Dependence of additive-solvent on bulk-heterojunction organic photovoltaic cell fabricated by electrospay deposition method

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1. Introduction

Since an organic thin film 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 [1–3]. Recently, several solution processes have been investigated for further low-fabrication cost [4]. Therefore solution-processed organic devices will be used as organic light-emitting diodes, organic photovoltaic cells (OPVs), and organic thin-film transistors.

In general, an organic multilayer structure is difficult to fabricate with different polymers using conventional solution-processes, such as the gravure printing, the dip-coating, the screen printing, and the inkjet printing. This is because the underlying organic layer is dissolved while coating the upper organic layer. Nowadays, we investigated an electrospay deposition (ESD) process for organic photovoltaic/photoconductive devices [5-6]. 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 [7]. As a result, the solvent easily evaporates before reaching the substrate due to the small-droplet size. Therefore, the organic multilayer can be deposited like a thermal evaporation method. Other advantages of this technique are that it has (1) a simple experimental setup without special conditions (high temperature and vacuum chamber) and (2) the potential for thick films with a high uniformity and a smooth morphology.

A surface roughness of the organic layer is important factor to improve the photovoltaic performance of the OPV. However, the smooth surface is difficult to form by the ESD process. Our previous paper demonstrated the drastically improved photovoltaic characteristics of the bulk-heterojunction OPV by using the additive-solvent technique [6]. However, further reduced surface roughness is necessary for the practical application.

In this paper, we investigated the relationship between the additive-solvent of the ESD process and the surface roughness of the poly-3-hexylthiophene (P3HT): (6,6)-phenyl-C61-butyric acid methyl ester (PCBM) thin film. Furthermore, we also estimated the device performance of the bulk-heterojunction OPV fabricated by the ESD method with different additive-solvent in o-DCB, and discussed the influence of the surface roughness on the device performance of the bulk-heterojunction OPV.

2. Experimental

Figure 1 shows a schematic configuration of the experimental setup for the ESD method. A tip of the glass capillary was approximately 50 μm in size. A red light was irradiated around the tip of the glass capillary, and the spray distribution was captured using a charge coupled device (CCD) camera. The inset of Fig. 1 shows the CCD image while spraying an organic solution.

The device structure of the OPV was indium tin oxide (ITO) / PEDOT:PSS (32nm) / P3HT:PCBM / Al (130nm). At first, the PEDOT:PSS layer was spin-coated on the ITO-glass substrate. After annealing at 140°C for 10 min, the P3HT:PCBM film was prepared from the o-dichlorobenzene (o-DCB) solution by the ESD method. Concentrations of PCBM and P3HT in o-DCB were 1.2 and 1.0 mg/ml. In addition, dimethyl sulfoxide (DMSO) (device A), N,N-dimethylformamide (DMF) (device B), and acetonitrile (device C) were added into the resulting solution at 10 vol%, respectively. The distance from the glass capillary to the ITO-glass substrate was 10 cm, and the applied voltage was 4.5 kV. The deposition time was fixed 60 min for all the ESD processes. Finally, the Al-electrode was thermally evaporated, and then the fabricated device was annealed at 140°C for 25 min to form the bulk-heterojunction structure.

![Figure 1 Schematic configuration of the experimental setup of the ESD method.](image-url)
3. Results and Discussion

Figure 2 shows the current density-voltage characteristics of the fabricated OPVs by the ESD method under the illumination (AM1.5). The measured thicknesses of the P3HT:PCBM layers were 50, 100, and 150 nm, for devices A (DMSO), B (DMF), and C (acetonitrile), respectively. Among the tested additives in o-DCB, the best photovoltaic performance was obtained from the device with the acetonitrile-additive. We achieved the power conversion efficiency of 2.2%, the short-circuit current density of 7.42 mA/cm², the open-circuit voltage of 0.59 V and the fill factor of 0.49 by using acetonitrile. In our previous paper, the dielectric constant and the vapor pressure are important factors to reduce the surface roughness of the organic thin film [6]. Therefore, this result indicates the control of the evaporation speed is important technique for the high-device performance. Figure 3 shows the spectral response of the fabricated OPVs. We observed the peak wavelength at 560nm, corresponding to the absorption of P3HT.

In general, the device performance is influenced by the surface roughness of the P3HT:PCBM layer. Figure 4 shows the atomic force microscope (AFM) images of the P3HT:PCBM thin films fabricated by the ESD method with different additive-solvents. The root mean square (RMS) roughness were 10.8, 6.32, 2.23, and 3.17 nm for the devices A (DMSO), B (DMF), C (acetonitrile), and the reference device (spin-coated sample) respectively. In the case of the device A, the surface morphology of the active layer became rough compared to other samples. This is because the aggregated structure was obtained before reaching the substrate due to the fast evaporation speed. On the other hand, it is noted that the surface roughness of the device C was reduced compared to the devices A and B. This is because the dried particles were deposited on the PEDOT:PSS layer without aggregating of P3HT:PCBM. As a result, the performance of the device C is relatively higher than that of the devices A and B. Therefore, the smooth surface morphology of the P3HT:PCBM layer is important in the high-photovoltaic performance of the ESD-based OPV. Our experimental results indicate the additive-solvent is important to control the surface morphology of the organic film and the photovoltaic performance.

4. Conclusions

We investigated the relationship between the additive-solvent of the ESD process and the surface roughness of the P3HT:PCBM thin film. In addition, we demonstrated the high-efficiency from P3HT:PCBM bulk-heterojunction OPV fabricated by ESD method with the mixed organic solvent technique. Especially, acetonitrile is found to be the best additive-solvent to improve the photovoltaic performance.

References