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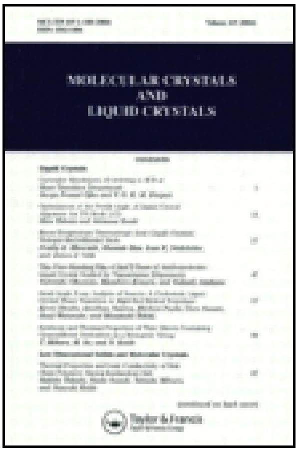

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Intensity Sensitive Organic Photodiodes Patterned by Inkjet Method

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Intensity Sensitive Organic Photodiodes Patterned by Inkjet Method

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In this work, intensity sensitive organic photodiodes were made based on the drop-on-demand piezoelectric inkjet printing of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) blend on the ITO substrates. Inkjet conditions for printing the P3HT:PCBM/chlorobenzene solution were studied and the influences of concentration and inkjet parameters such as pulse voltage and the method of stacking spots were systematically investigated under the goal of optimizing the morphology and uniformity of P3HT:PCBM spots on various kinds of ITO substrates. P3HT:PCBM films in any shape and size were prepared by overlapping the neighboring spots and bulk heterojunctions were fabricated after the deposition of a thin Al film as cathode on their top. Under the excitation of a 532 nm pulse laser source, the open-circuit voltage (Voc) between the ITO and Al electrodes could be detected. Intensity sensitive photo-diodes were obtained with a quantum yield of ∼0.35% and the time constant was estimated to be ∼1.0 μs. Ways for further improvement on the performance of the photo-diodes were also suggested.

Keywords Inkjet; morphology; open-circuit voltage; photodiode

1. Introduction

During the past several years, inkjet printing has attracted extensive research attention as a direct patterning technique for the cost-effective fabrication of organic electronic devices such as organic light-emitting diodes, organic field-effect transistors, organic solar cells, and radiofrequency identification devices [1–3]. As compared with other film deposition techniques for organic chemicals, the inkjet method was highly preferable owing to its versatility, miniaturization, and high-precision [4–7]. On the basis of this knowledge, it was suggested that drop-on-demand inkjet printing may be the most suitable technical pathway for the fabrication of photodiodes on the disposable integrated flowcytometry chip, as proposed in our previous reports [8–10]. And it should also be noted that for the fabrication of this kind of disposable and miniaturized organic photodiodes on the flowcytometry chips, other techniques

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such as spin-coating was not applicable because of the complicated structures of the flowcytometry chips, risk of contamination, and the infeasibility to integrate various kinds of photodiodes, for instance, photodiodes in various spectral region on one single chip. Under this aim, several kinds of wavelength sensitive organic photodiodes in the visible region have been developed by the inkjet printing technique recently, as one of the latest application of inkjet method in our group, which we suggest, may monitor the laser output from the tunable solid-state dye laser waveguides or the laser induced fluorescence from the micro fluid channel on the integrated cytometry chips [9,10]. However, the quantum efficiency of this kind of wavelength sensitive organic photo-diodes base the J-type aggregates of cyanine dyes were very low, merely on the level of 10^{-6}. Moreover, on the integrated laser chips, intensity sensitive photodiodes were also needed.

As considering the suitable materials for the intensity sensitive photodiodes printed by inkjet method, blended P3HT and PCBM was suggested to be one of the best candidates due to the high performance of the nanostructured polymer solar cells based on the P3HT:PCBM system in terms of efficiency and long-term stability [11–13]. The 3 dimensional nanoscale networks formed by the P3HT and PCBM accounted for the energy conversion efficiency of the bulk heterojunction increased significantly. So, in this work, the fabrication of a kind of intensity sensitive organic photodiodes patterned by a drop-on-demand piezoelectric inkjet system were introduced, which might also be used as a miniaturized photodetector on the proposed integrated flowcytometry chips, and ways to optimize the morphology and uniformity of the inkjet printed films were discussed. Further improvement on the performance of the intensity sensitive organic photodiodes was expected.

2. Experimental Details

In this work, the P3HT (Merck Lisicon SP001 EF430602) and PCBM (Nanom Spectra E100) were used as received. First, the P3HT and PCBM were dissolved into chlorobenzene at the fixed ratio of 30 mg: 21 mg. The concentration of P3HT:PCBM blend in the final solutions were mentioned in the following discussion. After ultrasonic treatment to prompt the dissolution and uniformity, the P3HT:PCBM/chlorobenzene solutions were filtered (Whatman filter PTFE, 0.2 μm) before use.

The fabrication process of the bulk heterojunction photodiodes was shown in Figure 1. A piezoelectric inkjet system (Microjet IJK-200 s) with a nozzle size of 70 μm was used in this work. ITO coated polyethylene terephthalate (PET) films were used as the substrates, which has been etched by 10% of aqua regia (120 s) with masks to obtain designed pattern. To avoid the environmental turbulence interference on the droplet, the distance between the jet nozzle and ITO substrate was kept to less than 1 mm. Large-area films in the designed shape or patterns were made by overlapping the neighboring spots delicately. At last, a thin Al layer was vapor deposited on the top of the P3HT:PCBM layers after the inkjet printing (ULAC, 6×10^{-3} Pa). The Voc between the cathode and anode of inkjet printed photodiodes was measured by oscilloscope (Tektronix TDS 3032) under the excitation of a passively-Q-switched and frequency-doubled Nd:YAG laser (0.5 ns, 532 nm) with the maximum pump energy and repetition rate at 30 μJ/pulse and 500 Hz, respectively. The absorption spectrum of the inkjet printed films was measured with an ultraviolet-visible-near-infrared (UV-vis-NIR) absorption spectrometer (Shimadzu UV-160A).

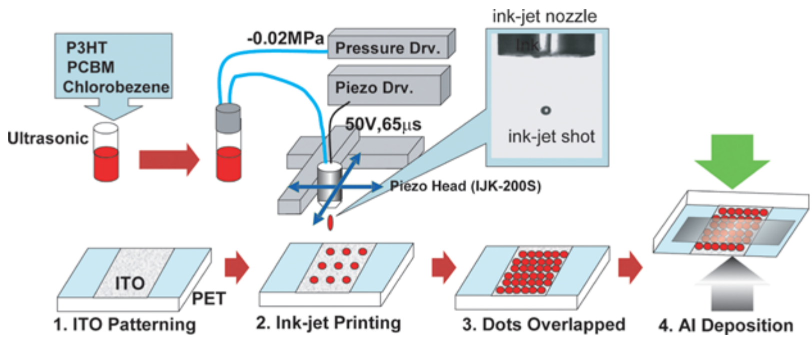

Figure 1. Fabrication process of photo-diodes by inkjet printing.

3. Results and Discussions

As the active layer of the photovoltaic devices, the absorption spectrum of the inkjet printed P3HT:PCBM film printed by the P3HT:PCBM/chlorobenzene solution at the concentration of 2.32 wt% was measured, as shown in Figure 2. Broad absorption band from the ultraviolet to until 650 nm could be observed, indicating the wide response range of the photodiodes based on P3HT:PCBM. With the ITO as the anode, while the thin Al layer deposited on the top of P3HT:PCBM films as the cathode, the photodiode behaved as a bulk heterojunction. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of each chemical and workfunctions of the electrodes were also summarized in Figure 3.

As the ink materials for printing, the viscosity of the P3HT:PCBM/chlorobenzene solutions at various concentration and their influence on the output droplets from the inkjet nozzle and spots on the ITO substrates were investigated. The images of P3HT:PCBM spots printed by the concentration of 1.16, 2.31 and 3.46 wt% were shown in Figure 4(a), (b) and (c), respectively. It was found that at

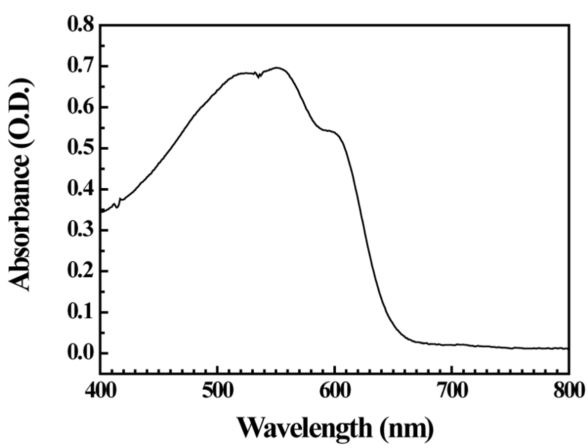

Figure 2. Absorption spectrum of inkjet printed P3HT:PCBM film at the concentration of 2.31 wt%.

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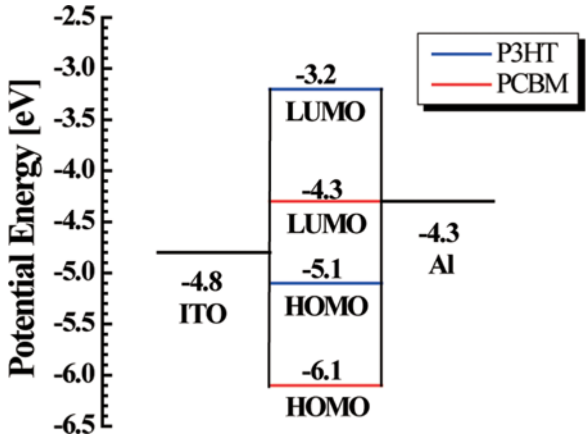

Figure 3. The HOMO and LUMO energy levels, and the workfunctions of electrodes of the P3HT:PCBM photo-diodes.

the lower concentration, for instance, 0.51 or 1.16 wt%, clear coffee-ring structures were observed. At the same inkjet condition, a wider edge of ~80 nm and a smaller spot size of 371.3 μm in diameter were observed at the concentration of 3.46 wt%, in comparison with the 384.3 μm of spot size in the case of 2.31 wt%, indicating the

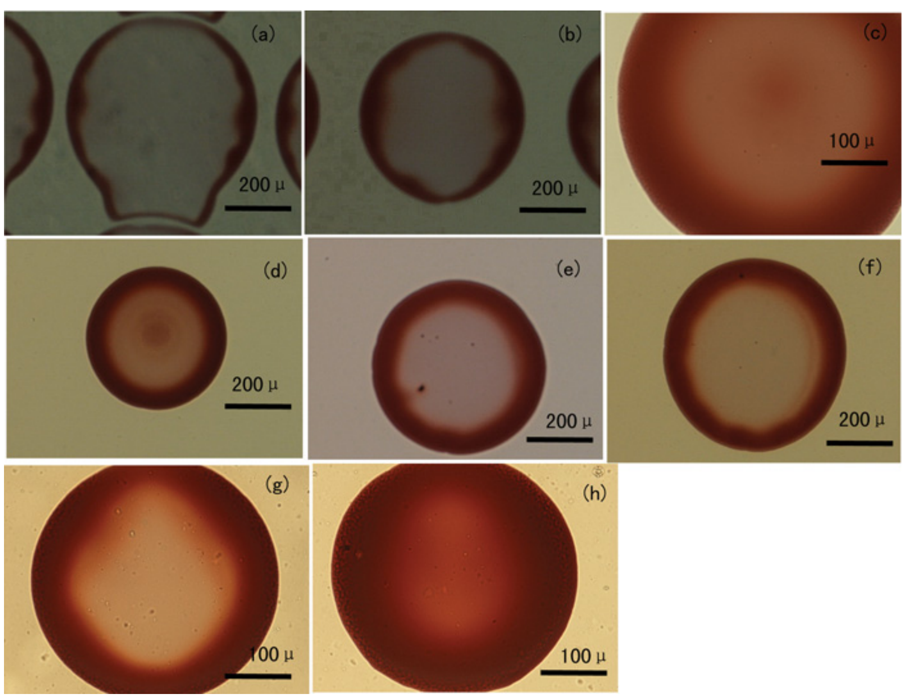

Figure 4. Image of inkjet printed P3HT:PCBM spots at various concentration and inkjet conditions: (a) 1.16 wt%; (b) 2.31 wt%; (c) 3.46 wt%; (d) 65 V (3.46 wt%); (e) 70 V (3.46 wt%); (f) 75 V (3.46 wt%); (g) 1-layer (3.0 wt%); (h) 2-layers (3.0 wt%).

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better morphology and uniformity at higher concentration. At the concentration of 4.61 wt%, the inkjet output might be ceased easily, due to the high viscosity of the solution.

So, at the fixed concentration of 3.46 wt%, the influence of the inkjet conditions such as pulse voltage on the morphology of the P3HT:PCBM spots were studied, as shown in Figure 4(d), (e), and (f). It was found that at the pulse voltage of 65, 70 and 75 V, the diameter of the spots was 326.9, 403.4 and 441.6 µm, respectively. With the decrease of the pulse voltage, the size of the spots' edge increased from 66 µm at 75 V to 80 µm at 65 V. So, it could be suggested that better morphology could be obtained at lower pulse voltage, which might be due to the lower droplet speed at lower voltage, as shown in Figure 5. However, at the concentration of 3.46 wt%, the pulse voltage could only be adjusted in the range of 65~75 V, pulse voltage lower than 60 V might result in the instability and abrupt cease of the output droplet. In contrast, the pulse voltage in the case of 2.31 wt% could be tuned easily from 45 to 75 V, while the droplet speeds at different concentration were similar, as shown in Figure 5. In this work, it was found that by slightly decrease the concentration to 3.0 wt%, the pulse voltage could still be adjusted in the range of 50~75 V. So, 3.0 wt% was selected as the optimized concentration of P3HT:PCBM for inkjet printing.

For the further improvement on the morphology, stacking of the P3HT:PCBM spots were adopted. As shown in Figure 4(g) and (h), at the concentration of 3.0 wt% and 50 V of pulse voltage, the size of the 1-layer spot and 2-layers spot were 274.2 and 274.7 µm, respectively. There was almost no change on the spot size after stacking, while the morphology of the spot improved significantly after stacking while the thickness increased to about 100 nm.

So, based on the above optimization on the P3HT:PCBM spotted films, the bulk heterojunction photodiodes were made and the Voc between the electrodes was measured under the excitation of the 532 nm pulsed laser beam. Figure 6 showed the dependence of the Voc of the P3HT:PCBM photodiode based on a 3 ∗ 2 mm overlapped film on the input energy, which was composed by 12 ∗ 8 spots with the least

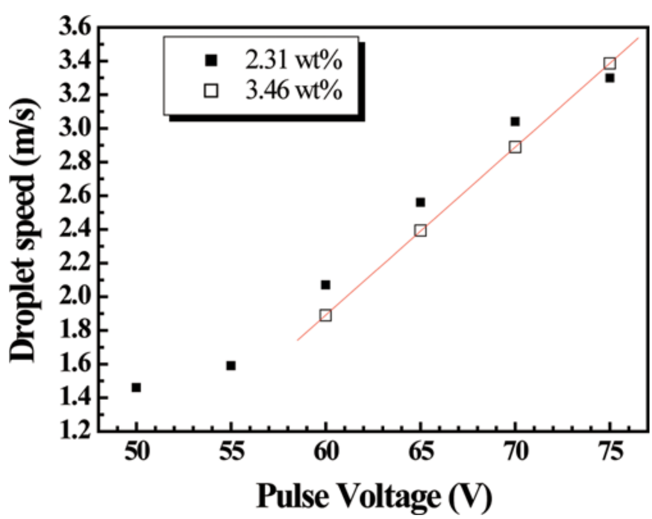

Figure 5. Dependence of droplet velocity on the pulse voltage at various concentrations.

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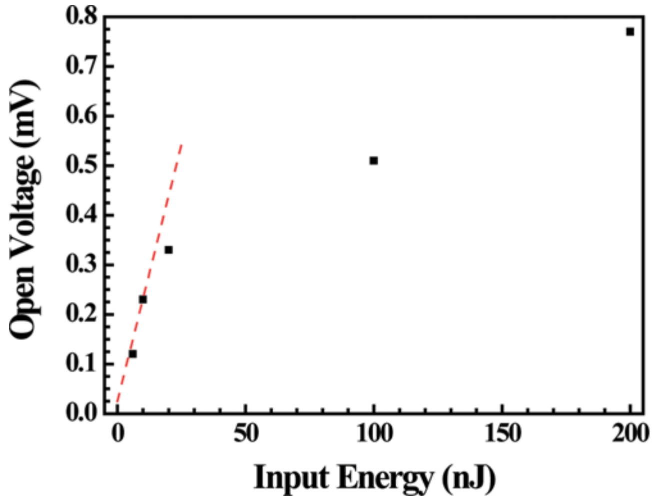

Figure 6. Dependence of Voc on the input excitation energy.

overlapping area. It could be found that at lower input density, the Voc increased almost linearly to the input energy. However, saturation was observed when the input energy was higher than 10 nJ, corresponding to 0.8 nJ/mm^2. At the input energy of 10 nJ, 0.23 mV of Voc was detected. According to the 200 kΩ resistance of the photodiode, 0.35% of quantum efficiency could be calculated. The time constant of the Voc was fitted to about 1 μs, as shown in Figure 7.

In comparison with the about 10^{-6} of quantum yield of the wavelength sensitive organic photodiodes based on cyanine dyes, the sensitivity of the photodiodes based on P3HT:PCBM was improved significantly. However, in contrast to the several percent of quantum yield of the organic solar cell, it was suggested that the performances of the P3HT:PCBM photodiodes could be further improved. For instance,

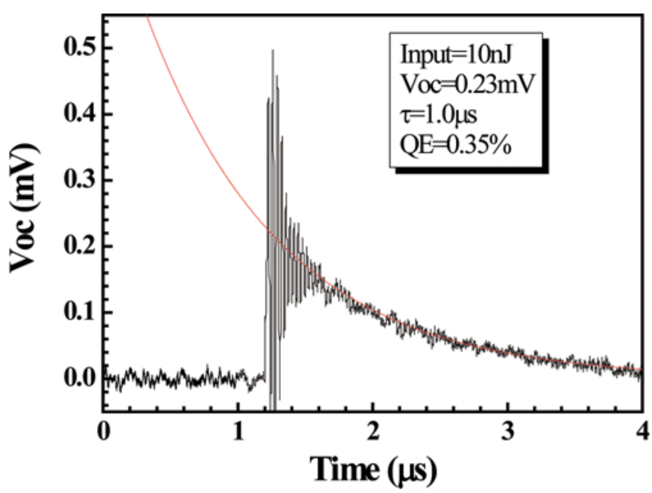

Figure 7. The waveform of the P3HT:PCBM photo-diode under the excitation of 10 nJ of laser pulses.

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in this work, the annealing was not applied in the fabrication process and the overlapping area of the films, which had much worse morphology compared with the single spot of P3HT:PCBM. As an ideal case, organic photodiodes based on the single spot of P3HT:PCBM were suggested to have more smooth morphology than the overlapped films and the time constant might be much shorter due to the smaller capacity resulted from the smaller film size. This work is now underway.

4. Conclusions

In summary, in this work, P3HT:PCBM films have been fabricated with a piezoelectric inkjet system and the influence of some key fabrication parameters including the blend concentration, and inkjet parameters are systematically investigated. Intensity sensitive organic photodiodes were made based on the bulk heterojunction of P3HT:PCBM. Under the excitation of 532 nm laser pulses, about 0.35% of quantum efficiency and 1 μs of time constant were obtained. Ways for the further improvement on the performance of the P3HT:PCBM photodiodes were also suggested.

Acknowledgment

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References

[1] Yoshioka, Y., & Jabbour, G. E. (2006). *Adv. Mater.*, *18*, 1307.
[2] Lim, J. A., Lee, W. H., Lee, H. S., Lee, J. H., Park, Y. D., & Cho, K. (2008). *Adv. Funct. Mater.*, *18*, 229.
[3] Hoth, C. N., Schilinsky, P., Choulis, S. A., & Brabec, C. J. (2008). *Nano Lett.*, *8*, 2806.
[4] Tekin, E., Holder, E., Kozodaev, D., & Schubert, U. S. (2007). *Adv. Funct. Mater.*, *17*, 277.
[5] Yoshioka, Y., Calvert, P. D., & Jabbour, G. E. (2005). *Macromol. Rapid Commun.*, *26*, 238.
[6] Yoshioka, Y., & Jabbour, G. E. (2006). *Synth. Met.*, *156*, 779.
[7] de Gans, B., Hoeppener, S., & Schubert, U. S. (2006). *Adv. Mater.*, *18*, 910.
[8] Oki, Y., Ogawa, Y., Yamashita, K., Miyazaki, M., & Maeda, M. (2007). *Mol. Cryst. & Liq. Cryst.*, *463*, 131.
[9] Yang, Y., Imaoka, H., Yamashita, K., Kamogawa, N., Watanabe, H., Miyazaki, M., & Oki, Y. (2010). *Jpn. J. Appl. Phys.*, *49*, 010204.
[10] Yang, Y., Omi, S., Goto, R., Yahiro, M., Era, M., Watanabe, H., & Oki, Y. *Org. Electron*, submitted.
[11] van Bavel, S. S., Sourty, E., de With, G., & Loos, J. (2009). *Nano Lett.*, *9*, 507.
[12] Marsh, R. A., Hodgkiss, J. M., Seifried, S. A., & Friend, R. H. (2010). *Nano Lett.*, *10*, 923.
[13] Lin, C., Lin, E. Y., & Tsai, F. Y. (2010). *Adv. Funct. Mater.*, *20*, 1.

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