In situ monitoring of organic solar cells during thermal annealing

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1. Introduction

Poly (3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₁ (PCBM)-based organic solar cell (OSC) has been shown to possess high power conversion efficiency (PCE) of ~5% [1]. Thermal annealing, control of casting rate of active layer, solvent annealing and mixed solvent are key techniques to obtain high-efficiency [2-5]. Among them, thermal annealing has been regarded as the most effective way to improve PCE in earlier years. Exact understanding of the role of the thermal annealing by using the general ex-situ measurement is not possible. Recently, several have been used to explore the crystallinic, optical and morphological changes of OSCs during thermal or solvent annealing [6-10]. All of these studies provide useful dynamic information that is screened in most *ex-situ* results. However, these methods are indirectly associated with the cell properties of OSCs and expensive.

This work reports a real-time technique that *in situ* monitors the electrical properties of the P3HT:PCBM-based OSCs during thermal annealing. The thermal annealing was clearly divided into five stages, explaining the detailed variations of cell parameters. The proposed method is practical and useful for optimization, modeling, and in-depth investigation of the influence of thermal annealing on the performance of OSCs.

2. Experimental details

The mixed P3HT:PCBM was spin-coated on the PE-DOT:PSS covered and patterned ITO substrate in a N₂ filled glove box. After depositing the Al cathode by a thermal evaporator, the samples were transferred back to the glove box and placed on a hot-plate, in which the *in situ* measurement was performed. The whole process was oxygen and H₂O free (O₂, H₂O < 1ppm). The area of device for irradiation was ~0.065 cm². The power of light and the time interval between measurements were well-chosen so that the decay of PCE of device under multiple measurement and long-time irradiation was minimized (<3%).

3. Discussions

Figure 1 (a) shows the temperature profile of the thermal annealing. The device was heated from room-temperature (RT) to 165 °C with a linear ramping rate (~15.3 °C/min), held for 30 min, linearly cooled down to 127 °C (~3.8 °C/min), and quickly cooled to room temperature (20 °C/min). The thermal annealing was divided into



Fig. 1(a) Temperature profile of thermal annealing. In situ variations of (b)Voc, (c) Jsc, (d) FF and (e) PCE.

five stages: (I) The open-circuit voltage (V_{OC}) drops, but the short-circuit current (J_{SC}), fill factor (FF) and PCE increased as the temperature increased from RT to 127 °C, which is the glass transition temperature of P3HT. (II) All of the parameters increased with temperature from 127-165 °C. (III) When the temperature was held at 165 °C for 30 min, the *Jsc* increased slightly in the first seven minutes, and then became unchanged. The V_{OC} and *FF* were unchanged, making the PCE increased slightly in the first few minute. (IV) Because the change of Voc has an obvious turning point around 127 °C, the temperature was decreased from 165 °C to 127 °C. All of the parameters increased gradually except the *FF*. (V) As the temperature was decreased to RT, the parameters decreased excluding the V_{OC} .

The series resistance (\mathbf{R}_s) was associated with the *FF* through the relation, $FF_s = FF_0(1-r_s)$, where FF_0 is the ideal fill factor [11]. Consequently, the PCE was mostly increased in the stages (I), (II) and (IV), particular the first two stages. Figure 2 shows the *in situ* curves with different annealing temperatures. Interestingly, 127 °C was the turning point of V_{OC} for all of the samples that were annealed at elevated temperatures (>127 °C). Moreover, the V_{OC} was increased after annealing only for those devices. The temperature-dependent V_{OC} is described by the following equation [12],

$$V_{OC} = \frac{nk_BT}{q}\ln\left(\frac{I_{SC}}{I_0} + 1\right) - - -(1)$$



Fig.2 In situ measurement of V_{OC} with various annealing temperatures.

In the stage I, the V_{OC} and n decreased when the temperature was increased (Fig. 1(b)). In the stage II, the n was near constant and the V_{OC} increased with temperature. The P3HT started to alignment and became flat because the annealing temperature exceeded its glass transition temperature [13]. Additionally, the PCBM starts to accumulate on the P3HT, improving the band alignment at PCBM/P3HT interface and increasing the V_{oc} . Subsequently, the V_{OC} was unchanged in stage III, and increased little in stage IV. The increase of V_{OC} in the rapid cooling stage (V) was the reverse process of stage I, but without changing the microstructure of the active layer. Accordingly, the increase in V_{OC} during thermal annealing came mostly from stages II and IV.

The increase in J_{SC} had two steps in the stage I, became slower from stage II to first seven minutes of stage III (Fig. 1(d)). In the stage IV, the J_{SC} increased again. The increase in J_{SC} in stage I and II was further investigated by *in situ* monitoring the dark current-voltage (I-V) relation for the electron-only and hole-only devices. Figures 3(a) and (b) show the mobility of electrons (μ_e) and holes (μ_h), which were derived from I-V relationship and using the space-charge limiting current model [4]. The rapid increase in μ_e started from ~73°C, indicating that the release of bottle-necking of the blend was arisen from the clustering of PCBM. The rapid increase in μ_h started from ~93°C, which was associated with the crystallization of P3HT. Because the J_{sc} was proportional to $(n_e\mu_e+n_h\mu_h)$, the fast increase in mobility of electrons and holes in



Fig.3 In-situ measurement of hole (a) and electron (b) mobility. (c) and (d) are the Arrhenius-plot of (a) and (b).

~73-140°C consistently explained the rapid increase in J_{sc} in ~70-140°C (Fig. 1(d)). The $\mu_{\rm e}$ has two linear steps, while the $\mu_{\rm h}$ has three from RT to 160 °C, indicating that the transport of electrons and holes in each linear step behaved as a thermal-activated process. The transport of carriers can be described as $\mu_{\rm h}$ (or $\mu_{\rm e}) \propto {\rm e}^{-\Delta Q/k_{\rm B}T}$, where ΔQ was the activation energy and was labeled in Fig. 3(c) and (d).

In our case, the PCE became constant after 7 minutes from the beginning of stage III, suggesting that 7 min is the optimal time for thermal annealing. Additionally, the PCE was increased by the slowly cooling-down stage (IV) but was unchanged when a faster cooling rate was used.

4. Conclusion

In conclusion, this work reported *in situ* monitoring of the photovoltaic and transport properties of the P3HT:PCBM-based OSCs during thermal annealing. The thermal annealing was divided into five stages, from which the improvement of PEC was found mostly from the changes in stages I, II and IV. A dip of open-circuit voltage (V_{oc}) was observed at the glass transition temperature of P3HT (~127 °C), which is a critical temperature for the improvement of V_{oc}. The *in situ* monitoring of the electron/hole transport explained the initial variation of J_{SC} and was a thermal-activated process.

Acknowledgements

This work was supported by the National Science Council under contract no. 97-ET-7-006-006-ET.

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