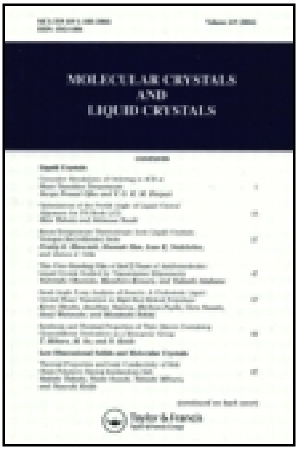

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Self-Aligned Multifunction Diodes Using Ink-Jet Printing Method

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We have investigated self-aligned multifunction diodes (SA-MFDs) using an ink-jet printing (IJP) method. The MFD is defined as the diode exhibits functions of emission and photo-sensing. A special organic material of pyrazoline derivative was dissolved and a solution was printed on a transparent indium-zinc-oxide (IZO) coated glass substrate covered with an insulating poly-methylmethacrylate (PMMA) layer. The PMMA was dissolved in a solvent. Then, organic materials were formed at the same position as that of the ink-jet-printed region, that is, SA-MFD was realized. For light emitting operation, a luminance obtained was $810\,cd/m^2$ *under forward-biased condition. For photo-sensing operation under xenon lamp illumination, a photocurrent density was* $0.84\,\mu A/cm^2$ *and the ratio of photoconductivity to dark conductivity was* 10^2 *under reverse-biased condition.*

Keywords: ink-jet printing method; organic electroluminescent device; organic photodiode; self-alignment technology

1. INTRODUCTION

Recently organic electronic devices such as, high-efficiency organic light-emitting diodes (OLEDs) [1,2] and organic photodiodes (OPDs)

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have been actively studied [3,4]. Stacked organic device structures have also been reported [5,6]. In our previous study, we have investigated multifunction diodes (MFDs) with both emission and photodetection function using a special organic material of pyrazoline derivative. We have also demonstrated prototype 16×16 MFD panel using evaporation technique and shadow mask [7]. This evaporation method will be limit its market due to lower resolution, mismatching of a back-plane and difficulty of large-size (over $1\,m^2$) panel fabrication. Therefore, the drop-on-demand system of the ink-jet printing (IJP) method has attracted much attention. For fabricating organic devices using the ink-jet printing method, a bank formation is commonly used to prevent shorting of the device. Shimoda *et al.* reported a prototype OLED fabricated using the IJP method [8]. Previously we proposed and investigated the self-aligned bank formation of OLEDs using the ink-jet printing method as a new fabrication process [9]. In this study, we have investigated self-aligned multifunction diodes (SA-MFDs) using the ink-jet printing method suitable for higher resolution, good relevancy for back-plane and suitability of larger area panel.

2. EXPERIMENT

Figure 1 shows process steps in the self-alignment device fabrication. An insulating film was formed on a glass substrate with an anode of an indium zinc oxide (IZO)-coated glass substrate. It is necessary for this insulating material to be soluble in an organic solvent and to exhibit good insulating characteristics. The ink dissolved with organic materials was jetted on the insulating film from IJP head. The solvent of ink dissolved the insulator, and the organic materials contacted to the anode (IZO) and an active layer was formed alternately, that is, self-alignment fabrication was carried out. Finally, a cathode layer was evaporated onto the organic layer.

In this study, we used a pyrazoline derivative 4-[2-[5-[4-(diethylamino)phenyl]-4,5-dihydro-1-phenyl-1*H*-pyrazol-3-yl]-ethenyl]-*N*,*N*-diethylaniline (PPR) for multifunction material. PPR was known as hole transport material [10]. Figure 2 shows organic materials under study. Poly(methyl methacrylate) (PMMA) was used as an insulating materials. For ink-jet printed materials, small molecules of the PPR with hole transport material *N,N*′-bis(3-methylphenyl)-(1,1′-biphenyl) 4,4′-diamine (TPD) was used. The mixing ratio of organic materials was PPR:TPD = 90:10. The solvent used was chloroform and the concentration of the solution was 1 wt%.

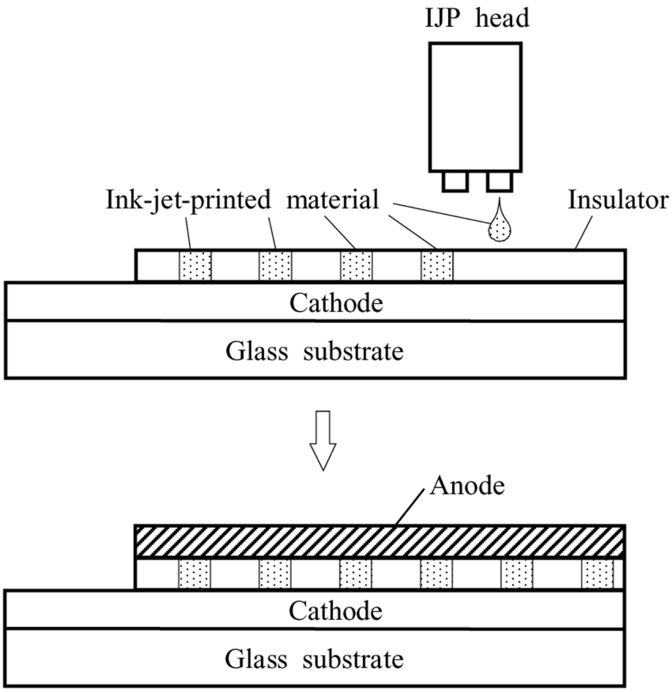

FIGURE 1 Process steps in self-alignement process.

The details of the stacking structure of organic materials and the fabrication process are as follows: First, IZO-coated glass substrate was patterned and cleaned. Second, after ultraviolet ozone treatment,

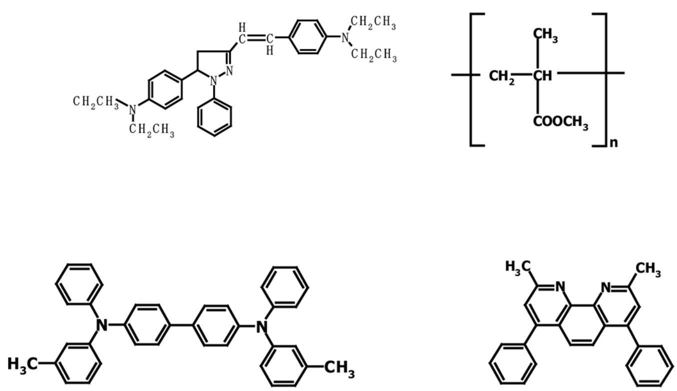

FIGURE 2 Molecular structure of organic materials under study.

the insulator (PMMA: 80 nm) was spin-coated on the IZO-coated glass substrate. Next, the organic mixture was printed on the substrate. After IJP, the substrate was then baked at 60°C for an hour in the vacuum ($\approx 10^{-5}$ Torr).

The description of the ink-jet printing apparatus (Brother Industries Ltd.) is as follows: ink-jet head, made of ceramics: number of nozzles 128; driving method, piezodriving; nozzle diameter, 40 μm; resolution, 150 dots per inch; and volume of droplet, 50 pℓ. The number of ejected droplets was 100 shot/s, the velocity of the substrate was 25 mm/s, and the pitch of the printed dots was 170 μm. The diameter of each organic region was 100 μm.

Finally, a hole-blocking layer of bathocuproine (BCP: 20 nm) and stacking layer of cathode LiF (1 nm)/Al (70 nm) were evaporated. The structure of the MFD dot was IZO/ink-jet printed materials/BCP BCP (20 nm)/LiF (1 nm)/Al (70 nm).

Current density versus voltage (*J*-*V*) characteristic was measured using a semiconductor parameter analyzer (HP, 4155B). A light source for measuring OPD characteristics was a xenon lamp (33 mW/cm^2) and irradiated to organic layer through the glass substrate. Emission intensity was also measured using a luminance meter (Topcon BM-3). For comparison, the spin-coated device was also fabricated without the insulator, and the structures were IZO/PPR + TPD [90:10] (100 nm)/BCP (20 nm)/LiF (1 nm)/Al (70 nm). The device area of device was 4 mm^2.

3. RESULTS AND DISCUSSION

Figure 3 shows an optical micrograph of the emission pattern. Clear emission was obtained, and a smoother surface was obtained. The periphery of the dot was thicker than the center of the dot. Emission was not observed at the periphery of the dot because the periphery of the organic layer was thick possibly due to drying condition, as already discussed in Ref. [9].

Figure 4 shows the current density (J) versus voltage (V) characteristics and luminance (L) versus voltage (V) characteristics. Reference device is spin-coated device. In the reference device, a maximum luminance ($L_{\max}$) of 4134 cd/m^2 ($J = 388$ mA/cm^2) was obtained. In the IJP device, $L_{\max}$ was 810 cd/m^2 ($J = 51$ mA/cm^2), which value was inferior to those of reference device, because of series resistance of the device. However, current efficiency of IJP device was identical to those of reference device. In reference and IJP device, η of 1.40 and 1.59 at $J = 30$ mA/cm^2, respectively. By optimizing a phase separation

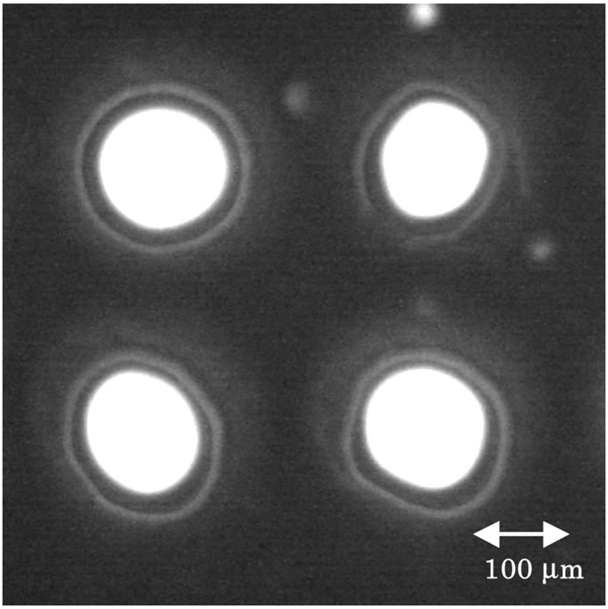

FIGURE 3 The optical micrograph of the emission pattern.

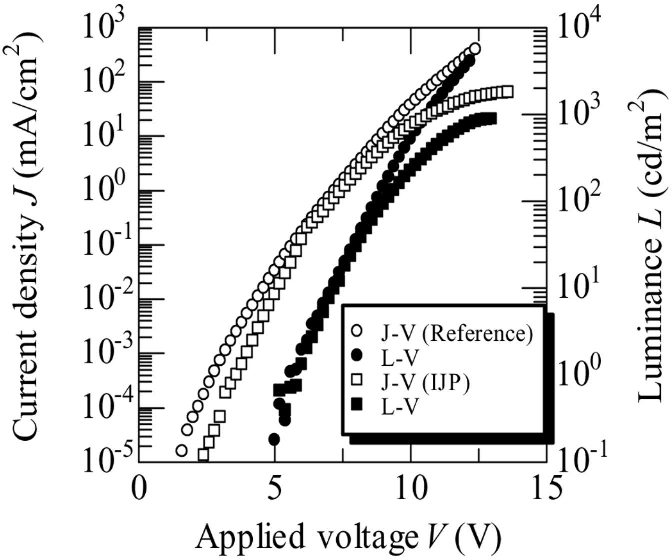

FIGURE 4 Current density and luminance versus voltage characteristics of OLED.

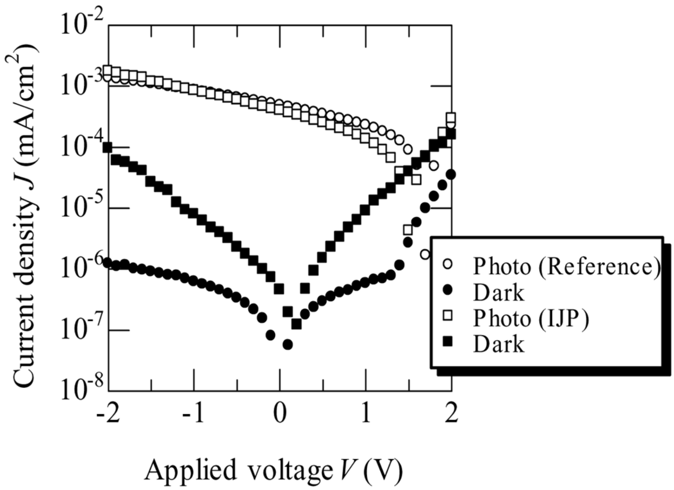

FIGURE 5 Current density versus voltage characteristics of OPD.

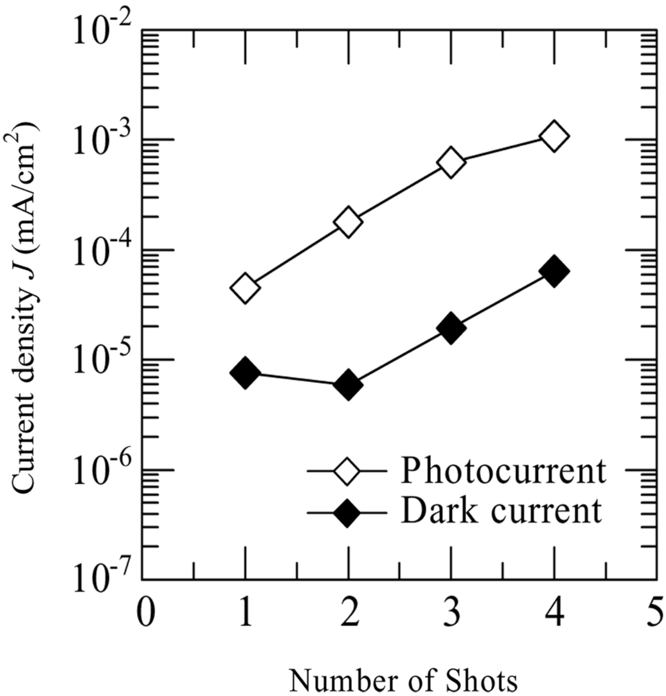

FIGURE 6 Photo and dark current of OPD varied with number of ink-jet printed shots.

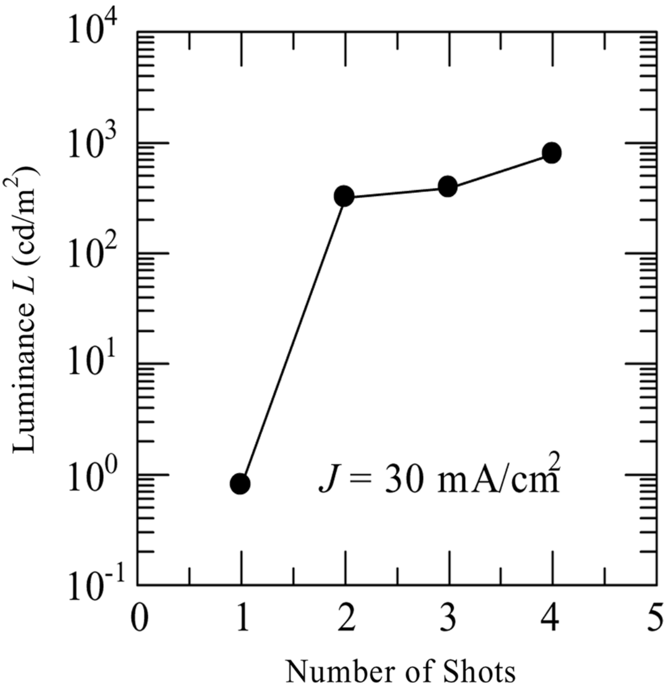

FIGURE 7 Variation of the luminance, number of ink-jet printed shots as a parameter.

condition between ink-jet printed material and insulator, the device performance of IJP device will be improved due to reduction of series resistance. Figure 5 shows J-V characteristics of OPD. Open circles, squares and triangles and filled circles, squares and triangles show J-V characteristics under illumination and dark conditions, respectively. In the reference device, J_{photo} and the ratio of photoconductivity to dark conductivity σ_{R} were $0.84\,\mu\mathrm{A/cm^2}$ and 1.3×10^3, respectively, at the voltage of $-1\,\mathrm{V}$. In IJP device, J_{photo} and σ_{R} were $0.84\,\mu\mathrm{A/cm^2}$ 2 and 10^2, at the voltage of $-1\,\mathrm{V}$. For sensing device operation, higher resistivity of the insulator was important to reduce the dark current of OPD characteristics. In IJP device, the dark current was higher than that of the reference device, because of the leakage current in PMMA layer and thinness of the middle edge of emission dot. For decreasing the dark current, optimization of insulating layer and ink-jet printing condition have to be optimized.

Figure 6 shows the photo and dark current of OPD varied with number of ink-jet printed shots (N). The number of shots was varied from one to four times. Photocurrent was increased with increase of number of shots. However, dark current was further increased with increase of number of shots. These results that a fraction of PPR molecule and ratio of thin area were simultaneously suggested increase in the dots. Figure 7 shows variation of luminance with varied number of ink-jet printed shots. Luminance was improved greatly by increasing the number of ink-jet printed shots. It is considered that this mixing ratio of PMMA, PPR and TPD is optimized, by changing the number of ink-jet printed shots. In the one-shot device, little emission was observed because of insufficient through-hole formation between the anode and organic materials. Although the sensing characteristics became worse, the luminance value was increased by increasing the number of shots.

4. CONCLUSION

We had investigated the self-aligned MFDs using the IJP method. Using the special material of pyrazoline derivative, the luminance obtained was 810 cd/m^2 under forward-biased condition. The photocurrent density was 0.84 $\mu A/cm^2$ and the ratio of photoconductivity to dark conductivity was 10^2 under reverse-biased condition. In this way, we will be expected for higher resolution active-matrix panel with the merit of simple fabrication.

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