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Improvement of Electrical Conductivity by Low-temperature Solvent Annealing Method for High Performance Organic Solar Cells

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Abstract

The crystallinity of photoactive layer for organic solar cells is a key factor for improving the stable charge carrier transport. For forming highly crystalline photoactive layer, we used a solvent annealing method at low temperature of 0°C for the stable growth of conductive polymer without the interruption from other molecule diffusion. The solar cells fabricated by this method shows 36% improved crystallinity and extremely higher conductivity than a device using normal fabrication method. Higher conductivity leads to improve the power conversion efficiency up to 5.36% with the fill factor increase.

1. Introduction

Organic solar cells have been actively studied because of its low-cost alternatives, light weight, and flexible application. Recently, the power conversion efficiency (PCE) organic solar cells were reported using the bulk hetero junction (BHJ) photoactive layer with the blend of thieno [3,4-b] thiophene /benzodithiophene (PTB7) as electron donor and [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) as electron accepter [1-2]. Actually, the conductivity of photoactive layer is relatively low in the BHJ structure, because the disordered structure with the low crystalline and small sized polymer domains could interrupt the charge carrier transport [2]. Thus there are some efforts to enhance both crystallinity and size of polymer domains using thermal annealing with specific temperature for crystallization for the photoactive layer with the lower ratio of accepter such as 1:0.8 or 1:1 [3-4]. However, in the case of higher ratio of accepter such as 1:1.5 for the organic solar cells for higher PCE, this thermal annealing could not form highly crystalline domains stably due to the numerous accepter molecules which diffuse through inside of donor domains. High temperature during the thermal annealing could improve to form crystalline domain of donor, but also enhance the accepter's diffusion during annealing process. In this study, to form highly crystalline photoactive layer with 1:1.5 ratio of accepter, the low-temperature solvent annealing method is introduced. To confirm the effect of this method, the crystallinity, conductivity, and solar cell performance of fabricated devices were characterized using the grazing incidence X-ray diffraction (GI-XRD) analysis, the hall's effect measurement and I-V source meter, respectively. In addition, the optimum annealing method of BHJ organic photoactive layer is discussed.

2. Experimental details

An indium tin oxide-coated glass substrate was prepared for the deposition of organic layers. First a poly- ethylene dioxythiophene:poly-styrenesulfonate (PEDOT:PSS) was spin-coated at 4000 rpm for 30 sec as a hole transport layer. Then a mixture of PTB7 and PCBM was blended with a weight ratio of 1:1.5 and stirred in chlorobenzene. This blended solution was also spin-coated at 900 rpm for 30 sec to be a thickness of 110 nm. Then three different annealing methods were applied to control the crystallinity in the photoactive layer. First, the low-temperature solvent annealing was performed in a chamber at 0°C with the controllable conditions of temperature and humidity. In this case, the fabricated device was carried out in a glass petri dish for 20 min under the solvent atmosphere with a small boat containing chlorobenzene (S00). To compare the crystallinity of photoactive layer as the effect of temperature, the normal solvent annealing was carried out at 25°C with the annealing time for 20 min (S25) as shown in Fig. 1. Both solvent annealing processes were followed the final treatment at 70°C for 10 min. In addition, a reference device was also prepared using only a thermal annealing at 70°C for 10 min (T70) to compare the difference of annealing method. Finally, an aluminum back electrode was deposited by thermal evaporation.

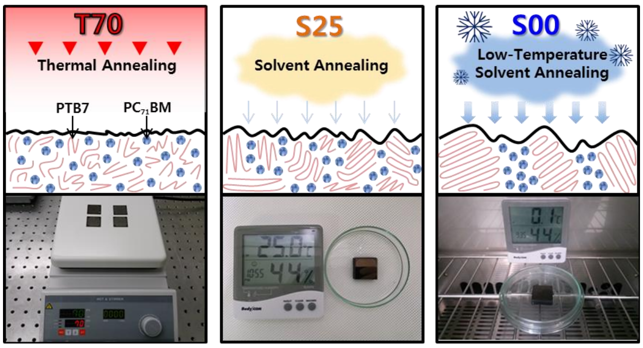
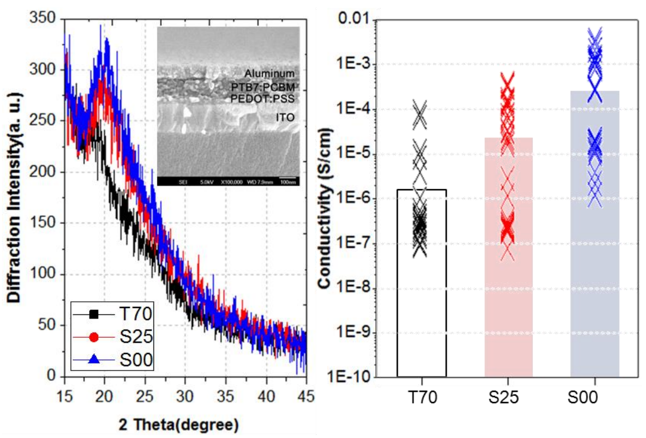


Fig. 1 Schematic diagrams of three different annealing processes in the PTB7:PCBM layer after the thermal annealing at 70°C(T70; left), solvent annealing at 25°C(S25; center) and low-temperature solvent annealing at 0°C (S00; right).

3. Results and discussion

To observe the crystallinity changes in the photoactive layers as a function of annealing temperature as well as annealing method, GI-XRD analysis was performed at the surface of PTB7:PCBM layer. In this analysis, 2 theta angles of peak diffraction intensity for PTB7:PCBM layers was observed as 19°~21°, which reflect the crystallinity of lamella stacking structure into photoactive layers. As shown in Fig. 2(a), the diffraction intensity of photoactive layer fabricated by thermal annealing (T70), normal solvent annealing (S25), and low-temperature solvent annealing (S00) resulted in the values of 250, 313, and 342, respectively. Because this diffraction intensity mainly implies the amount of crystalline lamella structures [3-5], we considered that the low-temperature solvent annealing method is very effective method for forming crystalline lamella structure to improve the exciton diffusion length, and enhance the solar cell performance compared to the normal solvent annealing method.



(a) (b)

Fig. 2 PTB7:PCBM blend films fabricated using different annealing methods were characterized by (a) GI-XRD analysis and (b) electrical conductivity mesurement.

On the other hand, to understand the effect of annealing methods on the electrical performance of PTB7:PCBM layers, the electrical conductivity of devices was measured by the four-point Van Der Pauw's method [6]. As shown in Fig. 2(b), the average conductivity of photoactive layer fabricated by T70, S25, and S00 were measured as 1.2×10^{-6} S/cm, 2.0×10^{-5} S/cm, 2.7×10^{-4} S/cm, respectively. From these results, we believe that the low- temperature solvent annealing help to improve not only the crystallinity also the electrical conductivity, which means the better charge carrier transport characteristic.

Fig. 3 shows how the improved crystallinity and electrical conductivity enhance the J-V characteristics of solar cells. Interestingly, the open circuit voltage (Voc) and the short circuit current (Jsc) were not changed as a function of annealing method as well as annealing temperature. However, the fill factor (FF) of devices fabricated by S25 and S00 were increased from 52.65% to 55.32% and 57.72%, respectively. This improvement of FF also leads to enhance the PCE from 4.84% to 5.01% and 5.36%, respectively. Because it is generally known that the FF is strongly related to electrical properties such as the stability of electrode contact and conductivity, we think that this improved FF are mainly affected by improving the electrical conductivity, which was caused by crystallinity change. From these results, we also considered that the low-temperature solvent annealing is one of powerful fabrication method for high performance BHJ organic solar cells.

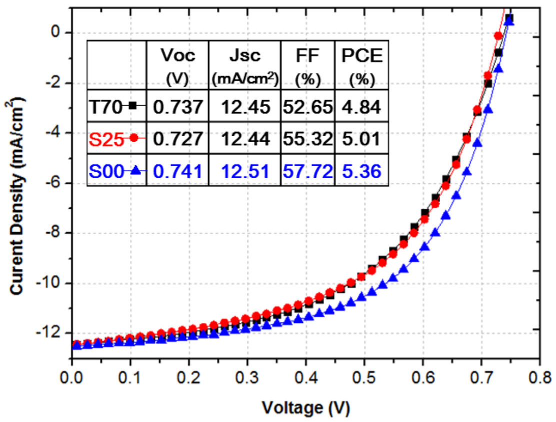


Fig. 3 J-V characteristic of PTB7-based organic solar cells fabricated by various annealing methods

4. Conclusions

To improve the electrical conductivity of PTB7:PCBM based organic solar cells, the low-temperature solvent annealing was introduced. As a result, the photoactive layer fabricated by the low-temperature solvent annealing resulted in the enhanced crystallinity about 36.8% compared to the device treated by thermal annealing. We think that this increase of crystallinity is caused by reducing molecular diffusion of PCBM at low temperature environment. The higher crystallinity of photoactive layer leads to increase the electrical conductivity from 1.2×10^{-6} S/cm up to 2.7×10^{-4} S/cm. And the device PCE was also enhanced from 4.84% to 5.36% with the improvement of only FF, which mainly affected by the electrical characteristic. Thus we conclude that the low-temperature solvent annealing is very simple and effective method for the FF increase, and should be an essential fabrication process for high performance BHJ organic solar cells.

Acknowledgements

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