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Highly Efficient Inkjet-Printed Organic Photovoltaic Cells

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In this article, we report the development of inkjet printing technique for the fabrication of bulk heterojunction organic photovoltaic cells (OPVs). We have demonstrated highly efficient OPV with a mixture of poly(3-hexylthiophene)s (P3HT) and 1-[3-(methoxycarbonyl)propyl]-1-phenyl[6.6]C61 (PCBM) as an inkjet-printed photoactive layer. Especially, 3.8% of power conversion efficiency (PCE) and 0.68 V of open circuit voltage (V_{oc}) can be obtained by using the chlorobenzene as a solvent. This value is the highest performance in P3HT:PCBM based OPV system by now. We reveal that substantial improvements can be realized by nano-structured heterojunction after inkjet printing and this technique is one of the promising fabrication methods for organic photovoltaic cells. Also, we have designed and fabricated five-series connected large area (18 cm²) inkjet-printed OPVs using the patterned indium tin oxide (ITO) with Au bus-electrode to minimize the efficiency drop due to the surface resistance of ITO. Consequently, 1.25% of power conversion efficiency can be obtained with a short circuit current of 1.24 mA/cm², a fill factor of 0.32, and an open circuit voltage of 3.2 V. © 2010 The Japan Society of Applied Physics

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1. Introduction

Polymer based organic photovoltaic cells (OPVs) have gained more and more interest over the past two decades, as reported by a steady increase in the reported power conversion efficiency (PCE).^{1–5} Among the alternative fabrication technologies for large area OPVs on flexible substrates, printing is one of the attractive fabrication processes that have several advantages such as low cost, direct patterning, low wastage, and close composition control.^{6,7} Fortunately, most organic photovoltaic materials can be made to be soluble and/or solution processable. Also the alternative technologies, for example, screen printing and inkjet printing have been studied during the past several years. Direct inkjet printing has been utilized for the area of organic electronics [organic light-emitting diodes (OLEDs), organic thin-film transistors (OFETs), and OPVs] as well as convenient graphic printing field. In the end of 2007, Brabec and his coworkers reported 2.9% PCE OPVs⁸ with inkjet printing technology and the improved the PCE of inkjet-printed OPV about 3.15%, which is the highest efficient printed OPVs by now.⁹

In this work, we demonstrate the use of inkjet-printing technology for deposition of an active layer of OPVs using a mixture of poly(3-hexylthiophene) (P3HT) and 1-[3-(methoxycarbonyl)propyl]-1-phenyl[6.6]C61 (PCBM). In inkjet-printing method, ink drops are ejected when required by pulse flow through nozzle of typically 30 μ m orifice. The ejecting drops have volumes about 10 pL. The mechanism by which a piezoelectric drop on demand (DOD) ink-jet print-head generates droplets has been a study for a several years.^{10,11} The principle of operation is the generation of pressure waves in a fluid-filled channel behind an orifice. At the orifice, fluid is normally retained by surface tension at the fluid/air interface, hence the action of the pressure wave is to overcome the surface tension and project a finger of fluid from the orifice. Above some critical value of this pressure, determined by the rheological properties of the fluid and the mechanical properties and dimensions of the channel and orifice, the protruding liquid finger will pinch off under surface tension to eject a droplet.¹²

Table I. Vapor pressures, boiling points, and surface tension of the solvents.

Liquid	Vapor pressure at 20 °C (mmHg)	Boiling point (°C)	Surface tension (mN m ⁻¹)
<i>o</i> -Dichlorobenzene	1.2	180	37
Chlorobenzene	8.8	130	33.6
Mesitylene	1.86	165	28.8

The vapor pressure, boiling point, and surface tension of the solvents are critical parameters for inkjet printing technology.¹³ Table I summarizes the vapor pressures, boiling points, and surface tensions for the solvents used in this study. For the solvents used in our studies higher vapor pressures at a defined temperature (20 °C) result in lower boiling points. This indicates a more rapid vaporization of chlorobenzene owing to the higher vapor pressure and the lower boiling point in contrast to *o*-dichlorobenzene, which vaporizes slowly. In addition, *o*-dichlorobenzene is a high surface tension solvent (37 dyn/cm). Therefore, its use resulted in a suppressed film formation and therefore a non-uniform film with strong thickness variation in the micrometer scale within one printed area, showing a dewetting behavior.⁹ This could be due to the lower surface energy of the poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) underlayer. Therefore, the inkjet-printed P3HT:PCBM blend active layer from *o*-dichlorobenzene shows clear limitations regarding the wetting and spreading of the solution on the PEDOT:PSS layer used in this study. The authors suggested chlorobenzene solvent can overcome the above limitations due to its lower surface tension of 34.9 dyn/cm compared to *o*-dichlorobenzene. From now on, we propose the inkjet-printing method using chlorobenzene solution for an active layer of OPVs and discuss the effect of the solvent vapor pressure and surface tension to the inkjet-printed P3HT:PCBM blend morphology.⁸

2. Experimental Procedure

2.1 Materials

P3HT was purchased from Rieke Metals and PCBM was synthesized in the same methods described in the literature.¹⁴

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Table II. Devices performance comparison as a function of printing condition and solvent species.

Device	Resolution (dpi)	Solvent	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor	PCE (%)
2-1	550	<i>o</i> -Dichlorobenzene	0.69	8.15	0.64	3.61
2-2	750	<i>o</i> -Dichlorobenzene	0.69	9.08	0.53	3.30
2-3	550	Chlorobenzene	0.69	6.15	0.61	2.61
2-4	750	Chlorobenzene	0.68	9.05	0.62	3.80
2-5	1000	Chlorobenzene	0.66	10.6	0.51	3.55
1-1 (ref.)	Spin-coated	<i>o</i> -Dichlorobenzene	0.67	9.4	0.59	3.75
1-2 (ref.)	Spin-coated	Chlorobenzene	0.65	8.9	0.55	3.17

*Under 100 mW/cm² AM 1.5G simulated light illumination

Other chemicals including solvents were purchased from Aldrich Chemicals and used without further purification.

2.2 Device fabrications

A typical polymer photovoltaic device in this study was consisted of a layer of polymer thin film sandwiched between a transparent anode (indium tin oxide, ITO) and a LiF/Al cathode. The active polymeric material was a mixture of P3HT and PCBM. To fabricate the OPVs, the patterned ITO glass substrate (2.5 × 2.5 cm², Samsung Corning Fine Glass, sheet resistance: <7 Ω/square) was cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol sequentially. After treatment of Ar Plasma on the surface of ITO surface, fabricated with spin-coated PEDOT:PSS (AI 4083, 45 nm), followed thermal treatment of the substrates at 140 °C for 15 min. And then, solutions of P3HT and PCBM (5 : 3.5 mg) in *o*-dichlorobenzene (1 mL) or chlorobenzene (1 mL) were inkjetted by using inkjet printer (Unijet UJ2100) and dried at 90 °C for 10 min in an Ar atmosphere. The cathode consisting of LiF (0.5 nm) and Al (120 nm) layer was thermally deposited via metal mask on top of the active layer under vacuum of around 10^{−6} Torr. The thickness of films was measured with a Tencor Alpha-Step Profiler. The surface morphology of active layer films of OPVs was measured on an atomic force microscope (AFM; Seiko Instruments SPM-9500). All of our OPVs were encapsulated under UV curing with a glass cap including desiccant (CaO) and annealed at 150 °C for several minutes. In case of large area OPV fabrication, two types of ITO glass substrates were used with or without Au bus-electrode and all other processes were exactly same with the previous description.

2.3 Current density–voltage measurements

The current density–voltage (J – V) characteristics were measured by a Keithley 2400 source-measure unit. The photocurrent was obtained under illumination from an Oriel solar simulator (AM 1.5G, 100 mW/cm²). The illumination intensity was calibrated by a standard Si photodiode with KG-5 filter (Bunkoh Keiki BS520). The calibration method based on IEC-69094-1 spectrum followed the procedures described in the literature.¹⁵⁾

3. Results and Discussion

3.1 Performances of inkjet-printed OPVs

The organic photovoltaic cells were fabricated in a structure of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al in which active

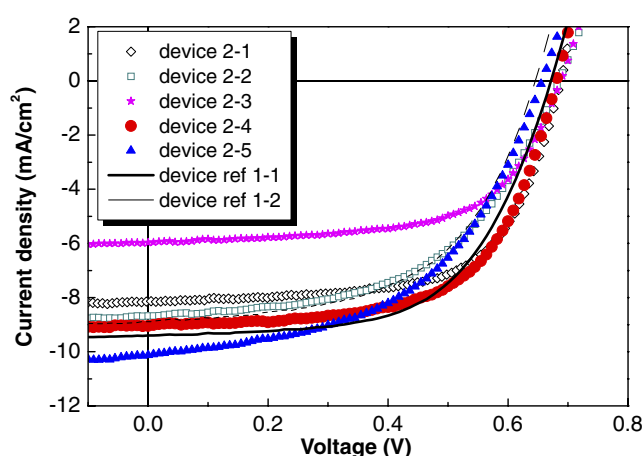


Fig. 1. (Color online) J – V characteristics for inkjet-printed OPVs fabricated with variation of printing condition and solvent of active layer (ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al).

layer was variation with different inkjet printing resolution (550, 750, and 1000 dpi) and solvents (*o*-dichlorobenzene and chlorobenzene). Also, spin-coated reference device using a mixture of P3HT:PCBM in *o*-dichlorobenzene and chlorobenzene solvent as an active layer was fabricated to be compared. The J – V characteristics of fabricated OPVs measured under 100 mW/cm² AM 1.5G simulated light illumination as shown in Fig. 1. And other device performance of OPVs as a function of printing condition and solvent were summarized and compared with spin-coated OPVs in Table II. In our study, it is confirm that the chlorobenzene solvent is more useful than *o*-dichlorobenzene solvent and the resolution of 750 dpi is more adoptable compare to those of 550 and 1000 dpi. With increasing the resolution, a short circuit current density (J_{sc}) was linearly increased, however, the overall device performance was lowered due to the decrease of V_{oc} and fill factor. Consequently, we can obtain the highest PCE about 3.8% by using the chlorobenzene solvent at the inkjet printing condition of 750 dpi, which device showed a J_{sc} of 9.05 mA/cm², a V_{oc} of 0.68 V, and a fill factor of 0.62. Consequently, device 2-4 shows almost same performance with reference device 1-1 that have fabricated by optimized spin-coating condition. In addition, inkjet-printed OPVs (devices 2-4 and 2-5) show higher power conversion efficiency above 3.5% than spin-coated OPV (reference device 1-2, 3.2%), because effective bulk-heterojunction can be formed after inkjet-printing due to

appropriate solvent evaporation. From these results, we can confirm that inkjet-printed OPVs show the equal performance with spin-coated device by control the printing resolution and use of chlorobenzene solvent.

Actually, 3.8% PCE was slightly higher than the result of Brabec.⁸⁾ Brabec and his coworker's were struggled to minimize the surface roughness of inkjet-printed active layer and they found the proper printing condition, which was using the combined solvent of *o*-dichlorobenzene and mesitylene and elevating the substrate temperature to 40 °C. However, we can find the unique printing condition using the single solvent of chlorobenzene without substrate heating. The vapor pressure and surface tension of chlorobenzene solvent are 8.8 mmHg and 33.6 mN/m at 20 °C, respectively and these values are expected to be the same with those of combined solvent of *o*-dichlorobenzene and mesitylene at 40 °C. Consequently, the chlorobenzene inkjet-printed active layer shows a much more uniform mixing of the P3HT and PCBM components within the blend and we can obtain the very high power conversion efficiency of 3.8%, which is the highest value in the world by now.

Comparing to the result of Brabec,⁹⁾ in this work, the V_{oc} of our inkjet-printed OPVs were significantly increased from 0.53 to 0.68 V. But the fill factor and the current density were marginally decreased from 0.64 to 0.62 and from 10.05 to 9.05 mA/cm², respectively. There are two major possibility of increased V_{oc} , one is mixing ratio of donor and acceptor and the other is the thickness of active layer. As changing the mixing ratio of P3HT and PCBM from 1 : 1 to 1 : 0.7 and film thickness of active layer from 200 to 80 nm, our OPVs can show the improved V_{oc} from 0.53 to 0.68 V. And additional study to understand the increased V_{oc} will be proceeded.

3.2 Analyses of printed active layer films

To understand the bulk-heterojunction morphology of our inkjet-printed active layer, we did the AFM analyses of printed films using *o*-dichlorobenzene and chlorobenzene as a solvent with a variation of printing resolution. First, the AFM images of the pristine (with no thermal treatment) films show surfaces for the inkjet-printed active region (1.5 × 1.5 μm²) compare to that of annealed films at 150 °C for 10 min. Figures 2(a) and 2(b) show the AFM images of the inkjet-printed P3HT:PCBM blend films using *o*-dichlorobenzene at pristine [Fig. 2(a)] and after annealing at 150 °C for 10 min [Fig. 2(b)] which the resolution of inkjet-printing is 750 dpi. The mean roughness is changed from 5.780 nm at pristine condition to 2.982 nm after annealing at 150 °C for 10 min, which is the distinctive tendency with the spin-coated device.¹⁶⁾ However, in the case of *o*-dichlorobenzene solvent, 750 dpi inkjetted film shows large agglomerate due to the slow solvent evaporation resulted from low vapor pressure and high surface tension of *o*-dichlorobenzene. Finally, we have compare two inkjetted films which are deposited by 750 dpi resolution in chlorobenzene solvent and 550 dpi resolution in *o*-dichlorobenzene solvent. Figures 2(c) and 2(d) show the AFM images for films that have inkjet-printed using chlorobenzene solvent at 750 dpi resolution. For the pristine film the surface using chlorobenzene solvent is smoother with an rms roughness of 4.638 nm compare to the

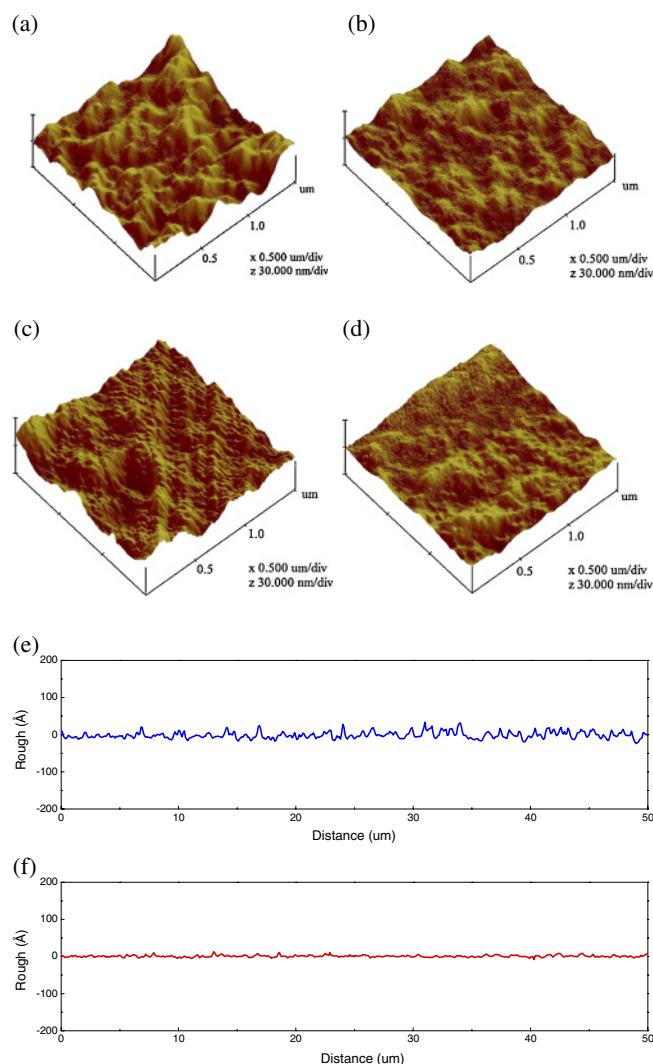


Fig. 2. (Color online) AFM images of inkjetted P3HT/PCBM film surfaces with a variation of solvent and printing resolution: (a) pristine film (550 dpi) with *o*-dichlorobenzene, (b) annealed film (550 dpi) at 150 °C for 10 min with *o*-dichlorobenzene, (c,e) pristine film (750 dpi) with chlorobenzene, and (d,f) Annealed film (750 dpi) at 150 °C for 10 min with chlorobenzene.

surface using *o*-dichlorobenzene (5.780 nm). In addition, after undergoing thermal treatment at 150 °C for 10 min, the rms roughness becomes 2.561 nm, which is slightly decreased compared to the case of *o*-dichlorobenzene solvent. There is significant improvement of surface roughness when solvent is changed from *o*-dichlorobenzene to chlorobenzene for inkjet-printed OPVs.

Figures 2(e) and 2(f) show the change in the large area (50 × 50 μm²) of printed film using chlorobenzene solvent after thermal annealing. The pristine film in Fig. 2(e) shows not only a higher roughness compared to the annealed film in Fig. 2(f) but also a much coarser texture with broad hill-like features compared to the annealed film in Fig. 2(f). Thus, the resulting surface morphology is dependent on the fabrication method chosen for the preparation of the active layer, that is to say, the chlorobenzene solvent can provide reliable inkjet printing with uniform coating. The mean roughness of film in the large area is changed from several ten nm to several nm which is almost same with the published result of Brabec.⁸⁾ This means that chlorobenzene

Table III. Devices performance and resistances of large area inkjet-printed OPVs with/without Au bus-electrode.

Device	Type	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor	PCE (%)	Shunt resistance	Series resistance
3-1	Without Au electrode	3.08	0.75	0.33	0.77	4.42×10^2	1.44×10^2
3-2	With Au electrode	3.17	1.24	0.32	1.25	2.84×10^2	9.69×10^1

*Under 100 mW/cm² AM 1.5G simulated light illumination

single solvent is useful to the fabrication of inkjet-printed organic photovoltaic cell and we can obtain the similar film morphology with the combination of *o*-dichlorobenzene and mesitylene.

3.3 Five-series connected large area inkjet-printed organic photovoltaic cells

In general, large area OPV showed definitely poor power conversion efficiency due to the high sheet resistance of ITO electrode. To resolve this problem we have incorporated a bus-electrode using the vacuum deposited Cr/Au on the patterned ITO electrode. And we have designed and fabricated large area (7×7 cm², active area of 18 cm²) inkjet-printed OPVs with/without the Au bus-electrode coated ITO glass which device consisted of five-series connected pixels. The active layer was inkjet-printed by using the chlorobenzene solvent at the same printing condition of 750 dpi. The performance of large area inkjet-printed OPVs was measured and compared with reference device without Au bus-electrode after annealing at 150 °C for 10 min under 100 mW/cm² AM 1.5G simulated light illumination.

As shown in Fig. 3 and Table III, the performance of large area device was drastically decreased due to the increase of sheet resistance with increase of pixel size. In case of device 3-2, however, the J_{sc} became doubled in the presence of increased (about 0.09 V) V_{oc} but the fill factor was marginally decreased from 0.32 to 0.31. Consequently, the PCE of device 3-2 was increased from 0.77 to 1.25% by 1.6 times with incorporation of Au bus-electrode on ITO. In addition, series resistance (R_s) for device 3-2 was measured to be lower than that of device 3-1. Thus, device 3-2 having Au bus-electrode showed the PCE of 1.25% with a J_{sc} of 1.24 mA/cm², a V_{oc} of 3.17 V, and a fill factor of 0.32. Under illumination, low shunt resistance is related to a recombination of photogenerated-carriers unless it is limited by the current leakage through local shorts.¹⁷⁾

4. Conclusions

We have fabricated the P3HT:PCBM based inkjet-printed OPVs which showed world best power conversion efficiency of 3.8% with a J_{sc} of 9.05 mA/cm², a V_{oc} of 0.68 V, and a fill factor of 0.62 under 100 mW/cm² AM 1.5G simulated light illumination. From this study, we can confirm that chlorobenzene is the most adequate solvent to fabricate the inkjet-printed OPVs considering the vapor pressure and surface tension. Also, we can conclude that the efficiency of OPVs is closely relying on the printing conditions such as printing resolution (750 dpi). Also, we have designed and fabricated five-series connected large area (18 cm²) inkjet-printed OPVs using the patterned ITO with Au bus-electrode. Consequently, 1.25% of power conversion

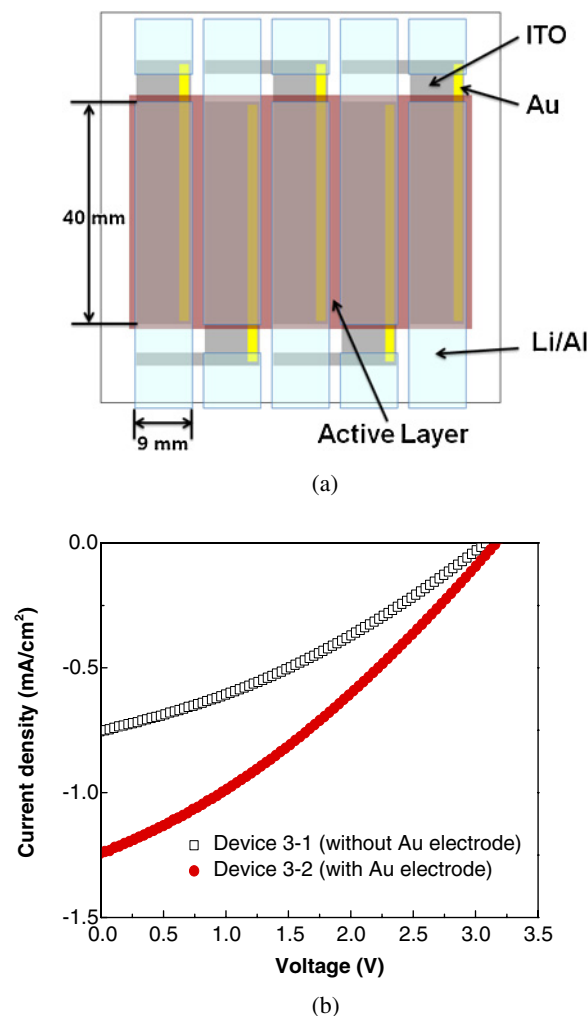


Fig. 3. (Color online) (a) Device layout and (b) J - V characteristics of five-series connected large area (active area: 18 cm²) inkjet-printed OPVs (ITO/PEDOT-PSS/P3HT:PCBM/LiF/Al) fabricated with or without Au bus-electrode.

efficiency can be obtained with a short circuit current of 1.24 mA/cm², a fill factor of 0.32, and an open circuit voltage of 3.2 V.

Acknowledgement

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