# Annealing Effects on Polymer Solar Cells with High Polythiophene- fullerene Concentrations

Chiu-Sheng Ho<sup>1</sup>, E-Ling Huang<sup>1</sup>, Wei-Chou Hsu<sup>1</sup>, Ching-Sung Lee<sup>2</sup>, Ying-Nan Lai<sup>1</sup>, and Wen-Hsuan Lai<sup>1</sup>

<sup>1</sup>Institute of Microelectronics, Department of Electrical Engineering, and Advanced Optoelectronic Technology Center,

National Cheng Kung University, Tainan 70101, Taiwan, R.O.C.

Phone: +886-6-2757575 #62350 / E-mail: wchsu@eembox.ncku.edu.tw

<sup>2</sup>Department of Electronic Engineering, Feng Chia University,

Taichung 40724, Taiwan, R.O.C.

## 1. Introduction

Polymer solar cells are of tremendous interests as potential sources of renewable energy because of their low cost in large-area fabrication, light weight, and compatible processing on flexible substrates.<sup>1</sup> The power conversion efficiency (PCE) of polymer solar cell based on conjugated polymer and fullerene has been improved significantly with the introduction of the bulk-heterojunction (BHJ) concept.<sup>4-7</sup> The BHJ design, consisting of an interpenetrating network of electron donor (conjugated polymer) and electron acceptor (fullerene), can provide efficient dissociation of excitons within the whole photoactive layer. In particular, poly(3-hexylthiophene) (P3HT) has been studied extensively due to its promising physical properties over other polymers, including high hole mobility of around 10<sup>-3</sup> cm<sup>2</sup>/V-s, extended absorption in red region, and good environmental stability.<sup>8-11</sup> Efforts has been devoted to improving PCE characteristics of P3HT-based polymer solar cells by performing thermal annealing to obtain close-packed crystalline structure and strong interchain interaction of P3HT.<sup>12-13</sup> Nevertheless, low concentrations (1~2 wt%) of photoactive layer were commonly used in order to obtain the high degree of molecular order. In this letter, we will investigate different thermal annealing effects, with the temperature ranging from 110°C to 200°C, on absorption, electrical, and morphology properties of polymer solar cells based on P3HT:fullerene blend films with high concentrations of 3 wt% and 5 wt%.

## 2. Experimental Results and Discussions

Figures 1(a) and 1(b) show the temperature-dependent UV-Vis absorption spectra of P3HT:PCBM blend films prepared in 3 wt% and 5 wt% solvents, respectively. The observed absorption peaks at 330 nm and 510 nm are believed to be due to contributions of PCBM and P3HT, correspondingly. Besides, two shoulders at 550 nm and 600 nm in the absorption spectra in Fig. 1(a) were observed for the as-casted, 3 wt% sample. This is not obvious as shown in Fig 1(b) for the as-casted, 5 wt% film. The above difference indicates the orientation of P3HT was forced by the short timescale such that it was not thermodynamically stable at high concentration, and consequently resulted in increased defect density and decreased conjugation length<sup>14</sup>.

Considering the temperature-dependent absorption spectra in Fig. 1(a), the 3 wt% film showed similar dependences as the annealing temperatures were within the range of  $110^{\circ}$ C- $150^{\circ}$ C. However, the optical intensity decreased apparently as the annealing temperatures were higher than  $170^{\circ}$ C, and a shift to short-wavelength spectrum occurred at 200°C. The changes indicate the internal molecular orientation of P3HT was effected by the thermal treatment.



Fig. 1 UV-Vis absorption spectra of as-casted and annealed P3HT:PCBM blend film with (a) 3 wt% and (b) 5 wt% concentrations at different temperatures. The annealing time is 10 min for all samples.

On the other hand, optical intensities in absorption

spectra of the 5 wt% film were increased after annealing at high temperatures, as shown in Fig. 1(b). The enhancement of intensity indicates more excitons were generated within the photoactive layer. Therefore, the increased photocurrent of polymer solar cell is expected, which will be discussed later.

Figures 2(a) and 2(b) show the temperature-dependent photocurrent-voltage characteristics for polymer solar cells made of 3 wt% and 5 wt% blend films, respectively. The insets show the corresponding PCE variations. As shown in Fig. 2(a), the short-circuit current density ( $J_{sc}$ ) and PCE of the as-casted, 3 wt% device were 4.78 mA/cm<sup>2</sup> and 1.43%, and were increased to 6.02 mA/cm<sup>2</sup> and 1.95% after annealing at 110°C. Increases in  $J_{sc}$  are believed to be due to the increased optical intensity as shown in Fig. 1(a).



Fig. 2 *J-V* characteristics of polymer solar cells made of (a) 3 wt% and (b) 5 wt% photoactive layers annealed at different temperatures. The insets show the temperature-dependent PCE characteristics.

The device showed similar performance after annealing at 130°C, but degraded as the annealing temperatures are higher than 170°C. The  $J_{sc}$  and PCE were decreased to 2.29 mA/cm<sup>2</sup> and 0.71% at 200°C. The observed degradation may be attributed to the variation of absorption intensity after annealing at temperatures higher than 170°C. On the other hand, the performance of the 5 wt% polymer solar cell has shown substantial improvements after thermal annealing, as shown in Fig. 2(b). Upon annealing at 150°C, the  $J_{sc}$  increases from 1.19 mA/cm<sup>2</sup> to 7.53 mA/cm<sup>2</sup> and the PCE increases from 0.31% to 2.42%. The improvement may be attributed to the apparent change in absorption spectrum, as shown in Fig. 1(b). This indicates the modification of molecular order in P3HT:PCBM mixture after annealing, and hence enhance the carrier mobility.<sup>13-15</sup>

## 3. Conclusions

In summary, we have investigated the annealing effects on the performance of polymer solar cell with high-concentration active layers. As compared to the as-casted sample, the 3 wt% blend film has shown increased optical intensity of absorption after annealing within 110°C-150°C, but degraded as the annealing temperature is higher than 170°C. On the other hand, apparent annealing effects on the absorption spectra and electrical property were observed for the 5 wt% blend film.

#### Acknowledgements

This work was supported by the National Science Council of Republic of China under the contract no. NSC 97-2221-E-006-240-MY3, and would like to thank the LED Lighting and Research Center, NCKU, for the assistance regarding measurements.

#### References

- [1] J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, and A. J. Heeger, *Science*, **317**, 222 (2007).
- [2] S. S. Kim, S. I. Na, J. Jo, G. Tae, and D. Y. Kim, Adv. Mater., 19, 4410 (2007).
- [3] C. J. Bradec, N. S. Sariciftci, and J. C. Hummelen, *Adv. Funct. Mater.*, **11**, 15 (2003).
- [4] J. Y. Kim, S. H. Kim, H. H. Lee, K. Lee, W. Ma, X. Gong, and A. J. Heeger, *Adv. Mater.*, **18**, 572 (2006).
- [5] R. A. J. Janssen, J. C. Hummelen, and N. S. Sariciftci, *MRS Bulletin*, **30**, 33 (2005).
- [6] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, *Appl. Phys. Lett.*, **78**, 841 (2001).
- [7] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science*, **270**, 1789 (1995).
- [8] C. W. Chu, H. Yang, W. J. Hou, J. Huang, G. Li, and Y. Yang, *Appl. Phys. Lett.*, **92**, 103306 (2008).
- [9] V. D. Mihailetchi, H. Xie, B. de Boer, L. M. Popescu, J. C. Hummelen, P. W. M. Blom, and L. J. A. Koster, *Appl. Phys. Lett.*, **89**, 012107 (2006).
- [10] X. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels, and R. A. J. Janssen, *Nano Letters*, 5, 579 (2005).
- [11] D. Chirvase, J. Parisi, J. C. Hummelen, and V. Dyakonov, *Nanotechnology*, **15**, 1317 (2004).
- [12] K. Kim, J. Liu, M. A. G. Namboothiry, and D. L. Carroll, *Appl. Phys. Lett.*, **90**, 163511 (2007).
- [13] W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger, Adv. Funct. Mater., 15, 1617 (2005).
- [14] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Nature Materials*, 4, 864 (2005).