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Comprehensive Studies of Solvent Annealing on Organic Photovoltaics

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1. Introduction

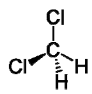
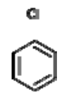
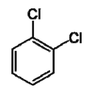
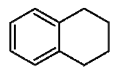
Poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM)-based bulk heterostructure has shown great potential for use in the organic photovoltaic (OPV). Various methods have been proposed to improve the cell efficiency, which has achieved 4-5% [1-4]. Among these successful approaches, solvent annealing plays an important role that increases the crystallinity of the polymer, induces effective phase separation, promotes the dissociation of excitons and enhances carrier transport behaviors. Because the solvent has different solubility of the donor and acceptor materials, the re-distribution of the donor and accepter materials should occur and influence on the transport behaviors. Additionally, thermal annealing increased the power conversion efficiency (PCE) of the solvent-annealed device further. However, comprehensive studies of the difference between solvents and their effects after thermal annealing are still lack [5-6].

This work systematically studied the solvent annealing that was followed by thermal annealing of the active layer for the improvement of OPVs. Various solvents that have different solubility of the P3HT and PCBM were attempted and compared. OPVs that were solvent annealed by dichloromethane (DCM) showed marked improvement of the fill factor (>60%), increasing the power conversion efficiency (PCE) to ~3.4%. The PCE of the DCM-annealed device increased to ~4% by thermal annealing. The mechanism of the solvent annealing was studied by using mixed solution method, indicating that the improvement of the solvent annealing was associated with the surface re-arrangement and redistribution of the PCBM and crystallinity of P3HT.

2. Experimental details

Solar cell devices were fabricated on indium-tin oxide (ITO) glass each with an area of 2.1×2.1 cm^2. Each piece of glass has six cells. The size of a cell (0.3×0.2 cm^2) was defined by the area of overlap between the strip cathode (Al) and the anode (ITO). The filtered (0.45 μm) poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Baytron P, HC Stark) was spin-coated (5000 rpm) on the patterned ITO, with a thickness of 30 nm, from aqueous solution. The 1:0.8 P3HT:PCBM (w/w) solution was prepared in chlorobenzene, and subsequently spin-coated at 500 rpm on the top of the PEDOT:PSS layer. Before Al cathode evaporated, the sample was solvent-annealed for 15 min in solvent atmosphere. Finally, the devices were thermal annealed at 150 °C for 5 minutes. The solvents that were studied included dichloromethane (DCM), chlorobenzene (CB), dichlorobenzene (DCB), and 1,2,3,4-tetrahydronaphthalene (tetralin), and fundamental properties of solvents were listed in Table 1.

Table 1 Properties of DCM, CB, DCB, and tetralin.

	DCM	CB	DCB	Tetralin
Structure				
Molecular Formula	CH_2Cl_2	C_6H_5Cl	$C_6H_4Cl_2$	$C_{10}H_{12}$
Density (g/cm^3)	1.33	1.11	1.3	0.97
Boiling Temp. (°C)	39.6	131	180.5	207
Solubility to P3HT (mg/ml)	≈0	30	30	0.5
Solubility to PCBM (mg/ml)	16	>50	100	>50

3. Results and Discussion

Figure 1(a) show the current-voltage relationship of the devices that were solvent-annealed. Obviously, the solvent-annealing improved the cell parameters by increasing the fill factor (FF) and short-circuit current. After thermal annealing, cell parameters of all of the samples that were solvent-annealed in different solvents became similar, but DCM was the most efficient one among the tested solvents (Fig. 1(b)).

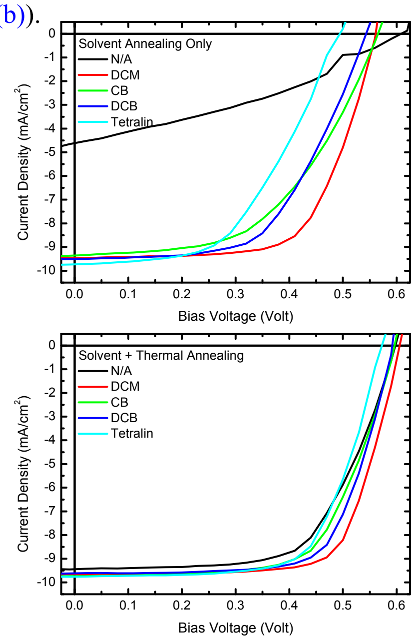


Fig. 1 Light I-V curves of (a) solvent annealed devices. (b) solvent annealed and thermal annealed devices.

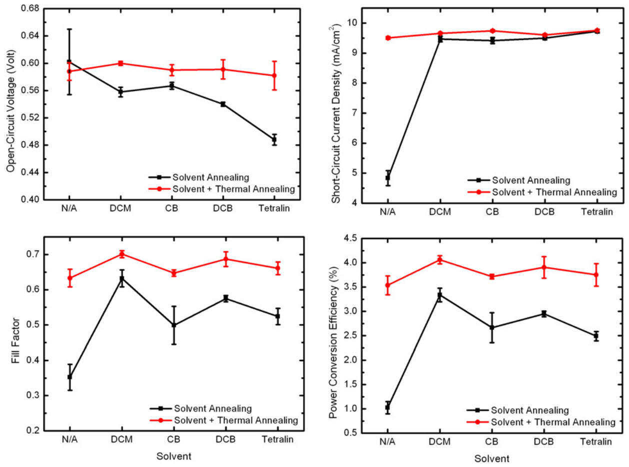


Fig. 2 Performance of devices annealed in DCM, CB, DCB and tetralin solvent (black square) and properties of devices that were thermal annealed after solvent annealing (red circle) were shown.

The summarized cell parameters of the OPVs that were solvent-annealed and thermal annealed were plotted in Fig. 2, revealing several interesting issues. First, the solvent annealing decreased the open-circuit voltage (Voc), which was recovered after the thermal annealing. Second, the short-circuit current was increased only for the device that was not solvent-annealed. Moreover, the solvent annealing markedly improved the fill factor, which was increased again after the thermal annealing, increasing the PCE. Cause of selective solubility to PCBM, the reason for better performance of DCM-annealed device is possible associated with the redistribution of the PCBM molecular near the Al cathode, which contributes to the transport of electrons.

The solubilities of P3HT and PCBM in DCM are zero and ~16 mg/ml, respectively. Additionally, the solubilities of P3HT and PCBM in tetralin are similar with those of the DCM, but less volatile. However, the DCM is more efficient than tetralin for the PCE improvement, indicating the volatility of solvents should be one of the important factors for the improvement of PCE of OPVs. On the other hand, DCB is also less volatile solution, but the DCB-annealed device got better performance. It is indicated that appropriate solubility to P3HT is needed for less volatile solvent. Therefore, we design another experiment to verify this phenomenon.

The DCB (30-100 volume percent) was mixed with tetralin as the solution of the P3HT:PCBM blend. The OPV devices were fabricated using the mixed solution and were thermal annealed. Figure 3 shows the incident photon to current efficiency (IPCE) of the OPVs. Interestingly, the IPCE increased in the wavelength ~600 nm but decreased in the wavelength around 370 nm, indicating that carrier collection by the absorption of PCBM and P3HT were decreased and increased, respectively. This factor indicated that the alteration of the solubility of P3HT for less volatile solvent changed the IPCE of devices. Accordingly, the solvent annealing played similar role as the mixed solution that increased the concentration of the PCBM near the surface of the active layer and promote the crystallinity of P3HT.

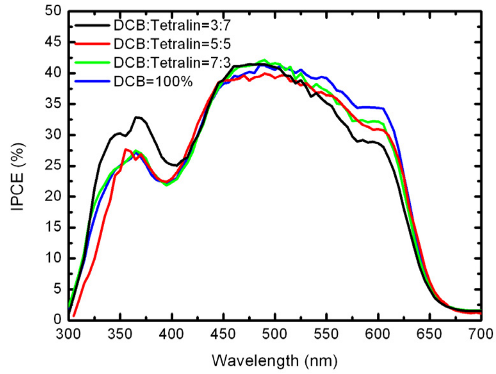


Fig.3 IPCE of the OPVs using various DCB:tetralin ratio.

4. Conclusion

The solvent annealing followed by thermal annealing of the active layer for the improvement of OPVs was studied. Various solvents that have different solubility of the P3HT and PCBM were attempted and compared. OPVs that were solvent annealed by dichloromethane (DCM) showed marked improvement of the fill factor (>60%), increasing the power conversion efficiency (PCE) to ~3.4%. The PCE of the DCM-annealed device increased to ~4% by thermal annealing. The mechanism of the solvent annealing was studied by using mixed solution method, indicating that the improvement of the solvent annealing was associated with the surface re-arrangement and redistribution of the PCBM and crystallinity of P3HT.

Acknowledgements

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References

[1] H. Kim, W. W. So, S. J. Moon, Solar Energy Materials & Solar Cells **91** (2007) 581–587

[2] F. C. Chen, Q. X, and Y. Yang, Appl. Phys. Lett. **84**, 16 (2004)

[3] D. M. Nanditha, M. Dissanayake, R. A. Hatton, R. J. Curry, and S. R. P. Silva Appl. Phys. Lett. **90**, 113505 (2007)

[4] Y. Kinoshita, T. Hasobe, and H. Murata, Appl. Phys. Lett. **91**, 083518 (2007)

[5] Y. Zhao, X. Guo, Z. Xie, Y. Qu, Y. Geng, L. Wang, J. Appl. Polym. Sci. 111, 1799 (2009)

[6] J. H. Park, J. S. Kim, J. H. Lee, W. H. Lee, and K. Cho, J. Phys. Chem. C 113, 17579 (2009)