Organic photoconductive device fabricated by electrospray deposition method

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Abstract

We demonstrated a blue-sensitive organic photoconductive device fabricated by an electrospray deposition method. Poly[9,9-dioctylfluorenyl-2,7-diyl]-co-1,4-benzo-(2,1,3)-thiadiazole (F8BT) was chosen as a blue-sensitive polymer, and a maximum external quantum efficiency of 0.22 % was achieved at the irradiated optical intensity of 3.9 mW/cm^2. The absorption spectrum of F8BT neat film showed that the selectivity of spectral responses at the blue wavelength region was good enough to divide the incident light into blue color components. These results indicate the possibility of a color separation without a prism for high resolution cameras by combination of green and red sensitive organic photoconductive devices.

Key words: Organic photoconductive device, Electrospray deposition, Polymer

1. Introduction

Since organic devices can be fabricated by a solution process, there have been considerable interests in organic devices for future printable electronics. [1, 2, 3]. Especially, organic photoconductive devices (OPDs) have attracted much attention from viewpoints of the lightweight and the thinness compared to other conventional image sensors, complementary metal-oxide-semiconductor sensors and charge-coupled devices. Recently, S. Aihara et al.

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proposed a novel type of an image sensor overlaid with three organic photo-conductive films, which are individually sensitive to only one of the primary color components, blue, green, and red light, respectively [4]. These devices were fabricated by a conventional thermal evaporation process, and the reported evaporation-based devices were realized good reliabilities and high device performances [5, 6]. However, the use of organic materials is motivated by several special advantages over inorganic materials, as for example large substrate formats, mechanical flexibility, easy to process at low-costs and furthermore the huge potential for monolithic integration of different organic devices onto one common substrate. In order to realize larger photoconductive area productivity with a lower cost, we need to develop solution-processed photoconductive devices. By now, little is known about color-separable organic photoconductive devices fabricated by a solution process.

Most of organic materials can be prepared using solution processes, such as a dip-coating, a screen printing, and a conventional spin-coating. One serious problem of the solution process is the dissolution of the under layer, and it makes difficult to prepare multilayer structures formed by different polymer layers using a conventional wet process. Recently, many spray technique have been developed to deposit organic multilayer films [7, 8, 9], and these methods are suitable to fabricate high performance in organic devices using the solution process. However, the smaller size of the polymer solution while spraying is important for further improvement in the surface roughness and the device performance. We investigated a novel spray process to fabricate organic films, called as an electrospray deposition (ESD). In this method, the high voltage approximately several kV is applied to the polymer solution, and then the polymer solution is divided to nano-particles. As a result, the organic solvent is evaporated before reaching the substrate, and the organic thin film can be deposited like a thermal evaporation method without dissolving the under organic layer. Other interesting properties of this technique are the simple experimental setup without special conditions (high temperature and/or vacuum chamber) and the possibility of thick films with a high uniformity and morphology.

The previous paper reported the organic and/or inorganic thin films [10, 11] and nano-size polymers [12, 13] by the ESD method. However, there are few study of the ESD-based organic photoconductive device, and the above-mentioned advantage of ESD method is useful for organic devices. In addition, the most advantage of ESD method is the particle size of organic solution compared to other spray method, therefore, the high density film

organic thin film can be deposited.

We deposited an organic photoconductive film sensitive to the blue light composed of a single layer structure with poly[9,9-dioctylfluorenyl-2,7-diyl]-co-1,4-benzo-(2,1,3)-thiadiazole (F8BT) using the ESD method. F8BT has the high carrier mobility [14] and the sharp spectral selectivity of photocurrent spectrum. Therefore, we selected F8BT as an organic photoconductive material. In this study, we investigated photoconductive characteristics of an electrospray-based OPD with F8BT, which has a color selectivity at the blue-wavelength region. We also estimated the influence of the applied voltage during the ESD method on the optical property of the F8BT neat film to optimize the deposition condition.

2. Experimental

A schematic configuration of the experimental setup for the ESD method is shown in Fig. 1. At first, F8BT was dissolved in tetrahydrofuran (THF) at a content of 0.45 g/l. The highly diluted organic solution was contained in a plastic syringe. A stainless steel nozzle with a 0.7 mm diameter was connected at the point of the plastic syringe. Then, the organic solution was supplied to the point of the stainless nozzle at a scanning speed of 3 μl/min using a mechanical stage. The distance from the stainless nozzle to a glass substrate was ranged from 8 to 10 cm.

An indium tin oxide (ITO) layer with the thickness of 150 nm was sputtered on the glass substrate, and the prepared glass substrate was cleaned in ethanol under ultrasonic waves, and was treated with ultraviolet ozone cleaning for 20 min. The positive voltage and ground lines of a high voltage source (HJPQ-30P1, Matsusada Precision) were connected to the stainless nozzle and an ITO layer sputtered on the glass substrate, respectively. By applying the high voltage, the F8BT solution was sprayed on the top of the ITO layer. All the processes were performed in a nitrogen atmosphere to avoid degeneration of F8BT. We fabricated two devices, called as devices A and B. The deposition times of devices A and B were 10 to 20 min, respectively. Finally, LiF (1 nm) and Al (100 nm) were thermally evaporated successively to realize efficient carrier transport between a metal cathode and an adjacent organic photoconductive layer (F8BT) [15]. The deposition rates of LiF and Al were 0.05 and 0.3 nm/s as determined using a quartz crystal monitor, respectively.

To investigate the optimized deposition condition of the F8BT layer, we measured the photoluminescence (PL) quantum efficiency of organic neat films using a luminance quantum yield measurement system (QEMS-2000, Systems Engineering Inc.) with the integrated sphere. The center wavelength of excited light was 400 nm. Ultraviolet-visible (UV-Vis) light absorption spectra of organic neat films were recorded with a UV-Vis spectrophotometer (V-550, JASCO). Monochromic light was irradiated through a glass substrate, and the transport light intensity was measured. Then, the thickness was measured using the surface profile meter (Dektak3, ULVAC).

Photocurrent and dark current-voltage characteristics of devices were measured by a DC voltage current source/monitor (6241A, ADCMT). The center wavelength of irradiated light was 470 nm, and the dark current was also measured without irradiating light. The external quantum efficiency (EQE), defined as the number of output electrons divided by the total number of irradiated photons, was estimated from the measured photocurrent and the optical intensity of irradiated light as follows,

$$\eta = \frac{I_p}{e} / \frac{P}{h\nu} \tag{1}$$

where I_p, e, P, h, and ν are the measured photocurrent, the elemental charge, the irradiated optical intensity, Planck's constant, and the frequency of vibration of irradiated light, respectively.

3. Results and discussion

Figure 2 shows PL quantum efficiencies of F8BT neat films, which were fabricated by applying different voltages ranged from 5 to 10 kV. The distance from the stainless nozzle to a glass substrate was 8 cm, and the deposition time was fixed at 60 min. The PL quantum efficiency was calculated as the PL intensity divided by the decrease in the excited light intensity by inserting the sample into the integrated sphere. At a lower applied voltage below 8 kV, the PL quantum efficiency showed little change by changing the applied voltage. The PL quantum efficiency of spin-coated F8BT neat film was 42 %, and the F8BT neat film by the ESD method was approximately same as the spin-coated sample. On the contrary, the PL quantum efficiency decreased with decreasing the applied voltage above 9 kV. The most likely cause of this result is that the molecular structure of F8BT is changed by applying the high voltage above 9 kV, resulting in the low PL quantum efficiency (see Fig.

2). On the other word, this result indicates that we can realize the F8BT neat film without degeneration of molecular structure less than 8 kV by the ESD method.

Thicknesses of F8BT neat films are also shown in Fig. 2. The measured thicknesses were 900, 1080, 1340, 500, and 600 nm corresponding to the applied voltage of 6, 7, 8, 9, and 10 kV, respectively. Generally, the amount of sprayed solution increases with the increase in applied voltage [16, 17]. Therefore, we observed that increasing the voltage tended to initially increase the thickness in the case of the low applied voltage. However, as the voltage increase further, the thickness decreased at the deposition condition of above 9 kV, as shown in Fig. 2, owing to the degeneration of molecular structure of F8BT.

Figure 3 shows the absorption spectra of the F8BT neat films, which were fabricated by an electrospray method and a conventional spin-coating method, respectively. In the case of the electrospray deposition, there was a peak in the absorption spectrum at 474 nm, and it remained low in both cases of wavelength regions below 400 nm and above 500 nm. The spectral width of the electrosprayed film was larger than that of the spin-coated film. This is because that the molecular weight and orientation of F8BT were varied widely by applying the high voltage during the electrospray deposition. Anyhow, this result indicates that this organic photoconductive device had sensitivity in only the blue wavelength region with little response in the green and red wavelength regions.

The thicknesses of the F8BT layers of devices A and B were 30 and 60 nm corresponding to the deposition times of 10 and 20 min, respectively. The applied voltage was fixed at 5 kV, and the distance from the stainless nozzle to the glass substrate was 10 cm to reduce the fluctuation of thickness. The measured thicknesses yielded the deposition rate of 3 nm/min, which is lower than that of the F8BT neat film (see Fig. 2). Since the longer distance between the stainless nozzle and the glass substrate causes the spread of F8BT solution over the glass substrate, the deposition rate was considered to be decreased.

The current density-electric field characteristics of the fabricated devices are summarized in Fig. 4. The applied electric field was calculated as the applied voltage divided by the thickness of the organic layer. The optical intensities of irradiated light were changed as 1.7, 2.6, and 3.3 mW/cm^2, respectively. The spin-coated device was also measured at the irradiated light intensity of 2.9 mW/cm^2. As clearly shown in Fig. 4, the current density was

increased with increasing the electric field. The carrier diffusion length for most organic materials is below 20 nm [18], which is less than the thickness of an organic photoconductive layer. In addition, the carrier mobility of organic materials is increased as the applied electric field increases [19]. Therefore, a higher electric field causes the dissociated hole-electron pairs in an organic photoconductive material with low recombination probability, resulting in higher EQE, as shown in Fig. 4. The current density of spin-coated device was higher than that of the device fabricated ESD method. This is because that the ESD-based F8BT layer has low density compared to that fabricated by the spin-coat process.

Figure 5 summarized the influence of the electric field on EQEs, which was calculated by the measurement result in Fig. 4. The EQEs of all the devices increased constantly with increasing the electric field, and the maximum quantum efficiencies were 0.22 % for both devices. The EQE of device B was approximately twice compared to that of device A at the same electric field. Since the carrier mobility of F8BT is high [14], the photo excited carrier efficiently move to the electrode sides. Therefore, the EQEs of both devices were independent of the thickness of F8BT, resulting in the same EQE-voltage characteristics. The EQE of reference device, which was fabricated by the spin-coat process, was higher than those of devices A and B. The multilayer stricture can be fabricated by the ESD method, therefore, the most important result of our experiment was the finding of optimized electrospray condition less than 8 kV, and the high PL quantum yield as same as the spin-coated sample was achieved by the ESD method.

Though the high applied voltage is considered to cause the molecular structure of F8BT, resulting in the low performance, it is noted that the ESD-based F8BT neat film shows the same PL quantum yield compared the spin-coated film by optimizing the deposition condition. In addition, the multilayer structure can be fabricated by the ESD method, therefore, the further improvement in the device characteristics will be realized in near future.

4. Conclusion

We demonstrated the ESD-based OPD with the external quantum efficiency of 0.22 %. Though the higher applied voltage is required for the fast deposition, we found that the molecular structure of F8BT was broken by applying the high voltage. The optimized voltage was less than 8 kV in the

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case of F8BT. The external quantum efficiency of device is not high enough for practical applications. However, this result suggests that the organic photoconductive device sensitive to blue lights was achieved using F8BT as a photoconductive layer by the ESD method. Further improvement will be realized by optimizing the fabrication process and the device structure.

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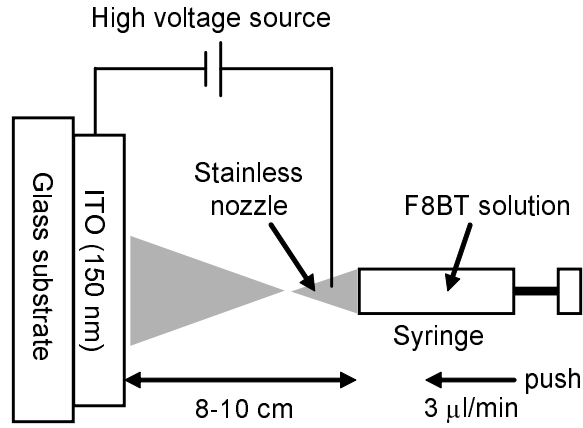
Figure captions

Figure 1 A schematic configuration of the experimental setup of the electrospray deposition method.

Figure 2 The influence of the applied voltage to the stainless nozzle on the PL quantum yield and the thickness of the organic neat film. The center wavelength of excited light for the PL quantum yield measurement was 400 nm.

Figure 3 Absorption spectra of F8BT neat films, which were fabricated by electrospray and spin-coating processes, respectively.

Figure 4 Current density-voltage characteristics for (a) device A and (b) device B.

Figure 5 The influence of the electric field on the EQEs of devices A and B. The deposition times of devices A and B were 10 and 20 min, respectively.

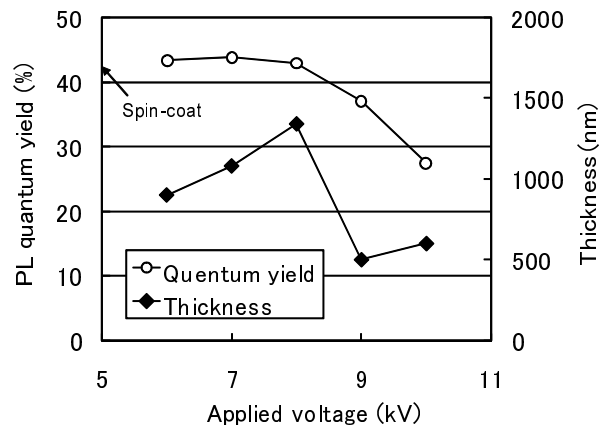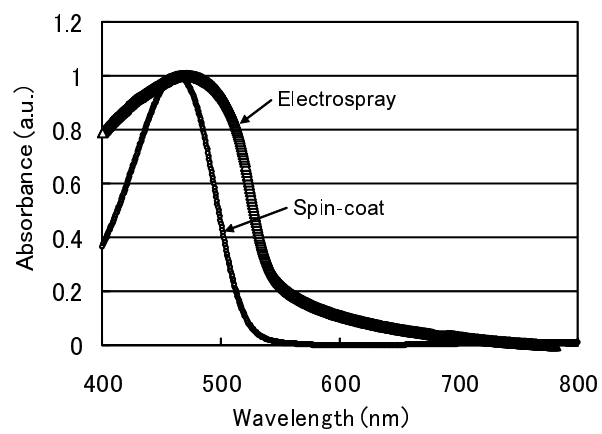Figure 1: A schematic configuration of the experimental setup of the electrospray deposition method.

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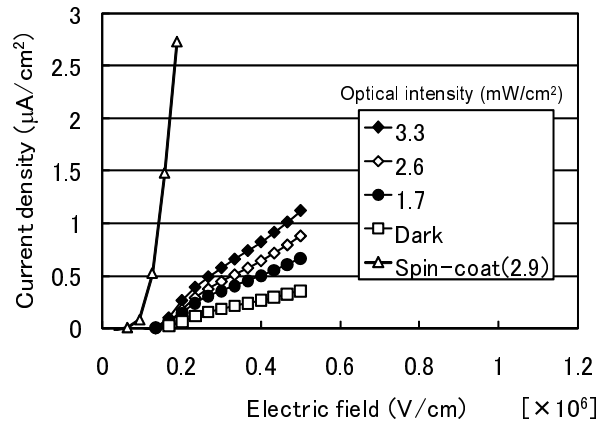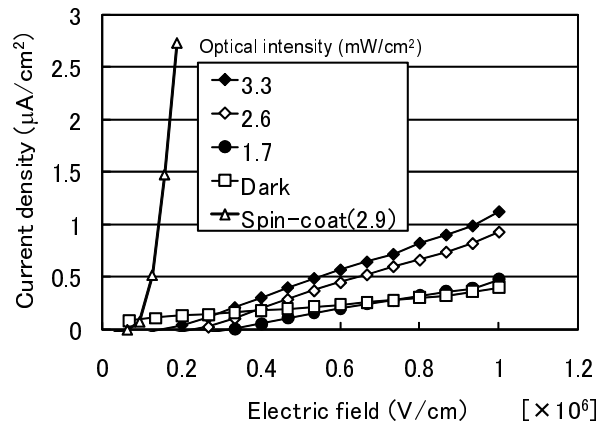
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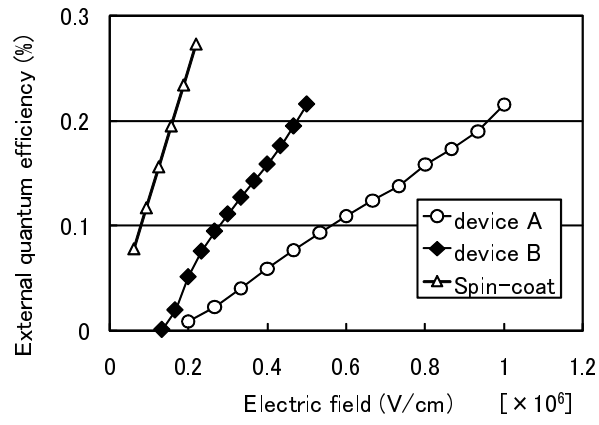Figure 4: Current density-voltage characteristics for (a) device A and (b) device B.

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