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Improved Crystallinity of Poly(3-hexylthiophene-2,5-diyl):[6,6]-Phenyl-C_{61} Butyric Acid Methyl Ester Film by Pulsed Electrospray Deposition

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We investigated crystallinity parameters and ordering domains of poly(3-hexylthiophene-2,5-diyl) blended in [6,6]-phenyl-C_{61}-butyric acid methyl ester films, which were fabricated by pulsed electrospray deposition methods. The crystallinity parameter and the ordering domain were estimated from Raman and optical absorption spectra, respectively. As a result, they were improved with decreasing the off time of pulse voltage, corresponding to the slow evaporation speed of solvent. In addition, both the space-charge limited current mobility and the photoconversion efficiency showed same trend. A highest photoconversion efficiency of 1.11 % was achieved without the thermal annealing process after depositing the active layer.

Introduction

Photoconversion efficiencies (PCEs) of organic photovoltaics (OPVs) have been drastically improved by optimizing molecular structures of p-type polymers and device architectures [1, 2]. In generally, the high temperature annealing causes aggregated fullerene derivatives; therefore, a solvent-vapor annealing process is often used to form the bulk heterojunction structure without the aggregation of fullerene derivative [3].

In generally, OPVs can be fabricated by several solution processes, and an electrospray deposition (ESD) method has gained interest as a novel coating process for organic devices. Previous researches demonstrated a smooth surface roughness using an additive solvent with the high dielectric constant [4–6] and high PCEs comparable to other solution processes like a spin-coating [7–9].

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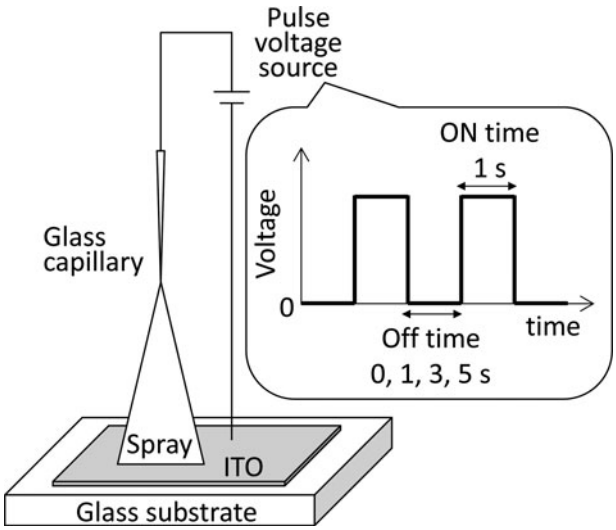

Figure 1. Schematic configuration of ESD setup and the pulse shape of applied voltage.

Nowadays, an ordered poly(3-hexylthiophene-2,5-diyl) (P3HT) domain and the crystallinity parameter (CP) were estimated from optical absorption [10] and Raman spectroscopies [11] for the ESD-film, respectively. By optimizing the ESD condition, such as applied voltage and solvent, the internal structure (the ordered domain and the crystallinity) of organic thin film can be controlled by the ESD without the thermal annealing process. Furthermore, the relationship between the device performance and the internal structure have been investigated as a basic research.

In this paper, we investigated the relationship between the off time of pules voltage and the internal structure of P3HT-doped-(6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) by the ESD. The space-charge limited current (SCLC) mobility and the PCE of OPV were also investigated to compare the internal structure of thin film and the device performance.

Experimental Method

Figure 1 shows the schematic configuration of ESD setup. An inner diameter of the glass capillary was approximately 50 μm. A positive high voltage was applied to a copper wire in the P3HT:PCBM solution using a high-voltage source (ETM3-20K01PN1, Element). P3HT and PCBM were dissolved in *o*-dichlorobenzene at concentrations of 1 mg/mL, and then acetonitrile (10 vol.%) was added into the resulting solution as an additive solvent [9].

At first, the P3HT:PCBM thin film was deposited on the ITO-coated glass substrate to measure ultraviolet-visible absorption and Raman spectra. Then, we fabricated the hole-only device (ITO/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)/P3HT:PCBM/MoO_3/Al) and the OPV (ITO/PEDOT:PSS/P3HT:PCBM/Al). Herein, only the P3HT:PCBM layer was deposited by the ESD. The PEDOT:PSS thin film was spin-coated at a thickness of 20 nm. For the deposition of P3HT:PCBM layer, the distance between the glass capillary and the substrate, the deposition time, and the voltage were 10 cm, 40 min, and 3.75 kV, respectively. The on time of pulse voltage was fixed at 1 s, and the off time was changed as 0, 1, 3, and 5 s to control the evaporation speed of

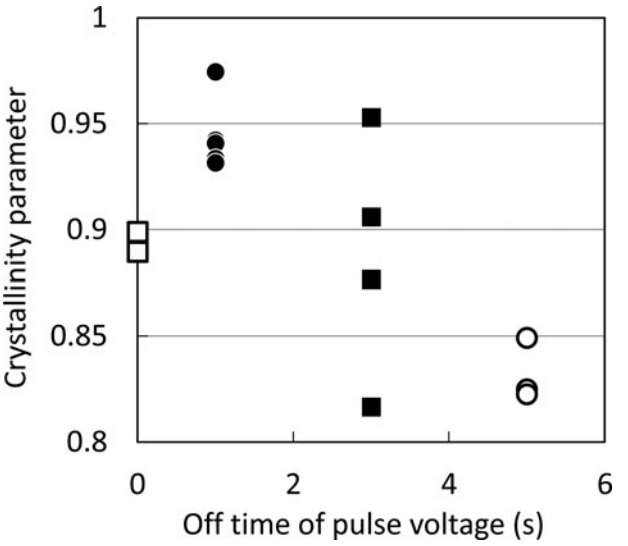

Figure 2. Relationship between crystallinity parameter of P3HT and off time of pulse voltage.

the solvent. Finally, a MoO_3 layer (10 nm) and an Al electrode (100 nm) were thermally evaporated.

The Raman spectrum was estimated using an inVia Raman microscope (Renishaw) with an excitation wavelength of 532 nm. The UV-Vis absorption spectrum was measured using an UV-Vis spectrometer (JASCO, V-650). The current-density-voltage characteristics were measured using a DC voltage current source/monitor (ADCMT, 6241A) under the standard solar spectrum (AM 1.5G, 100 mW/cm^2).

Results and Discussion

The CP was calculated as $CP=S_1/(S_1+S_2)$, where S_1 and S_2 are the integrated intensities of the crystalline and amorphous peaks of Raman spectra [12]. Figure 2 shows the relationship between the off time and the CPs, which were measured at 4 points for each sample. The CP increased with decreasing off time, which corresponds to the short evaporation time of solvent. Because the period between two deposited droplets becomes short when the off time of pulse voltage is short, and most of the solvent evaporate before the next droplet is reached. In addition, many aggregations were observed at an edge of droplet mark due to the solvent evaporation when the pulse voltage was used. In addition, the CP of aggregation is rather high compared to that of P3HT:PCBM thin film. Therefore, the higher CP at the off time of 1 s compared that of the sample fabricated by the DC voltage is caused by the aggregated P3HT in the deposited thin film.

Figure 3 shows UV-Vis absorption spectrum of P3HT:PCBM thin films fabricated with different off times. The broad peak at around 515 nm corresponds to disordered P3HT domains [13], and the low energy vibronic peak at 515 nm is caused by the ordered domains [14]. The relative absorbance of sub peak increased with decreasing off time. Shrotriya *et al.* demonstrated that self-organization in polymer/fullerene blend film is efficiently occurred at the slow glow speed, and this fact is well agreement with our experimental result in Fig. 3.

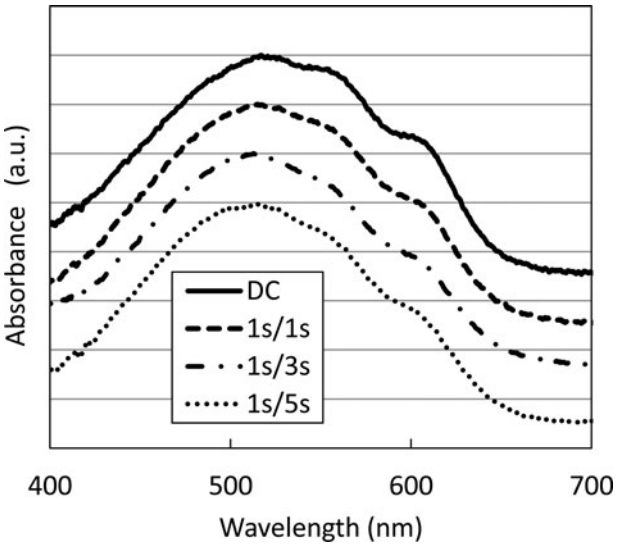

Figure 3. UV-Vis absorption spectra of P3HT:PCBM thin films deposited by pulsed ESD processes with different off times ranged from 0 (DC) to 3 s.

Figure 4 shows the SCLC mobility of P3HT:PCBM layer estimated from the hole-only device [15]. The SCLC mobility decreased with increasing off time of pulse voltage. This result can be explained by the ordered P3HT domain, as shown in Figs. 1 and 2. This is because that the ordered P3HT causes efficient hole transport in the P3HT:PCBM layer, resulting in the high SCLC mobility.

Finally, OPV performances were investigated. Table 1 summarizes the short circuit current density (J_{sc}), the open circuit voltage (V_{oc}), the PCE, and fill factor (FF) of OPVs fabricated by the pulsed ESD. These values were averaged for 4 devices. J_{sc} increased

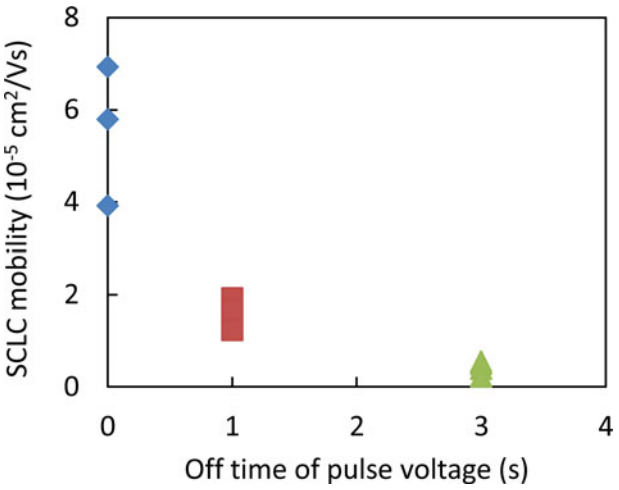

Figure 4. SCLC mobility of P3HT:PCBM layer deposited with different off times of pulse voltage.

Table 1. Performances of OPV devices fabricated by pulsed-ESD

off time	0 s (DC)	1 s	3 s
PCE	1.11	0.73	0.73
J_{sc}	5.62	3.95	3.52
V_{oc}	0.56	0.57	0.57
FF	0.35	0.32	0.36

with decreasing off time of pulse voltage, resulting in the high PCE without the annealing process to form the bulk heterojunction structure.

Conclusion

In this research, we investigated the internal structure of P3HT:PCBM thin film and the device performances of the hole only device and the OPV as a function of the off time of the pulse voltage for ESD. The short off time corresponding to the slow evaporation speed is found to improve the ordering domain of P3HT and the semiconductor characteristics.

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