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Dynamic Response of Charge Recombination from Post-Annealing Process in Organic Solar Cell Using Intensity Modulated Photovoltage Spectroscopy

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Abstract

Intensity modulated photovoltage spectroscopy (IMVS) analysis of organic solar cells (OSCs) with a bulk-heterojunction (BHJ) film composed of P3HT and $PC_{61}BM$ was performed. The dynamic response of charge recombination by the post-annealing approach in P3HT/$PC_{61}BM$ BHJ solar cells characterized by IMVS demonstrated that post-annealing reduced the recombination of electron carriers in the device. The recombination times of P3HT/$PC_{61}BM$ BHJ solar cells post-annealed at room temperature, 80, 120, and 140 °C were 0.009, 0.020, 0.024, and 0.030 ms, respectively, at a short-circuit current of 0.18 mA. The results indicated that the IMVS analysis can be effectively used as powerful.

Keywords: Organic Solar cells, Dynamic Response, Charge Recombination, and IMVS

1. Introduction

Scientific interest in organic solar cells (OSCs) is driven by their facile fabrication *via* various printing technologies such as roll-to-roll, inkjet, and doctor blade methods, their low-cost, and amenability to efficient mass production.[1-5] Over the past few decades, considerable effort has been directed towards obtaining high power conversion efficiencies (PCEs) of above 10% by developing OSCs using high performance semiconducting materials, such as low-band gap π–conjugated polymer donors and fullerene derivative acceptors. Several studies have focused on achieving effective function based on surface plasmon resonance, charge transport, optical spacing, and buffering in device structures. Morphological engineering of photosensitive films by post-annealing, manipulation of the drying conditions of casting solutions, and the use of processing additives have also been evaluated.[6-15] Recently, He *et al*. reported the most promising PCEs of up to 9.2% in OSCs, achieved with bulk heterojunction (BHJ) films from π-conjugated low-bandgap polymers containing the benzodithiophene (poly(thieno[3,4-*b*]thiophene-alt-benzodithiophene) (PTB) skeleton and [6,6]-phenyl-$C_{(61\ or\ 71)}$-butyric acid methyl ester ($PC_{(61\ or\ 71)}BM$).[14] Most OSCs have been evaluated in terms of three main characteristics: (1) the photovoltaic performance based on current-voltage (*J-V*) and incident photon-to-current efficiency (IPCE) curves, (2) the morphological features of the photoactive materials using atomic force microscopy (AFM), transmission electron microscopy (TEM), Kelvin probe microscopy,[16] or spectroscopic ellipsometry,[17] and (3) the charge carrier dynamics in BHJ films using transient absorption spectroscopy or time-resolved optical spectroscopy.[18,19] However, despite the variety of analytical instruments, not many of these analysis tools can be employed for holistic evaluation of devices. Furthermore, although outstanding performance of OSCs has continued to be achieved, the efficiency evolution is not yet fully understood from these characterizations. In this regard, recent research has focused on the use of new analytical tools such as impedance spectroscopy to provide deeper insight into electrical Phenomena in OSCs.[20,21] Because impedance analysis is well established for the characterization of the charge carrier lifetime in dye-sensitized solar cells (DSSCs), this technique can also be employed to determine the charge carrier mobility and lifetime in OSCs devices.[22] Considering such approaches, we propose

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that intensity modulated photovoltage spectroscopy (IMVS),[23-25] as well as impedance analysis, may be powerful tools for evaluation of the carrier lifetime in OSC devices based on their prior use to investigate the electron lifetime in DSSCs.

IMVS measures the photovoltage response, which is periodically modulated by the difference in the Fermi level in the dark and the quasi Fermi level under illumination, of the cell to a small sinusoidal perturbation of light intensity superimposed on a largely steady background level. This can be quite informative for determining the electron lifetime under open circuit conditions. Thusly, the charge recombination in OSCs with a BHJ film composed of poly-(3-hexylthiophene) (P3HT):$PC_{61}BM$ was evaluated using the IMVS analysis. Herein, we report the dynamic response of charge recombination by post heat-treatment in OSCs based on IMVS analysis. It is demonstrated that the post-annealing approach is a most effective method of increasing the PCE of the OSC device, and affects the morphology of the BHJ film.

2. Experiment Methods

2.1. Device Fabrication

The BHJ films were prepared and optimized according to previously reported methods.[21] PEDOT:PSS (Heraeus, Clevios P VP.AI 4083) was spin-cast on indium tin oxide (ITO)-coated glass substrates (thickness: ~40 nm), which were cleaned by sonication in detergent, acetone, and isopropyl alcohol, followed by drying for 10 min at 140 °C in air. P3HT (Reike) was mixed with $PC_{61}BM$ in a ratio of 1:0.8 w/w in chlorobenzene to give the BHJ composite. This mixed solution was spin-cast on a PEDOT:PSS film followed by drying for 10 min at 60 °C under inert atmosphere. Subsequently, the Al electrode (thickness: ~100 nm) was deposited on the BHJ film under a high vacuum of 10^{-7} Torr. The device samples were heat-treated in a glove box for 5 min at 80, 120, and 140 °C, where the temperature was incremented in a step-wise manner prior to measurement of the efficiency and IMVS response. These parameters were compared to those obtained without post-annealing.

2.2. Measurement and Instruments

The Current-Voltage (*J-V*) curves were measured under 100 mW/cm^2 AM 1.5G irradiation (Oriel 911193), the intensity of which was adjusted with a National Renewable Energy Laboratory (NREL)-calibrated Si solar cell (PV measurement Inc.), and recorded using a Keithley model 2400 digital source meter. The electron lifetime was measured *via* IMVS (Ivium stat). A diode laser (red LED source, 635 nm) with modulation control was used as the light source for IMVS. The amplitude of the light was calculated from the light intensity, determined with a calibrated reference Si solar cell. IMVS response curves were measured in the range of 5000 Hz to 100 Hz under modulated light intensities.

3. Results and Discussion

More than 100 solar cells were used in this study; the optimal ratio of P3HT to $PC_{61}BM$ was 1:0.8 in the most

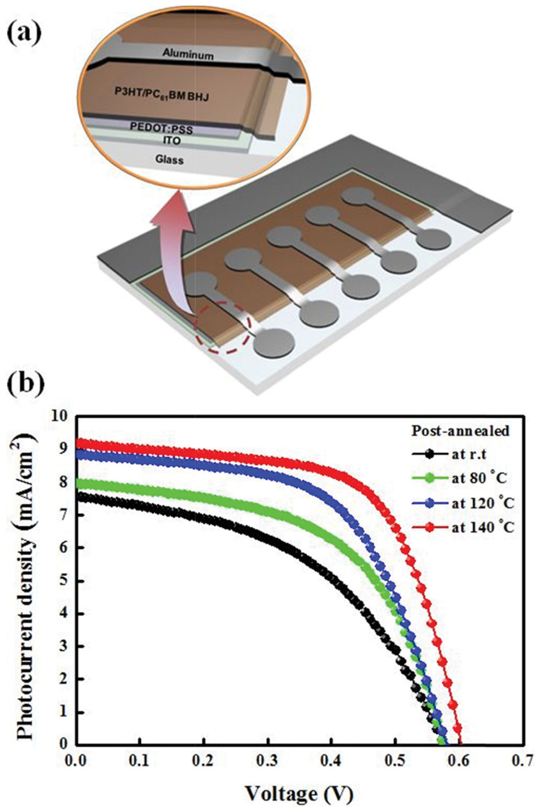

Fig. 1. (a) Schematic depict of conventional device structure and (b) its *J-V* curves under AM 1.5 irradiation (100 mW/cm^2) of the P3HT/$PC_{61}BM$ based solar cell, which were fabricated under optimized processing conditions, after post-annealing at 80, 120, and 140 °C for 5 min.

efficient BHJ photovoltaic devices, with a thickness of around 100nm. Fig. 1 shows (a) a schematic depiction of the conventional device structure and (b) the corresponding *J-V* curves of the P3HT/PC_{61}BM based solar cells under AM 1.5 irradiation (100 mW/cm^2); the cells were fabricated under the optimized processing conditions after post-annealing at 80, 120, and 140 °C for 5 min. These *J-V* curves were compared with that obtained without post-annealing. The corresponding results are summarized in Table 1. As shown in Fig. 1 and Table 1, post-annealing at the relatively higher temperature of 140 °C increased the PCEs, with improvements of all photovoltaic parameters, i.e., the short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*F.F*). These results are consistent with previously reported results and well-known effects from dramatic changes in the BHJ morphologies induced by post heat-treatment.

Table 1. Photovoltaic performances and lifetime of P3HT/PC61BM BHJ solar cells at various post-annealing temperatures.[a]

Post-annealing (°C)	J_{sc} (mA/cm^2)	V_{oc} (V)	F.F	η (%)	τ_r (ms)[b]
rt	7.56	0.58	0.47	2.05	0.009
80	7.96	0.58	0.55	2.52	0.020
120	8.85	0.58	0.58	2.97	0.024
140	9.19	0.60	0.63	3.51	0.030

[a]The performances were determined under simulated 100 mW/cm^2 AM 1.5G illumination. The light intensity using calibrated standard silicon solar cells with a proactive window made from KG5 filter glass traced to the National Renewable Energy Laboratory (NREL). The active area of device is 4 mm^2.

[b]*RI,I*+1 These values were calculated from 1/2 πf_{min} at 0.18 mA of the short-circuit current (I_{sc}) obtained under modulated light intensities.

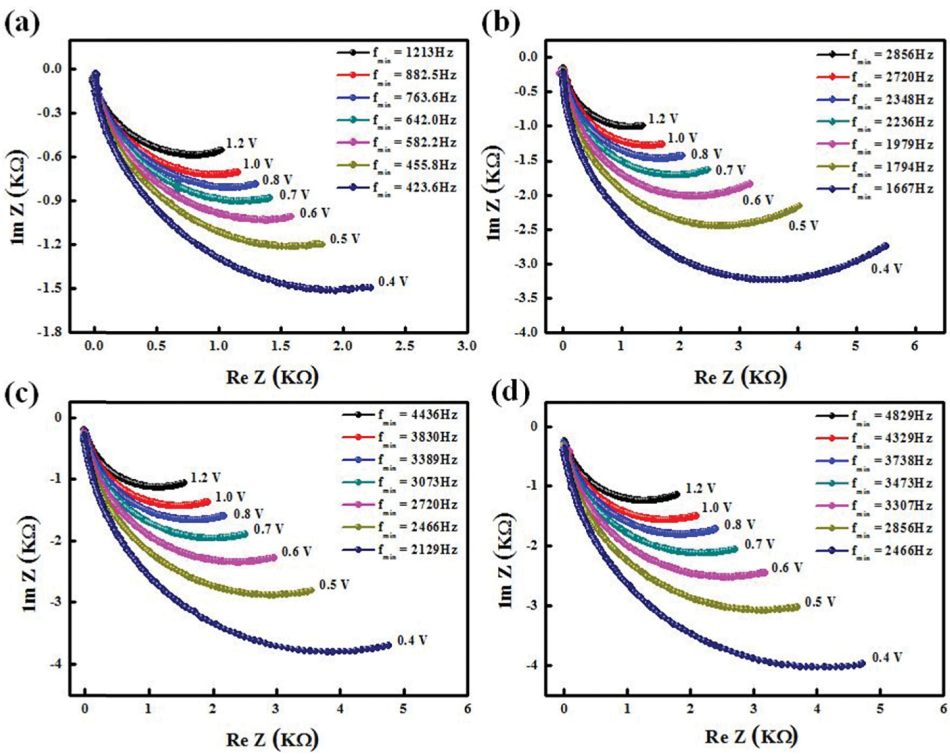

Fig. 2. IMVS spectra of P3HT/PC71BM BHJ solar cells post-annealed at (a) rt, (b) 80, (c) 120, and (d) 140 °C.

Fig. 2 shows IMVS spectra of the P3HT/$PC_{71}BM$ BHJ solar cells post-annealed at (a) rt, (b) 80, (c) 120, and (d) 140 °C. The curves exhibited semicircular profiles, and the phase lag possibly originated from recombination of electron carriers in the BHJ morphology or at the interfacial junction between the photoactive layer and the Al electrode. As shown in Fig. 2, the IMVS curves could be plotted with the frequencies measured under modulated light intensities, where the photovoltage lag leads to a response in the fourth quadrant (positive real and negative imaginary) of the complex plane. The minimum frequency (f_{min}) was observed in the lowest imaginary component. Furthermore, lower f_{min} values were obtained by reducing the light intensity. These f_{min} values can provide information related to the lifetime (τ_r), of the electron carriers, which is calculated from 1/2 πf_{min}.

Fig. 3 shows the lifetime (τ_r) values of the P3HT/$PC_{61}BM$ BHJ solar cells post-annealed at rt, 80, 120, and 140 °C for the short-circuit current (I_{sc}) obtained under modulated light intensities; the short-circuit current was determined using a reference cell (I = 0.624 mA at 100 mW/cm^2) to facilitate comparison at the same light intensity. As shown in Fig. 3, the τ_r values of the BHJ OSCs decreased at higher I_{sc} values. This feature is consistent with that observed in DSSCs. Interestingly, the τ_r values of the P3HT/$PC_{61}BM$ BHJ solar cells post-annealed at rt, 80, 120, and 140 °C were 0.009, 0.020, 0.024, and 0.030 ms, respectively, at an I_{sc} of 0.18 mA. These results suggest that the post-annealing approach to increasing the photovoltaic performance of the P3HT/$PC_{61}BM$ BHJ solar cell effectively reduces recombination of electron carriers, indication that the IMVS tool can be effectively used in analysis of OSCs. The reduced recombination of electron carriers may contribute to the increase of the J_{sc}, V_{oc}, and $F.F$ values of the device. Since the post-annealing approach can induce formation of more effective phase-segregated morphologies in the BHJ, these morphological modulations significantly affect all the parameters (J_{sc}, V_{oc}, and $F.F$) of the device. Specifically, the post-annealing approach generally reduces the resistance and trap sites in the BHJ morphology or at the interfacial junction between the photoactive layer and the Al electrode, resulting in an increase of the $F.F$ values. The IMVS response might be closely related to the $F.F$ values given that IMVS measures the variation of the frequencies under modulated light intensities using impedance. However, it is not yet fully understood whether the lifetime values determined by IMVS originated primarily from the reduced internal resistance in the BHJ film or from the reduced interfacial junction between the photoactive layer and the Al electrode.

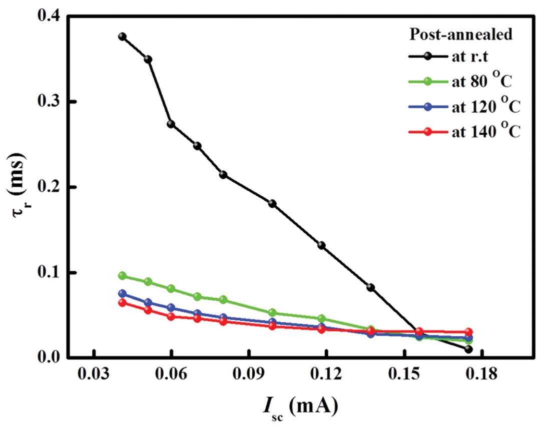

Fig. 3. Lifetime (τ_r) values of P3HT/$PC_{61}BM$ BHJ solar cells post-annealed at re, 80, 120, and 140 °C in the short-circuit current (I_{sc}) obtained under modulated light intensities.

4. Conclusion

An IMVS technique for analysis of BHJ OSCs was developed as a new, powerful characterization tool. The dynamic response of charge recombination *via* the post-annealing approach in P3HT/$PC_{61}BM$ BHJ solar cells was investigated by IMVS analysis. The charge recombination time, i.e., π_r value of the P3HT/$PC_{61}BM$ BHJ solar cells determined by IMVS, was significantly reduced with the use of higher post-annealing temperatures of up to 140 °C. The results showed that the IMVS response could provide information about the resistance and trap sites in the BHJ morphology or in the interfacial junction between the photoactive layer and Al the electrode. Further study is ongoing to determine the origin of the lifetime values determined *via* IMVS analysis of BHJ OSCs.

Acknowledgments

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