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Effect of Annealing Treatment and Surface Morphology on Power Conversion in Organic Photovoltaics

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We investigated the effect of annealing treatment and surface morphology on power conversion efficiency (PCE) of organic photovoltaic (OPV) devices. The bulk-heterojunction OPV devices were fabricated by using poly(3-hexylthiophene) (P3HT) and phenyl-C₆₁-butyric acid methyl ester (PCBM) as a donor and an acceptor material, respectively. Significant changes of surface morphology and grain size were observed by varying annealing temperature, which is possibly due to different diffusion rate of PCBM molecules into the bulk-heterojunction polymer films. From these results, we conclude that differences in surface morphology and grain size are responsible for the significantly different PCE in the OPV devices. Consequently, the PCE is improved from 0.5 to 2.6% combined with the increase of short-circuit current and fill factor by annealing treatment at 150 °C. © 2009 The Japan Society of Applied Physics

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1. Introduction

In recent years, organic photovoltaic (OPV) devices have been researched intensively due to their potential use in low-cost, large area, and arbitrary shaped applications. The performance of OPVs has been increased substantially in the last several years. In polymer bulk-heterojunction (BHJ) OPVs, an important factor in determining the device performance is the charge transport in the active layer. Since several groups have reported efficient charge transport in fullerenes and conjugated polymers interpenetrating network of BHJ polymer film,^{1–3)} lots of researches were performed to improve the performance of these systems. Recently, a power conversion efficiency (PCE) of up to around 5% has been demonstrated using a mixture of poly(3-hexylthiophene) (P3HT) and phenyl-C₆₁-butyric acid methyl ester (PCBM) polymer molecules. To achieve improved charge transport of holes and electrons through individual pathway of the interpenetrating network, annealing treatment has been considered as one of efficient ways. Annealing treatment may facilitate optimal nano-scale phase separation between donor and acceptor components, which enables the efficient transport of excitons to charge separation interface.^{4–7)}

Although several good results regarding significantly enhanced P3HT:PCBM OPV system by annealing treatment have been demonstrated,^{8–10)} the exact mechanism for the improvement of solar energy conversion was not clearly understood. In this report, we studied the influence of annealing treatment on the performance of BHJ OPV system over a range of various annealing temperatures. Moreover, the possible mechanisms were discussed in relation to surface morphology, molecular ordering, and light absorption efficiency of the BHJ polymer system.

2. Experimental Methods

All OPV devices used in these experiments were fabricated on indium–tin-oxide (ITO) glass substrates (from Corning) with a sheet resistance of 20 Ω/□. Prior to device fabrication ITO (150 nm) substrates were cleaned using ultrasonication in acetone following oxygen plasma treat-

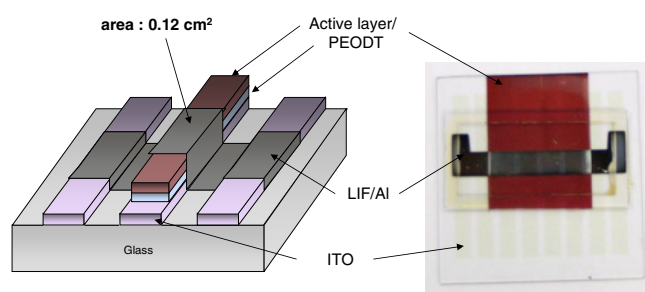


Fig. 1. (Color online) Schematic diagram and optical micrograph of fabricated organic photovoltaic device.

ment for 3 min (50 W). After cleaning the substrates, to obtain good interfacial properties between the active layer and ITO anode, thin (~10 nm) anode interfacial layer, poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), was spun over the ITO substrates and baked at 90 °C for 30 min. For the active polymer system, the blend of P3HT:PCBM (1 : 0.9 v/v) from 2 wt % chlorobenzene solution was spun over the PEDOT:PSS layer. The P3HT:PCBM blend was stirred to ensure complete mixture and filtered using 0.45 μm syringe filter. Finally, LiF (0.5 nm) and Al (100 nm) cathode was evaporated using shadow mask, making active device area of 0.12 cm². After fabrication process, the devices were annealed in convection oven at the temperature range of 60–180 °C. Light absorption and surface morphology were measured using a JASCO V-560 UV/vis spectrophotometer and PSIA XE-100 Advanced Scanning Probe Microscope, respectively. Photocurrent measurements were carried out under AM1.5G 100 mW/cm² illumination by a SAN-EI ELECTRIC XES-301S solar simulator. All the electrical and optical measurements were performed in air ambient and room temperature after glass sealing of OPV devices. Figure 1 demonstrates the schematic diagram and optical micrograph of the fabricated OPV device.

3. Results and Discussion

Figure 2 shows atomic force microscope (AFM) images of surface morphology of P3HT:PCBM polymer films which are annealed at various temperatures. As shown in these

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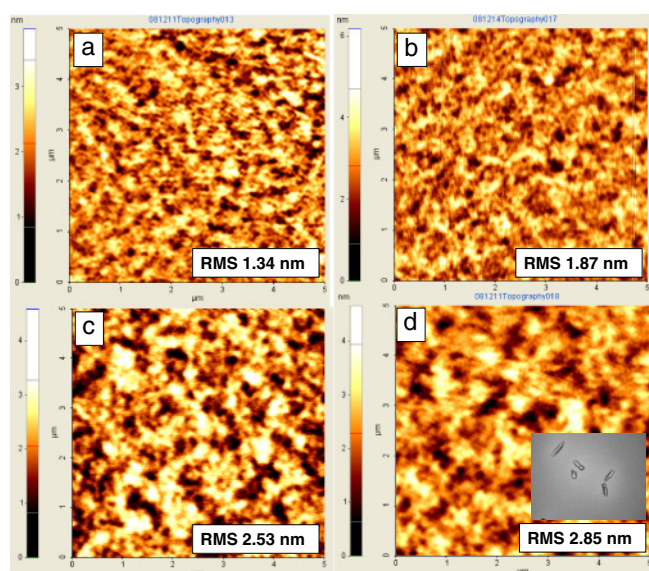


Fig. 2. (Color online) AFM images of P3HT:PCBM film morphology after thermal annealing (a) at room temperature, (b) at 90 °C for 30 min, (c) at 150 °C for 30 min, and (d) at 180 °C for 30 min.

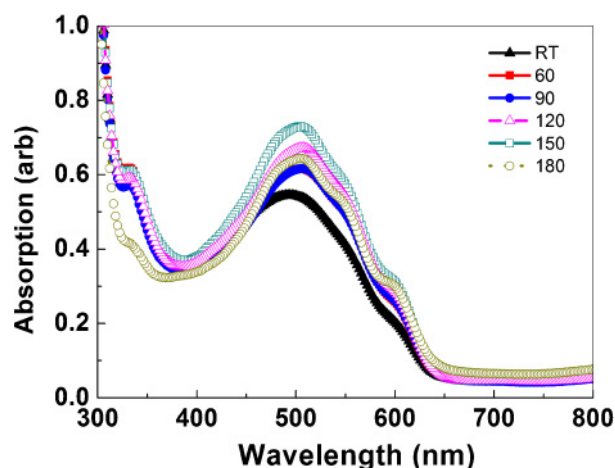


Fig. 3. (Color online) Absorption spectra of annealed P3HT:PCBM blend.

figures, as increasing annealing temperature, large grains and rough surface were observed in the polymer films, which indicates significantly rougher surface morphologies of the samples with annealing at 130–180 °C than without. At the annealing temperature of higher than 150 °C, crystal-like aggregates were appeared in the P3HT:PCBM films [inset of Fig. 2(d)]. It is likely that the aggregates are created at the expense of surrounding PCBM molecules, which is possibly due to the increased thermal diffusion of PCBM molecules at the elevated temperature.^{11,12)}

Figure 3 shows an absorption spectra of P3HT:PCBM polymer films on ITO glass substrates which were annealed at the temperature of 60, 90, 120, 150, and 180 °C for 30 min. As shown in Fig. 3, the solar radiation absorption was enhanced as increasing annealing temperature of up to 150 °C. PCBM is a derivative of C₆₀ where alkyl side chains are attached to C₆₀ molecule to increase the solubility in organic solvents. According to Yang's report,¹¹⁾ after annealing process, the alkyl side chains of P3HT and PCBM may be strongly intercorrelated, resulting in more ordered

Table I. Device characteristics of organic photovoltaic devices fabricated using different annealing temperatures (intensity: AM 1.5G, 100 mW/cm²).

Annealing temp. (°C)	J_{sc} (mA/cm ²)	FF (%)	V_{oc} (V)	PCE (%)
RT	1.72	0.46	0.65	0.5
60	5.31	0.42	0.62	1.4
90	5.85	0.54	0.58	1.83
120	6.49	0.58	0.58	2.16
150	7.1	0.60	0.61	2.62
180	6.49	0.55	0.64	2.34

individual P3HT and PCBM molecules and larger grains in BHJ system. It is not fully understood but we believe that the increase of the absorption spectra may be attributed to increase of grain size in the BHJ system as well as improved molecular ordering of P3HT and PCBM molecules. The sample annealed at 180 °C typically has shown decrease of absorption spectra which may be due to significantly enlarged crystalline aggregates of PCBM molecules.¹²⁾ The aggregates may reduce the interpenetrating network area of P3HT:PCBM possibly due to creation of large PCBM-rich area. Vanlaeke *et al.*¹³⁾ and Shrotriya *et al.*¹⁴⁾ reported that the PCBM-rich area induces disordering of P3HT chains and increase charge transferring between p-type polymer (P3HT) and n-type molecule (C₆₀), inducing quenching of absorption peak.

Table I and Fig. 4 show electrical characteristics of fabricated OPV devices which were annealed at various temperatures. While similar open circuit voltages (V_{oc}) were observed over the all samples, current density and fill factor (FF) were dramatically improved as increasing annealing temperature up to 150 °C. Enhanced spectral absorption which might be encouraged by annealing treatment may facilitate the improvement of FF and PCE in the OPV devices. The enlarged grain size and less grain boundaries are considered as possible contributors for the enhanced spectral absorption because polymer active layer including large grains typically shows efficient charge transferring with less loss at grain boundaries. Additionally, from the observation of dramatic variation of FF in Table I (theoretically FF varies only between 0.5 and 0.7), some other mechanisms such as contact properties between electrodes and active materials may be also related to the improved PCE of the OPV devices.

One more suspected reason for the improvement of the annealed OPV system is increased molecular ordering.^{15–18)} As shown in Table I and Fig. 4, the increased molecular ordering of the BHJ system may improve transport properties between the BHJ system and LiF:Al electrode, resulting in reduced series resistance and increased FF values. Since most of organic or polymer semiconductors have shown grain size and molecular ordering dependent charge carrier mobility,^{19,20)} polymer films with large grain and high molecular ordering typically have shown high charge carrier mobility. It is considered that unannealed P3HT:PCBM active layer may have a longer disordered zone, a higher energy barrier for hopping conduction, and therefore a lower carrier mobility¹⁶⁾ compared to annealed devices. This is

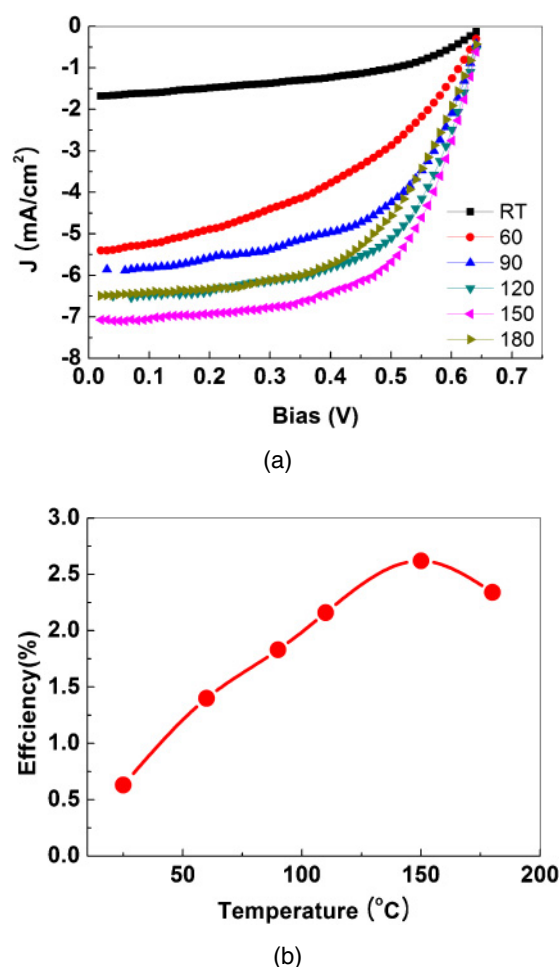


Fig. 4. (Color online) (a) Current density vs voltage characteristics of organic photovoltaic devices fabricated using different annealing temperatures and (b) power conversion efficiency versus annealing temperatures.

well consistent with previous studies of Kline *et al.*¹⁷⁾ and Zhang *et al.*¹⁵⁾ which demonstrated the correlation between field effect transistor (FET) mobility and the grain boundaries/nanofibril-widths of P3HT in FETs.

Although we observed higher molecular ordering and larger grain size in polymer films annealed at 180 °C, the OPV devices annealed at this temperature typically have shown slightly degraded performance compared to devices which is annealed at 150 °C. We suggest the degraded PCE may come from decreased absorption spectra and reduction of interpenetrating area due to large crystalline PCBM aggregates. Additionally, degradation of PEDOT:PSS is also likely to play an important role because the PEDOT:PSS is easily decomposed at high annealing temperature⁸⁾ and may inhibit the charge carrier transferring from active BHJ layer to ITO electrode, resulting in decrease of device performance.

4. Conclusions

We fabricated P3HT:PCBM based OPV devices over a range of annealing temperatures and investigated the influence of micro-structural changes in active layer on performance of the OPV devices. From the results, it is noted that the PCE of OPV devices may be closely related to surface morphology, especially grain size of BHJ polymer films. Large gains and high molecular ordering induced by annealing treatment may enhance spectral absorption and reduce charge carrier recombination, making improved OPV device performance possible. However, the active polymer films which are annealed at the temperature of higher than 150 °C typically have shown decreased spectral absorption and PCE, possibly due to decreased molecular ordering, decomposition of PEDOT:PSS layer, and reduced interfacial area of the BHJ polymer system.

- 1) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger: *Science* **270** (1995) 1789.
- 2) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl: *Science* **258** (1992) 1474.
- 3) G. Yu and A. J. Heeger: *J. Appl. Phys.* **78** (1995) 4510.
- 4) C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen: *Adv. Funct. Mater.* **11** (2001) 15.
- 5) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes: *Nature* **376** (1995) 498.
- 6) C. J. Brabec: *Sol. Energy Mater. Sol. Cells* **83** (2004) 273.
- 7) S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Romherz, and J. C. Hummelen: *Appl. Phys. Lett.* **78** (2001) 841.
- 8) X. Jiang, J. Dai, H. Wang, and D. Yan: *Thin Solid Films* **516** (2008) 6487.
- 9) M. Drees, K. Premaratne, W. Graupner, J. R. Hefflin, R. M. Davis, D. Marciu, and M. Miller: *Appl. Phys. Lett.* **81** (2002) 4607.
- 10) K. Kim, J. Liu, and D. L. Carroll: *Appl. Phys. Lett.* **88** (2006) 181911.
- 11) C. Yang, J. G. Hu, and A. Heeger: *J. Am. Chem. Soc.* **128** (2006) 12007.
- 12) H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner, and N. S. Sariciftci: *Adv. Funct. Mater.* **14** (2004) 1005.
- 13) V. Shrotriya, J. Ouyang, R. J. Tseng, G. Li, and Y. Yang: *Chem. Phys. Lett.* **411** (2005) 138.
- 14) P. Vanlaeke, A. Swinnen, I. Haeldermans, G. Vanhoyland, T. Aernouts, D. Cheyns, C. Deibel, J. D'Haen, P. Heremans, J. Poortmans, and J. V. Manca: *Sol. Energy Mater. Sol. Cells* **90** (2006) 2150.
- 15) W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger: *Adv. Funct. Mater.* **15** (2005) 1617.
- 16) T. Shimomura, H. Sato, H. Furusawa, Y. Kimura, H. Okumoto, K. Ito, R. Hayakawa, and S. Hotta: *Phys. Rev. Lett.* **72** (1994) 2073.
- 17) R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, and J. M. Frechet: *Adv. Mater.* **15** (2003) 1519.
- 18) R. Zhang, B. Li, M. Iovu, M. Jeffries-El, G. Sauve, J. Cooper, S. Jia, S. Tristram-Nagle, D. M. Smilgies, D. N. Lambeth, R. D. McCullough, and T. Kowalewski: *J. Am. Chem. Soc.* **128** (2006) 3480.
- 19) S. K. Park, D. A. Mourey, J. E. Anthony, and T. N. Jackson: *Appl. Phys. Lett.* **91** (2007) 063514.
- 20) S. Subramanian, S. K. Park, S. R. Parkin, V. Podzorov, T. N. Jackson, and J. E. Anthony: *J. Am. Chem. Soc.* **130** (2008) 2706.