependence of cw-PIA signals, and the results are shown in Fig. 3. At a pump intensity of 100 mW/cm^2, the peaks of out-of-phase curves are located at 6 kHz (P) and 40 kHz (DP) and carrier lifetimes are estimated to be 26 μs (P) and 4 μs (DP). This indicates that P and DP have different lifetimes. Free (mobile) carriers recombine in a bimolecular process so that their lifetimes are expected to be dependent on carrier density (or pump intensity). To verify this, we also measured modulation-frequency dependence at various pump intensities. Figure 3 also shows the results measured at a pump intensity of 5 mW/cm^2. Indeed, the peak frequencies of P and DP shift to 4 kHz (τ=40 μs) and 10 kHz (τ=16 μs), respectively. Thus, we attribute these carriers to free (mobile) ones. At lower pump intensities, additional peaks appear at around a few hundred Hz. Since their magnitude is virtually independent of pump intensity [5,7], these peaks are attributable to trapped carriers. It is known that the low density of states, fulfilled by even weaker pump intensity such as 5 mW/cm^2, is a characteristic feature of trapped carriers in polymer-based BHJ solar cells.

For a more precise determination of lifetime, we fit the data with a sum of Cole-Cole functions. The best fits are shown in Fig. 3. From the fits, we determine the carrier lifetime under excitation with a pump intensity of 100 mW/cm^2 to be 35 μs (free P), 12 μs (free DP), 0.4 ms (trapped P), and 0.3 ms (trapped DP).

Note that cw-PIA spectroscopy exhibits excellent sensitivity for signal detection. Hence, similar measurements can be performed to solar cells under the short-circuit condition, where carrier density is expected to be lower than that under the open-circuit condition. In the short-circuit case, transit time can be directly determined by this technique [8].

4. Conclusions

We carried out cw-PIA measurements for working devices with SCE of 2.3 % to determine carrier lifetimes. Although four types of carriers, i.e., free and trapped P and DP, exist in P3HT-based BHJ solar cells, we succeeded in determining them separately by this technique.

References

[1] C. Brabec, V. Dyakonov, and U. Scherf: Organic Photovoltaics (Wiley-VCH, Winheim 2008).
[2] S. R. Cowan, R. A. Street, S. Cho, and A. J. Heeger, Phys. Rev. B **83**, 035205 (2011).
[3] C. G. Shuttle et al., Phys. Rev. B. **78**, 113201 (2008).
[4] K. Kinoshita, T. Kobayashi, T. Nagase, and H. Naito, Mater. Sci. Forum **658**, 503 (2010).
[5] T. Kobayashi, K. Kinoshita, T. Nagase, and H. Naito, Phys. Rev. B **83**, 035305 (2011).
[6] R. Österbacka, C. P. An, X. M. Jiang, and Z. Z. Verdeny, Science **287**, 83 (2000).
[7] A. F. Nogueira et al., J. Phys. Chem. B **107**, 1567 (2003).
[8] T. Kobayashi, Y. Terada, T. Nagase, and H. Naito, Manuscript in preparation.