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Efficiency Improvement of Organic Solar Cells by Slow Growth and Changing Spin-Coating Parameters for Active Layers

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The derivatives of C₆₀, [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM), and 3-hexylthiophene (P3HT) were dissolved in *o*-dichlorobenzene (DCB) solvent, and then spin-coated as an active layer for polymer solar cells. The experimental parameters including the spin-coating speed and drying conditions for the active layer, were studied carefully to obtain the optimum power conversion efficiency (PCE). In the active layer drying procedure, the DCB solvent saturated/unsaturated vapor pressure was adjusted by controlling the amount of solvent at a half-open capacity. The DCB solution was used to enhance the self-organization of the active layer of P3HT and to reduce the number of pure PCBM clusters. In the DCB optimum solution, the PCE of a polymer solar cell can be increased from 1.36 to 1.79%. The structure corresponds to a nano-to-micron scale ordering in the unsaturation-treatment films. In the optimum unsaturation procedure, the PCE of a polymer solar cell can be increased from 1.79 to 2.53%. Using two steps with optimum rotation speeds in the active layer spin-coating, the surface uniformity can be improved, with the PCE increased from 2.53 to 3.13%. © 2011 The Japan Society of Applied Physics

1. Introduction

Conductive polymers usually possess π electron conjugate structures with single- and double-staggered-bond configurations, and thus are also known as organic polymer conjugates.^{1,2} These polymer materials, when neutral, are mostly insulators or semiconductors with limited conductivity. Once the material is treated by oxidation or reduction, it will form a semiconductor with good conductivity. Most small molecular organic photoelectric materials must be prepared using vacuum evaporation to form films, and the polymer materials must be dissolved in solvents to produce films. Poly(3-hexylthiophene) (P3HT) has excellent film formation and good semiconductor properties. For example, it contains a higher carrier mobility rate, and therefore, can be applied to the production of optoelectronic devices for flexible plastic substrates. It can also be produced to form a multi layer structure.^{3,4} In 1995, Yu *et al.* used a mixture of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]C₆₁ (PCBM) to form a single-layer, heterogeneous structure in which the PCE reached 1.5%.⁵ In 2001, Shaheen *et al.* used a mixture of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV), PCBM, and LiF/Al as the cathode to improve the efficiency to 2.1%.⁶ In 2005, Li *et al.* used the self-organization effect, and with slow growth treatment, reduced the resistance of devices connected in series resistance. This enhanced the carrier mobility rate and increased the efficiency to 4.37%.⁷ In the same year, Ma *et al.* produced devices in which the PCE reached 5%.⁸ This was performed mainly using poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) to create p-n junction structures for solar cell devices.^{9,10} Because organic solar cells have advantages such as low cost, light weight, deflectability, and the ability to easily produce large-area devices,^{11,12} they deserve further research. Using the self-organizational effect of the active layer with slow growth, including the required amount of solvent needed for

slow growth, saturated/unsaturated vapor pressure and a two-step spin-coating rotation speed, the problem of active layer unevenness can be improved to facilitate carrier transport.

2. Experimental Procedure

The sheet resistance and thickness of the Indium tin oxide (ITO) glass substrate were 5 Ω/\square and 280 nm, respectively. Photolithography was used to define the anode plot. The glass substrate was then placed within an ultrasound washer, with acetone, methyl alcohol and deionized (DI) water, each used in sequence for 10 min. The glass substrate was dried under a flow of nitrogen and placed in an oven for 30 min. The substrate was then placed within an oxygen plasma washing machine. The surface of the ITO glass was cleaned in an oxygen plasma environment with an oxygen flow rate of 10 sccm and an RF power of 30 W. The substrate was removed, and a layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was spin-coated to repair the ITO surface to assist with hole transfer to the electrode. The substrate was then removed and placed in a N₂ glove box. The active layer material (P3HT : PCBM = 1 : 1) was dissolved in *o*-dichlorobenzene (DCB) and placed on a hot plate at a temperature of 40 °C, with a rotation speed of 150 rpm for 24 h. The P3HT:PCBM solution was then spin-coated onto the PEDOT:PSS layer. After organic layer coating, the device was placed within a Petri dish 12.9 cm in diameter and 4.5 cm in height, as shown in Fig. 1. Active layer slow growth treatment produced a self-organized effect. Because of the coated active layer, the device was placed in a saturated vapor environment; thus, no film formation occurred on the active layer, and the layer remained in a solution state. This allowed P3HT and PCBM to self-organize. The sample was placed on a hot plate for the annealing treatment at 120 °C for 10 min. LiF/Al vaporization was used for cathode metal deposition. The device structure is shown in Fig. 2. The device area is 0.04 cm². After device production completion, AM G1.5 100 mW/cm² was used as the sunlight simulation. A Keithley 2400 was used to measure the current-voltage characteristics of the polymer solar cells.

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Table I. Device production parameters and characteristics.

Device	PEDOT:PSS		Active layer (P3HT : PCBM = 1 : 1, 1.7 wt %)					V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	
	Speed/time (rpm/s)	Stir Spin		Grown		Preannealing						
		Speed (rpm)	Time (s)	Capacity (cm ³)	Cap	Time (min)	Temp. (°C/min)					
A	2500/30	400	800	60	1	Close	50–	120/10	0.59	3.96	58	1.36
B					2.5				0.59	3.88	64	1.48
C		5	Close	0.59	4.89	62	1.79					
D		800	Open	0.59	6.38	67.2	2.53					
E		700	40–50	0.59	7.41	63.1	2.76					
F		600	Open	0.6	8.15	64	3.13					

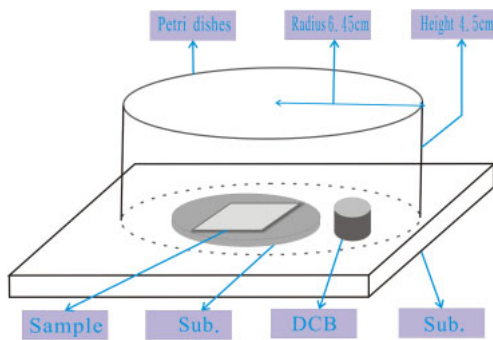


Fig. 1. (Color online) Illustration of slow growth (saturated vapor pressure).

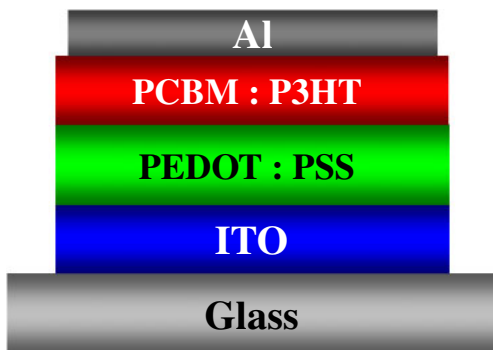


Fig. 2. (Color online) Device structure of polymer solar cell.

3. Results and Discussion

3.1 Effects of slow growth on polymer solar cells

Table I shows the device production parameters and characteristics. Figure 3 shows the short-circuit current density–voltage (J – V) characteristic curves for different slow growth solvents placed in Petri dishes. A slow growth time of the active layer affects the status of self-assembly. Because the slow growth time is too short, the active layer of P3HT cannot be arranged in the ordered formation of a self-organization structure and thus increases the number of pure PCBM clusters.^{13–15} However, the slow growth time is comparatively too long to result in the active layer of P3HT to be arranged in the ordered formation of a self-organization structure and thus decreases the number of pure PCBM

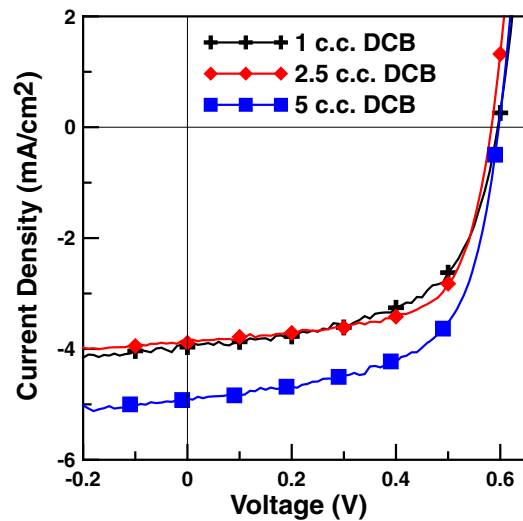


Fig. 3. (Color online) J – V characteristic curves for different slow growth solvents.

clusters. Comparisons were made among the slow growth solvents (DCB) used in 1, 2.5, and 5 cm³ in Petri dishes. The devices were placed in the Petri dishes for slow growth after spin coating. In the first stage (period of time), the vapor pressure within the Petri dish was unsaturated. Different amounts of solvent also affect the drying time of the active layer film. For Devices A and B, the amount of solvent was small. The gas molecules generated by the DCB solvent within the Petri dish were comparatively few, causing a weak self-organizing effect. The surface roughness of the active layer film was comparatively rough, as shown in Figs. 4(a) and 4(b). When the amount of solvent was increased to 5 cm³, the DCB concentration in the Petri dish became comparatively sufficient. Thus, the active layer self-organization effect became better and the surface smoother, as shown in Fig. 4(c). The type of active film markedly affects J_{sc} . A surface that is too rough is unfavorable for carrier transport, thus decreasing J_{sc} . When the active layer surface is smoother, the device series resistance is lower which is appropriate for carrier transport,⁷ thereby increasing the device short-circuit current density, as shown in Fig. 3. The short-circuit current density for 5 cm³ was greater than 1 and 2.5 cm³. The Device C characteristics are as follows: $V_{oc} = 0.59$ V, $J_{sc} = 4.89$ mA/cm², FF = 62%, and $\eta = 1.79\%$.

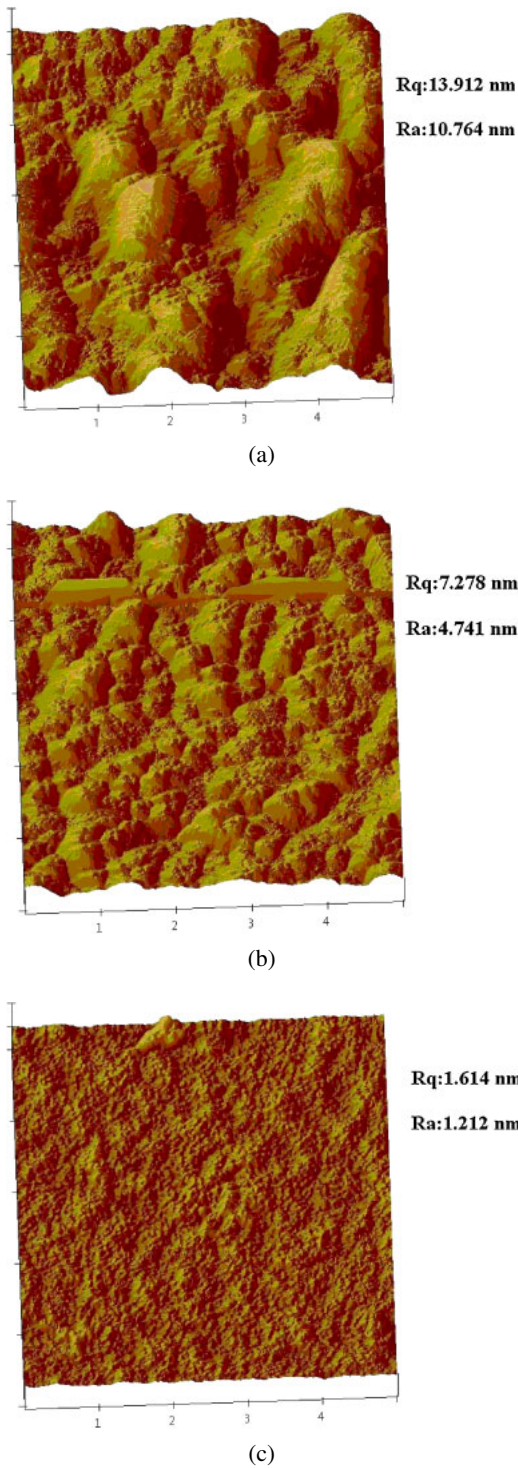


Fig. 4. (Color online) AFM for different amounts of slow growth solvents: (a) 1, (b) 2.5, and (c) 5 cm³.

3.2 Vapor pressure effect on polymer solar cells

Figure 5 shows the $J-V$ characteristic curves at vapor pressure. During the production of Device C, the Petri dish was sealed, as shown in Fig. 1. Because of the saturated vapor pressure, a longer drying time was required for the active layer (80–100 min), leading to a decrease in efficiency because of the lengthy production time. From the literature,¹⁶⁾ we find that the optimized duration for slow growth would be 30–40 min. To solve this optimization problem,

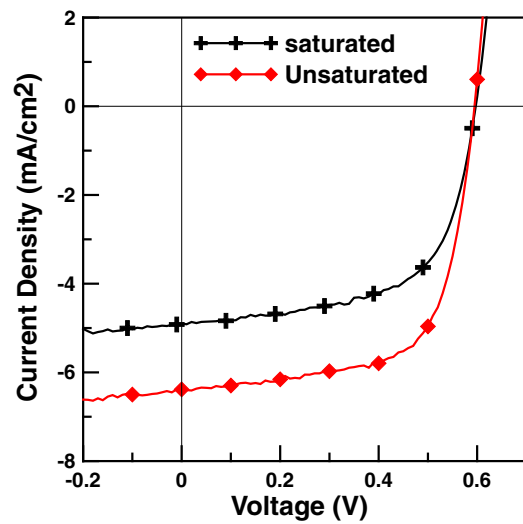


Fig. 5. (Color online) $J-V$ characteristic curve for different vapor pressures.

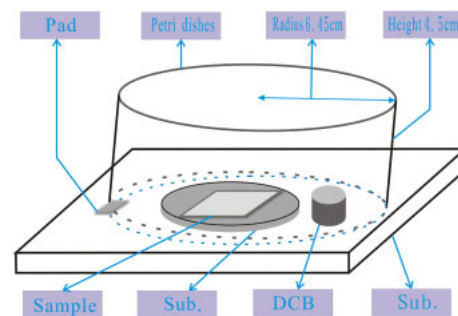


Fig. 6. (Color online) Illustration of slow growth (unsaturated vapor pressure).

Device D production was performed by leveling one side of the Petri dish (about 0.2 cm), as shown in Fig. 6. The vapor pressure inside the Petri dish was unsaturated and shortened the drying duration time to about 40–50 min. Figure 7 shows the surface roughness of the active layer at different vapor pressures. The surface roughness of Device D was greater than that of Device C, because entropy > 0, and therefore, the flatness area of Device D was larger than that of Device C, resulting in an enhancement of the device characteristics. The aggregated structure corresponds to a nano-to-micron scale ordering in the unsaturation-treatment films, in which the effect is consistent with the results presented in the literature for various treatments of P3HT:PCBM films.¹⁷⁾ The characteristics of Device D include the following: $V_{oc} = 0.59$ V, $J_{sc} = 6.83$ mA/cm², FF = 67.2%, and $\eta = 2.53\%$.

3.3 Spin-coating speed effect on polymer solar cells

Figure 8 shows the $J-V$ characteristic curves for different spin-coating rotation speeds. The active layer thickness directly affects J_{sc} . When the spin-coating speed was 800 rpm, the spin-coated film was rather thin and produced fewer excitons within the active layer after illumination. When the spin-coating speed was reduced so that the active layer formation became thicker, the short-circuit current density

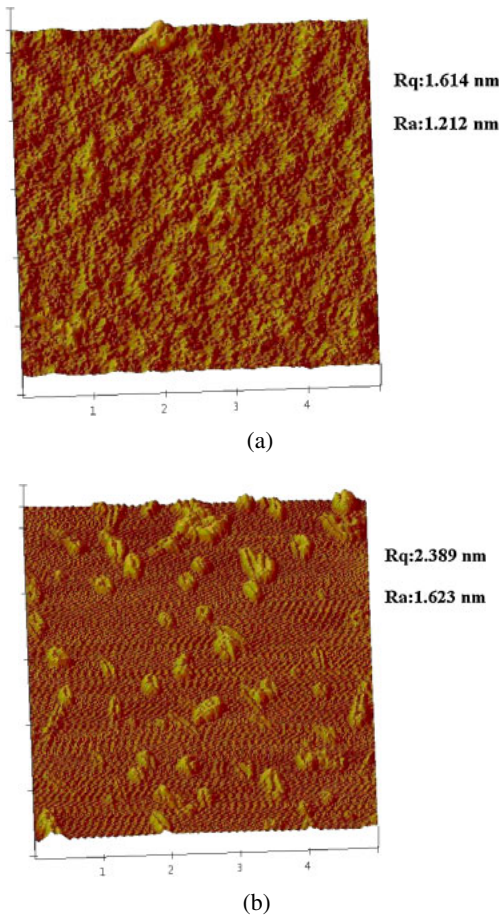


Fig. 7. (Color online) AFM images at different vapor pressures: (a) saturated vapor pressure (b) unsaturated vapor pressure.

increased. Although the active layer thickness can affect the generation of excitons, a layer that is too thick will cause problems with carrier transport and increase the series resistance, leading to reduced device efficiency.¹⁸⁾ Figure 8 shows that a 600 rpm spin-coating speed produced the best device characteristics: $V_{oc} = 0.6$ V, $J_{sc} = 8.15$ mA/cm², FF = 64%, and $\eta = 3.13\%$.

4. Conclusion

In this study, we used slow active layer growth conditions, various amounts of DCB solvents, and open as well as covered Petri dishes to evaluate the time and shorten the process duration for active layer film formation. The carrier transport rate improved and the series resistance decrease to increase device efficiency to 2.53%. The active layer thickness can be increased by lowering the second state spin coating speed. The increased layer thickness can generate enough excitons to enhance the short-circuit current density and increase the efficiency to 3.13%.

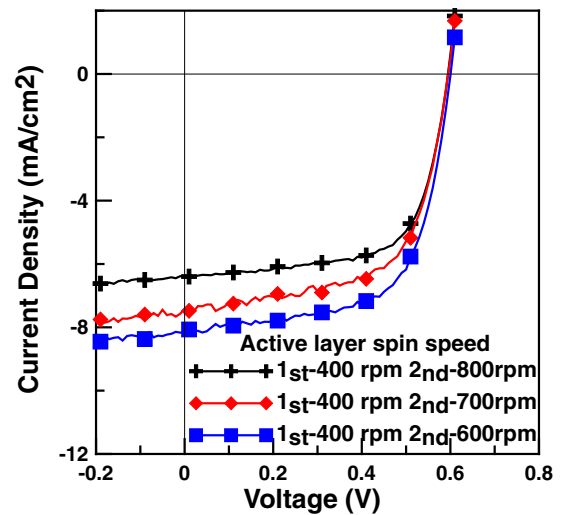


Fig. 8. (Color online) J - V characteristic curve for different spin-coating rotation speeds.

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