On-demand patterning for organic light-emitting diodes using laser irradiation

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We investigated the patterning of organic light-emitting diodes using a blue laser irradiation after making uniform device. Laser patterning was carried out in the atmosphere after the organic layer was deposited. The laser irradiation part was quenched, and it was shown that optional patterning was possible. This technique is expected as a fabrication technique for on-demand pattern emission.

Keywords: organic light-emitting diodes, laser patterning, on-demand patterning

Organic light-emitting diodes (OLEDs) ^{1,2} have attracted much interest, such as self-emission, high brightness, high contrast, and so on. ³⁻⁵ They have practically used in various applications such as lighting and a display for smartphones and televisions. For various device applications, a variety of simple patterning techniques are required. However, this is difficult with conventional mask patterning. This is because the cost of mask preparation could be large for various requirements, deterioration of the mask, and the like. Free patterning is required without photomasks or shadow masks. Inkjet printing method is being studied as one of the manufacturing methods to satisfy this requirement. Inkjet printing patterning methods such as dye doping, ⁶ charge injection layer patterning, ⁷ and self-alignment ⁸⁻¹² are being studied. The inkjet printing method has problems in the process of ink adjustment and drying. It has been studied as a patterning technology using light such as photo-bleaching, ^{13,14} photo-reaction ^{15,16} and color tuning ^{17,18}.

In this research, we have studied of patterned emission in OLEDs using photo-reaction of the organic semiconductors without the conventional mask. The patterned OLEDs were evaluated the characteristics of emission.

5,6,11,12-tetraphenyltetracene (rubrene) was used as an emission material. Rubrene is known to form endoperoxide by photo irradiation (Fig. S1). ¹⁹⁻²³ It has also been reported that rubrene functions as a light-emitting layer even in an extremely thin film. ²⁴⁻²⁷ Indium-tin-oxide (ITO) coated glass substrates were cleaned using ultrasonication and UV-ozone treatment. N,N'-di-1-naphthyl-N,N'-diphenylbenzidine (α -NPD) was used as a hole transport layer (70 nm), rubrene (1 nm) and bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy) aluminum (BALq) was used as an electron transport layer (30 nm) (Fig. S2). All layers were formed on the ITO substrate by vacuum evaporation. Subsequently, a blue laser (wavelength of 445 nm) was irradiated from the organic layer side in the atmosphere. The photo-patterning was performed using a FABOOL Laser Mini (SmartDIYs), which was x-y scannable and could be adjusted for the output power by pulse width modulation. The maximum output

Figure 1. Fabrication process and device structure.

power of the laser was 1.6W. In this study, it was used with maximum power continuous light to avoid discontinuous laser irradiation. After patterning, LiF (1 nm)/Al (70 nm) stack was formed as cathodes in vacuum. The device area was 2×2 mm². Figure 1 shows the fabrication and patterning processes. Current density and luminance versus applied voltage characteristics of devices were measured using a semiconductor parameter analyzer (B1500A, Keysight Technologies) and a luminance meter (BM-9, Topcon). The emission spectra were measured using an optical fiber spectrometer (Avaspec-UV/Vis/NIR, Avantes). Absorption spectra of the thin films were measured using an UV/VIS optical spectrometer (UV-1650PC, Shimadzu).

Figure 2 shows the absorption spectra of the materials used. The absorption coefficients of rubrene, α -NPD and BALq at 445 nm were 18,800, 2,600 and 1,900 cm⁻¹, respectively. Absorption coefficient at the laser wavelength of 445 nm is extremely high for rubrene, and the photo-reaction by laser irradiation can be expected. Figure 3 shows an example of the decrease in PL intensity of the rubrene after

Figure 2. Absorption coefficient of rubrene, α -NPD, and BALq thin films. The dash line is the wavelength of the blue laser at 445 nm.

Figure 3. Photoluminescent spectra of rubrene thin films before and after laser irradiation.

laser irradiation. It is indicated that the light degradation of the rubrene could be generated by the laser beam irradiation in the atmosphere.

The light emitting region was patterned by patterning the entire substrate. Figure 4 shows an emission photograph of device patterned at scanning speeds of 1,000, 5,000, and 8,000 mm/min. The grid pattern was successfully formed. The clarity of the pattern depended on the scanning speed. The line widened due to excessive light irradiation at slow scanning speeds (Fig. S3). In contrast, the pattern width at fast scanning speed was unclear and apparently widely. Many dark spots with the patterning devices were attributed to the contamination on the organic layers because the organic layers were exposed to the air, which is not a clean room, during the laser irradiation.

Figure 5 shows the characteristics of the device with and without patterning. No degradation of characteristics due to patterning was observed. No leakage current due to laser

Figure 4. Emission images of (a) pristine device and laser patterned devices with scanning speed of (b) 8,000, (c) 5,000, and (d) 1,000 mm/min.

Figure 5. Luminance versus applied voltage characteristics of the devices with and without patterning at scanning speed of 1,000, 5,000, and 8,000 mm/min.

irradiation was observed. This indicates that laser ablation does not occur, a photo-reaction occurs, and the altered material remains in place. If ablation occurs, the organic layer of the laser irradiation area disappears and a short occurs between the electrodes. The luminance values decreased with slow scanning speed because the luminance measurement area ($\phi 1.5\text{--}2.0$ mm) was almost the same as the device area, namely, the clear pattern led to decrease the emitting area. Other typical electrical characteristics are shown in Fig. S4.

Photo-oxidation mainly occurred in rubrene layer by light irradiation, and no light emission occurs in the light-irradiated area. However, the PL spectrum of the device changed by the laser irradiation and the spectral changes were from not only rubrene but also α -NPD (Fig. S5). In contrast, the pattern emission was also obtained in a device consisting of α -NPD/BAlq containing no rubrene since α -NPD has been known as the emitting material (Figs. S6 and S7).²⁸ α -NPD might also have the reduction of the carrier transport²⁹ and the photo-degradation³⁰ due to light irradiation. The decline of carrier transport properties led to a reduction in carrier recombination efficiency in the emitting layer, resulting in no light emission.

Pattern emission of OLED by laser irradiation was investigated. Though the degradation of the device characteristics was confirmed depending on the irradiation quantity of the laser, the characteristics equivalent to no laser irradiation were obtained under the condition of the appropriate laser irradiation quantity. This pattern was probably due to the photo-degradation and the reduction of the carrier transport. However, no significant degradation of the device was observed and the patterning process in this work may be expected to apply under a little oxygen, i.e., in a vacuum chamber or glove box. This method can be used as a wide range of on-demand patterning methods.

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1 Supporting Information is available on
 2 http://dx.doi.org/10.1246/cl.*****.

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