Solvent effects on gravure-printed organic layers of nanoscale thickness for organic solar cells

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Abstract–The effects of different solvents on the fabrication of organic photovoltaic cells by gravure printing are reported. Polymer bulk heterojunction solar cells were fabricated with ITO/PEDOT : PSS/P3HT : PCBM/Al layer structures using 4-9 wt% mixtures of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) in 1,2-dichlorobenzene to optimize solution viscosity for gravure printing. 7 wt% P3HT : PCBM showed optimal efficiency of 1.64% and resulted in an active layer 340 nm thick. Three solvents, 1,2-dichlorobenzene, chloroform, and chlorobenzene, were tested and a 1 : 1 ratio mixture of 1,2-dichlorobenzene and chloroform resulted in the best efficiency of 2.21%. This study demonstrates the importance of solvent effects in the gravure printing of organic photovoltaic devices.

INTRODUCTION

Solar cells are in increasing demand as they are hoped to alleviate the economic and environmental problems associated with traditional fossil fuels. Inorganic solar cells show higher energy conversion efficiency than organic photovoltaic devices, but typically require expensive equipment and large amount of energy during fabrication. Organic photovoltaic devices are of interest due to their low manufacturing costs and flexibility, despite having lower power conversion efficiency [1]. Considerable progress in the development of organic solar cells has been made in recent years, with >8% efficiency having been reported [2]. Roll-to-roll printing is considered a promising low-cost manufacturing process [3,4]. Various printing technologies have been developed for roll-to-roll processes, including doctor blading [5], screen printing [6,7], ink-jet printing [8,9] and gravure printing [10]. However, fabricating small patterns below 100 μm width is quite challenging by screen printing, and inkjet printing shows serious limitation in throughput. Gravure printing, which can achieve high throughputs of several meters per second in roll-to-roll processing, does not require high capital investment. It can produce resolutions of a few tens of micro-meters, better than high-throughput screen printing. It is considered economical as minimal materials are wasted. However, gravure printing for organic solar cells is in its early stages of development and the process development for a few hundred nanometer thick organic layers is required with a few nanometer scale surface roughness.

This work reports the fabrication of nanoscale organic layers by gravure printing for organic photovoltaic devices. The effects of different solvents on the resulting organic layers' thickness and roughness were investigated.

EXPERIMENTS

Organic photovoltaic devices were fabricated with stacked layer structures of glass/ITO/hole transfer layer/active layer/Al. *Ca.* 80 Å thick indium-tin oxide (ITO, M-M Tech.) was used as transparent anode layer with sheet resistance of 20-30 $\Omega/\square$. Anodes were formed by etching the ITO layers with HCl solution. After etching, the ITO glass was sequentially cleaned with deionized water, acetone, and isopropyl alcohol in an ultrasonic bath. Samples were then dried under a N_2 flow. The patterned ITO surfaces were exposed to oxygen and argon plasma for 5 minutes, before being spin-coated with PEDOT : PSS ([poly(3,4-ethylene dioxythiophene) - poly(styrene sulfonate)], Clevios P VP AI 4083) to form a hole transfer layer. Samples were then thermally annealed for 10 min at 120 °C.

For active layer formation, a 1 : 1 ratio of P3HT : PCBM was dissolved in a mixture of 1,2-dichlorobenzene and chloroform. Active materials were coated on the PEDOT : PSS layers by a custom-made gravure printer in a nitrogen filled glove box. The gravure printer consisted of a gravure roll, doctor blade, silicone roll, and substrate. The substrate was inserted between the patterned and silicone rolls and the pressure between the rolls was maintained at 6.5 MPa. A linear roll velocity of 217 mm/sec was maintained throughout. The patterns engraved on the printing roll were filled with drop inks. The gravure printer is described in detail elsewhere [11]. Organic photovoltaic layers formed by gravure printing were *ca.* 200-500 nm.

After the organic layers were coated, an 80 nm thick aluminum metal cathode layer was formed by thermal evaporation process. Each cell had an active area of 9 mm². After completion, each device was thermally treated for 10 minutes at 150 °C in a vacuum oven. Short circuit current, open circuit voltage, fill factor and power conversion efficiency were determined using a solar simulator (Luzchem, LZC-SSR, Keithley 2400 Sourcemeter) at AM 1.5, 100 mW/cm² and 25 °C.

RESULTS AND DISCUSSION

In the gravure printing of organic layers of nanoscale thickness, solution viscosity affects the resulting films, with the choice of solvents controlling the films' morphology and uniformity. [11]. This work compared the use of three solvents (chloroform, chlorobenzene and 1,2-dichlorobenzene) in the fabrication of organic photo-
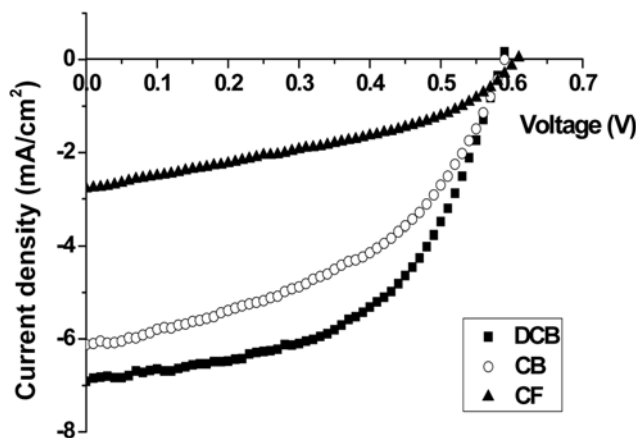
voltaic devices. The devices fabricated with chloroform showed the lowest efficiency of 0.59%; those made with 1,2-dichlorobenzene showed the highest efficiency of 2.1% (Figs. 1 and 2). Short circuit current (J_{SC}) was significantly affected by the solvent, increasing 2.3× when 1,2-dichlorobenzene was used rather than chloroform. The thickness of the organic layers was maintained at 330 nm for comparison. Layers formed using chloroform had roughness of over 150 nm, while using 1,2-dichlorobenzene resulted in 21.4 nm roughness. The improved roughness led to enhanced power con-

Fig. 1. J-V curves for different solvents (DCB - dichlorobenzene, CB - chlorobenzene, CF - chloroform).

Fig. 3. J-V curves for different active layer thicknesses.

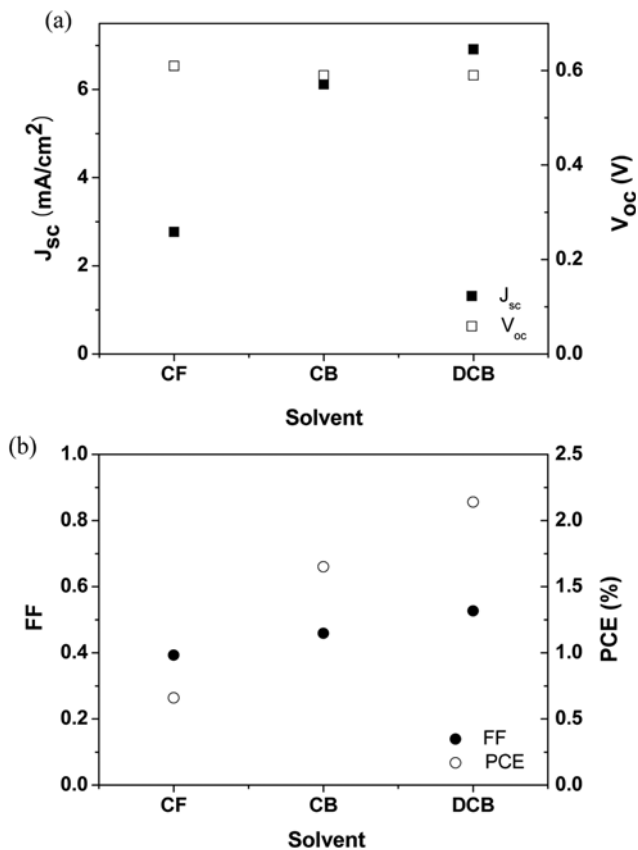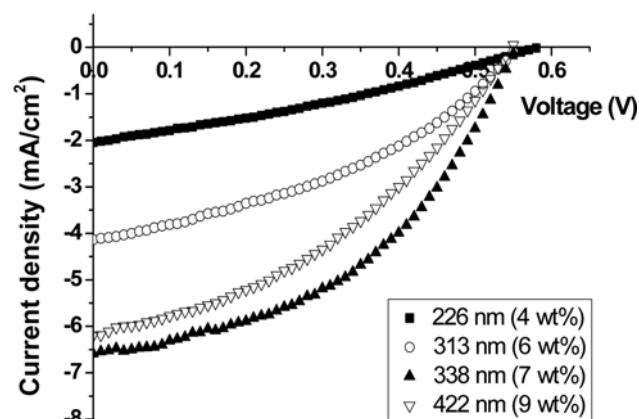**Fig. 2. Effect of solvent on device performance. (a) Short Circuit Current (Jsc) and open circuit voltage (Voc), (b) Fill factor (FF) and power conversion efficiency (PCE) (DCB - dichlorobenzene, CB - chlorobenzene, CF - chloroform).**

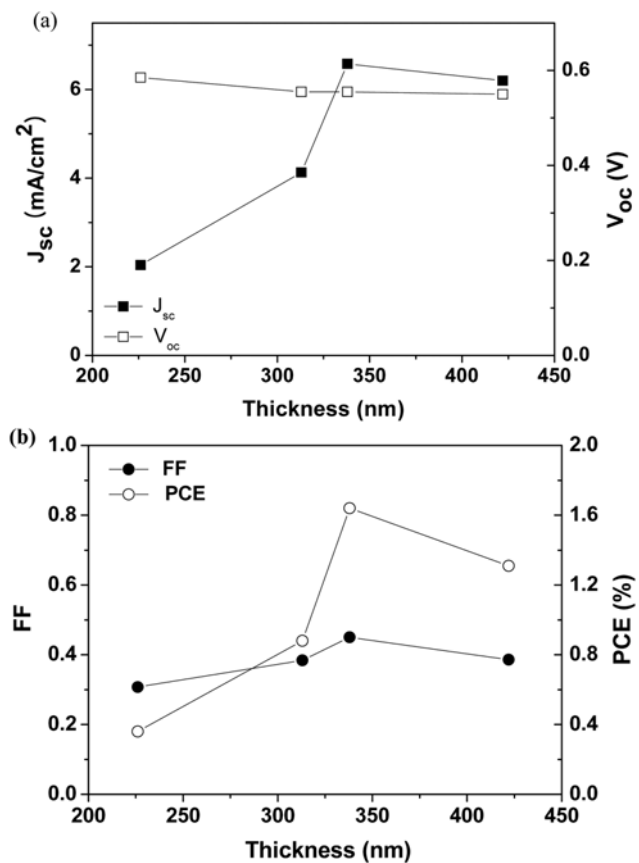**Fig. 4. Effects of active layer thickness on device performance. (a) Short circuit current (Jsc) and open circuit voltage (Voc), (b) Fill factor (FF) and power conversion efficiency (PCE).**

version efficiency.

Viscosity effect was tested by varying the concentration of P3HT : PCBM active materials in 1,2-dichlorobenzene as shown in Figs. 3 and 4. The P3HT : PCBM ratio was maintained at 1 : 1, and the amount of the active materials was tested at 4, 6, 7, and 9 wt%. The efficiency of solar cells with active layers 340 nm thick increased as concentration increased up to 7 wt%. This was mainly due to increased short circuit current and enhanced fill factor. Increasing the concentration of active materials to 9 wt% reduced energy con-
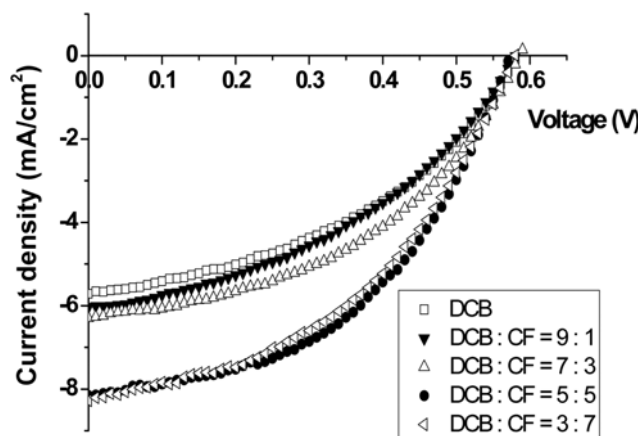
version efficiency, possibly due to increased charge recombination in the resulting thicker organic layers. The optimized condition of 7 wt% active material concentration was used in subsequent tests.

Organic photovoltaic cells were fabricated using various mixtures of chloroform and dichlorobenzene. Kawano et al. reported that solvent mixing affects the performance of resulting organic devices by affecting solubility [12]. Dichlorobenzene and chloroform were tested here at ratios of 9 : 1, 7 : 3, 5 : 5, and 3 : 7. Thicknesses of the organic layers ranged between 340 and 350 nm.

Fig. 5 and Fig. 6 show the effects of solvent mixing on the devices' power conversion efficiency, short circuit current, open circuit voltage, and fill factor. A 5 : 5 ratio of chloroform and dichlorobenzene resulted in the highest efficiency. Further addition of chloroform reduced power conversion efficiency slightly. Short circuit current increased from 5.7 mA/cm² to 8.2 mA/cm² with chloroform addition (Fig. 6(a)); open circuit voltage and fill factor were not clearly affected. Energy conversion efficiency improved from 1.4% to 2.2% when a 5 : 5 ratio of chloroform and dichlorobenzene was used. Chloroform's effect was attributed to the balancing of evaporation rate and solubility, as reported in gravure printed organic light emitting diodes by Lee et al. [11,13,14].

Fig. 7 shows AFM images of the gravure-printed organic layers when both chlorobenzene only and mixed chlorobenzene/chloroform were used. Both samples showed similar roughness: 21.9 nm with chlorobenzene only and 23.3 nm with the mixture. This indicates that the improvement of power conversion efficiency can be

Fig. 5. Effects of solvent mixing on J-V characteristics.

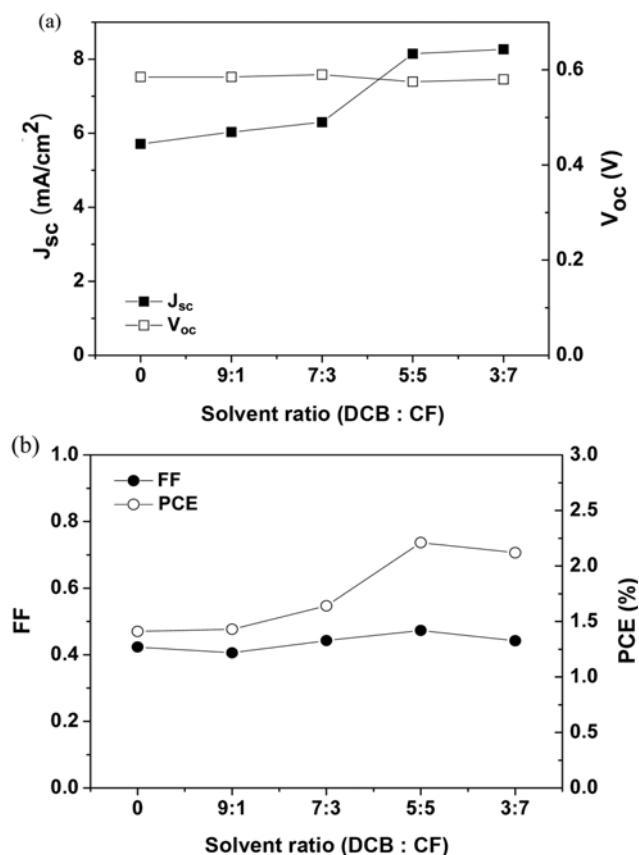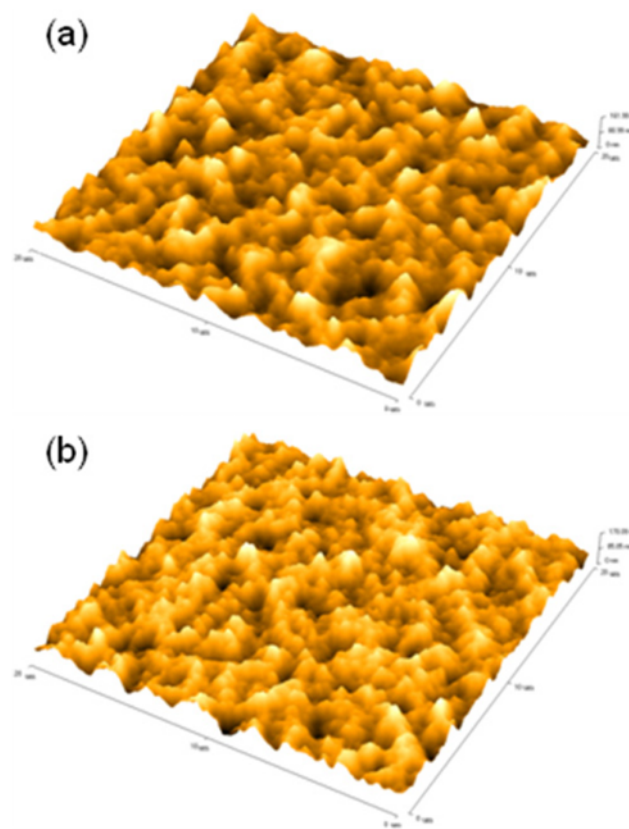**Fig. 6. Effects of solvent mixing on device performance. (a) Short circuit current (Jsc) and open circuit voltage (Voc), (b) Fill factor (FF) and power conversion efficiency (PCE).**

Fig. 7. AFM images of organic layers gravure printed using. (a) Dichlorobenzene solvent only (roughness 21.9 nm), (b) Dichlorobenzene : chloroform=5 : 5 (roughness 23.3 nm).

attributed to morphological changes and the degree of crystallization affected by solvent evaporation.

CONCLUSION

Gravure printing was tested in the fabrication of organic photovoltaic devices, and the effects of solvents were investigated with chloroform, chlorobenzene and 1,2-dichlorobenzene and with their mixtures. Solution viscosity was optimized for the gravure printing of P3HT : PCBM, and solvent effects were also investigated. Viscosity was varied by using different concentrations of the active materials 7% P3HT : PCBM was shown to be optimal in dichlorobenzene. Organic photovoltaic devices' power conversion efficiency was then improved to 2.2% by adding chloroform to the dichlorobenzene.

ACKNOWLEDGEMENT

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