

Bulk-heterojunction organic photovoltaic cell fabricated by electro-spray deposition method using mixed organic solvent

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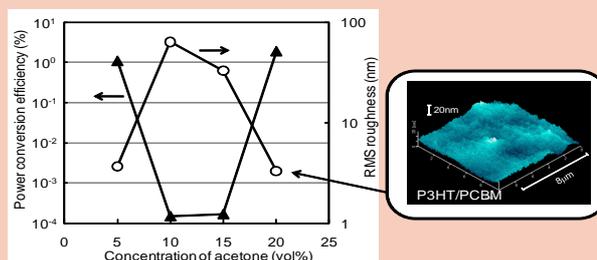
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A high-efficiency bulk heterojunction organic photovoltaic cell (OPV) was achieved by the electro-spray deposition method. The surface roughness of the P3HT:PCBM thin film can be reduced using the mixed solvent consisting of *o*-dichlorobenzene (*o*-DCB) and acetone. The effect of acetone concentration is related to its dielectric constant. Under optimized concentration of acetone in *o*-DCB (20 vol%), the P3HT/PCBM active layer with the smooth surface can be formed, and the power conversion efficiency of the OPV was 1.9%.



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1 Introduction Organic devices can be fabricated on a flexible substrate by a roll-to-roll printing process; therefore, solution-processed organic devices have been interested for future printable electronics [1–6]. Recently, several solution processes have been investigated to realize a lower fabrication cost and a larger device area [7]. This fact indicates that solution-processed organic devices will probably be used in practical applications, such as organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and organic thin-film transistors.

In general, a multilayer structure is difficult to form with different polymers using normal solution-processes, such as gravure printing, dip-coating, screen printing, and inkjet printing. This is because that these solution-

processes cause the dissolution of the underlying organic layer while coating the upper organic layer. However, several approaches were demonstrated to form the multilayer structure by the solution process [8]. Nowadays, we investigated an electro-spray deposition (ESD), a novel solution process, to fabricate organic photoconductive devices [9]. In this process, a high voltage of several kV is applied to the polymer solution, which is then divided into several particles with diameters of the order of a few μm [10]. As a result, the organic solvent evaporates before reaching the substrate. This fact indicates the multilayer structure can be deposited like an evaporation method using the ESD method, without dissolving the underlying organic layer.

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Recently, J. S. Kim reported an OPV fabricated by the ESD method [11]. The reported device performance is almost same as the reference device fabricated by the spin-coating process. However, the solvent vapor soaking technique is necessary to reduce the surface roughness of the poly(3-hexylthiophene) (P3HT)-doped-(6,6)-phenyl-C61-butyric acid methyl ester (PCBM) layer. Another approach is the mixed organic solvent technique. In a previous paper, J. Ju demonstrated that the surface roughness of the organic thin film was improved through the addition of *N,N*-dimethyl formamide in toluene with different vapor pressures [12].

In this letter, we investigated the relationship between the concentration of the solvent mixture (*o*-dichlorobenzene (*o*-DCB)/acetone) in the ESD coating process and the surface roughness of the P3HT:PCBM thin film. Finally, we also estimated the device performance of the OPV fabricated by the ESD method with the mixed organic solvent technique.

2 Experimental A glass capillary was fabricated using a puller (PC-10, Narishige) and a microforge (MF-900, Narishige). The inner diameter of the glass capillary was approximately 50 μm . A positive high voltage was applied to a copper wire in the P3HT and PCBM solution using a high voltage source (HJPQ-30P1, Matsusada Precision). The earthed line was connected to a patterned indium tin oxide (ITO) layer on top of the glass substrate.

An OPV was fabricated in a subsequent process. At first, 1.2 mg of P3HT and 1.0 mg of PCBM were mixed into 1 ml of *o*-DCB. Then, acetone was added into the resulting solution. Concentrations of acetone were 5 (device A), 10 (device B), 15 (device C), and 20 vol% (device D), respectively. In addition, an ITO-coated glass substrate was cleaned in solvent and deionized water under ultrasonic waves, and was treated with ultraviolet ozone cleaning for 20 min. After spin-coating PEDOT:PSS (Clevious PH500) at 5000 rpm for 1 min, the sample was annealed at 140 $^{\circ}\text{C}$ for 10 min in nitrogen atmosphere. The P3HT and PCBM layer was deposited by the ESD method in air, and the Al electrode (130 nm) was successively thermally evaporated in a vacuum chamber. The deposition time of the ESD process was fixed 40 min for all the ESD processes. Finally, the fabricated device was annealed at 140 $^{\circ}\text{C}$ for 20 min to form the bulk-heterojunction structure. The distance from the glass capillary to the glass substrate was 10 cm, and the active area was 8 mm^2 .

Current density-voltage characteristics were measured using a Keithley serious 2400 digital source meter under the standard solar spectrum (AM 1.5G, 100 mW/cm^2). In addition, the spray diameter was measured using a charge-coupled device camera (Watec, WAT-902B).

3 Results and discussion Figure 1 shows the current density-voltage characteristics of devices A, B, C, and D fabricated by the ESD method with different concen-

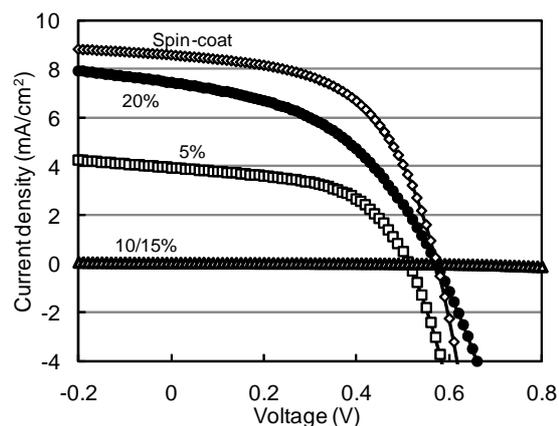


Figure 1 Current density-voltage characteristics of OPVs fabricated by the ESD method with different concentrations of acetone in *o*-DCB.

trations of acetone. The short-circuit current densities of devices B (10 vol%) and C (15 vol%) were quite low compared to the devices A (5 vol%) and D (20 vol%). The short-circuit current densities were less than 10 $\mu\text{A}/\text{cm}^2$ for both devices B and C, and the power conversion efficiencies (PCEs) were 0.00015% (device B) and 0.00017% (device C). On the other hand, the photovoltaic characteristics of the device D was drastically improved compared to the devices B and C. The PCE of the device D was 1.9%, and it was a little lower than the reference device fabricated by the spin-coating process (2.7%). The short-circuit current density of 0.57V, and the fill factor of 0.45 were achieved for the device D. In addition, the P3HT:PCBM solution was aggregated by adding the acetone over 20 vol%.

The measured thicknesses of the P3HT:PCBM layers were 120, 65, 75, 150, and 130 nm for devices A, B, C, D, and the reference device, respectively. In general, the device performance is influenced by the surface roughness of the P3HT:PCBM layer. In addition, the evaporation speed and spray diameter will be dominant factors affecting the surface roughness of an organic thin film. Figure 2 shows the relationship between the concentration of acetone on the spray diameter at 6 mm far from the tip of the glass capillary. The spray diameter increased with increasing concentration of acetone. This phenomena is caused by charged P3HT:PCBM droplets [13], which spread due to the static electrical force by applying the high voltage. Therefore, the large relative dielectric constant of acetone (20.7) compared to *o*-DCB (9.9) causes the spread spray diameter. In our experimental result, the thickest P3HT:PCBM layer was observed at 20 vol%. In general, the large spray diameter causes the slow deposition rate; however, the supply speed of the P3HT:PCBM solution tends to increase with increasing concentration of acetone.

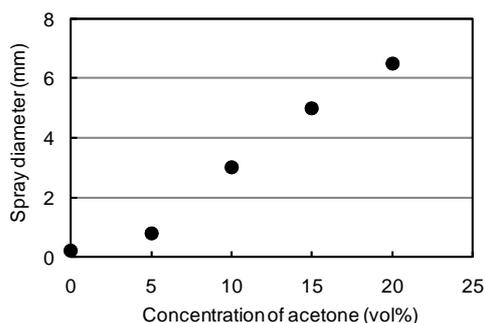


Figure 2 Relationship between the spray diameter measured at 6 mm far from the glass capillary and the concentration of acetone.

The most likely cause of the high-photovoltaic performance of the device D is the smooth surface morphology of the P3HT:PCBM layer by adding the optimized concentration of acetone. Figure 3 shows the atomic force microscope (AFM) images of the P3HT:PCBM layers fabricated by the ESD method with different concentrations of acetone. The root mean square (RMS) roughnesses of the P3HT:PCBM layer were 3.70, 63.8, 33.1, 3.31, and 2.63 nm for the devices A, B, C, D and the reference device, respectively. The wet droplet like a cast method was deposited on the ITO-coated glass substrate due to the narrow spray diameter at the concentration of 5 vol%, as shown in Fig. 2. Therefore, the surface structure of the P3HT:PCBM layer of the device A was almost same as that of the reference device. As a result, the performance of the device A is relatively higher than the devices B and C. In the case of the devices B and C, the surfaces of the active layers became rather rough. This is because that the aggregated

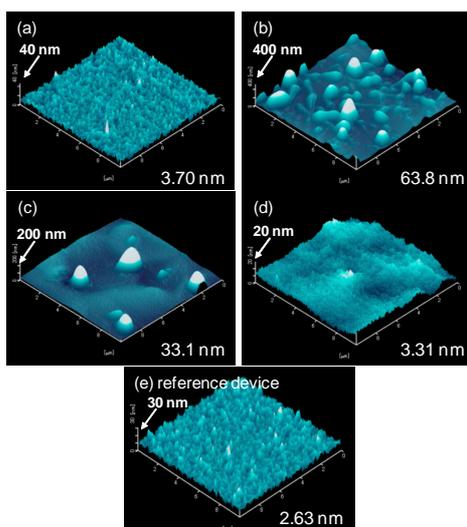


Figure 3 AFM image of the P3HT:PCBM layer. Concentrations of acetone were (a)5, (b)10, (c)15, and (d)20 vol%.

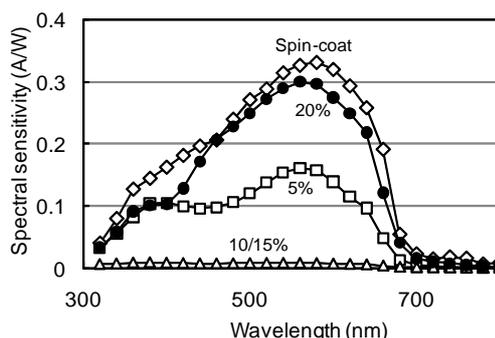


Figure 4 Spectral sensitivity of OPVs fabricated by the ESD method and the conventional spin-coating process.

structure was obtained before reaching the substrate due to the high evaporation speed of the droplet. On the other hand, it is noted that the surface roughness of the device D was drastically reduced compared to those of the devices B and C. The AFM image in Fig. 3(d) indicates the dried P3HT:PCBM particles were deposited on the PEDOT:PSS layer. The supply speed of the P3HT:PCBM solution increased with increasing concentration of acetone; therefore, the evaporation speed of the droplet was reduced by adding the large amount of acetone. As a result, the dried particles were deposited on the PEDOT:PSS layer without aggregating before reaching the substrate in the case of the device D, and the PCE of the device D was improved up to 1.9%.

Figure 4 shows the spectral sensitivity of OPVs. The peak-spectral sensitivities of all the devices were showed 580 nm corresponding to the absorption of P3HT. In addition, the quite low-spectral sensitivities were obtained for the devices B and C due to their low PCEs.

4 Conclusion We successfully achieved the smooth surface roughness of the P3HT:PCBM layer by the ESD method with the mixed organic solvent technique (*o*-DCB and acetone). Furthermore, the high-photovoltaic performance of the OPV was also demonstrated.

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