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Novel Patterning Techniques for Polymer Light-Emitting Devices: Optically Patternable Device and Maskless Dye Diffusion

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1. Introduction

Recently, several techniques to realize patterned emission from polymer light-emitting devices (PLEDs) have been reported. Bharathan and Yang successfully patterned emission from PLED by modulating the onset voltage of emission through the ink-jet printing of the hole-injection layer.[1] Another promising method is modulating the thickness of polymer layer by imprinting or molding. This method allows patterning in submicron scale.[2] Local photo-bleaching method was applied to patterning the emission color by Kido et al.[3] However, all of these methods modulate the surface of the emission layer directly, and must be applied before deposition of the metal electrode. Because no realistic methods for metal deposition on polymers except for vacuum evaporation are available at this stage, it seems hard to construct an "on-demand" system based on above methods to supply patterned PLEDs.

In this paper, we report a complete device whose emission can be optically patternable within several minutes. This was realized by using a quite thin metal film, which is semitransparent not only for light but also for atmospheric oxygen, as a cathode of the device.

On the other hand, it seems hard to realize a full-color display panel using PLEDs, because the most wet-processes are not compatible with local patterning of emission color, although they have great advantages in fabrication of a uniform film. Another technique reported in this paper is concerned with this problem. We have developed a novel method to pattern the emission color of PLEDs, maskless dye diffusion technique, and have successfully integrated RGB-devices on a glass substrate.

2. Optically Patternable Device

It is well known that conjugated polymers change their electronic, optical and other properties upon photo-irradiation in air. Yoshino et al reported photoinduced solubilization of the film of conducting polymer and proposed optical patterning of the film.[4] Photoinduced quenching of photoluminescence is also well studied by many researchers.[5] The main reason for these phenomena should be photo-oxidation of polymer main chain, resulting in scission of main chain as well as formation of quenching site for luminescence species. In this section, we report on the optical patterning of emission of complete device.

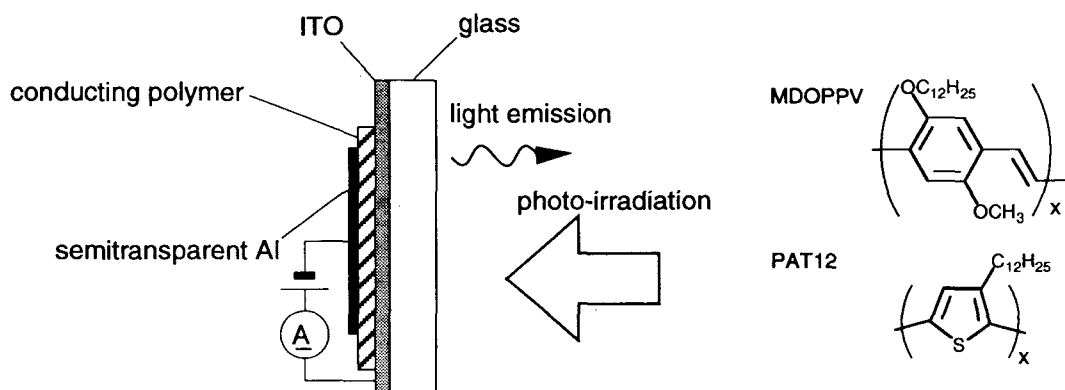


Fig. 1 Schematic structure of the optically patternable device proposed and the molecular structure of the polymers used.

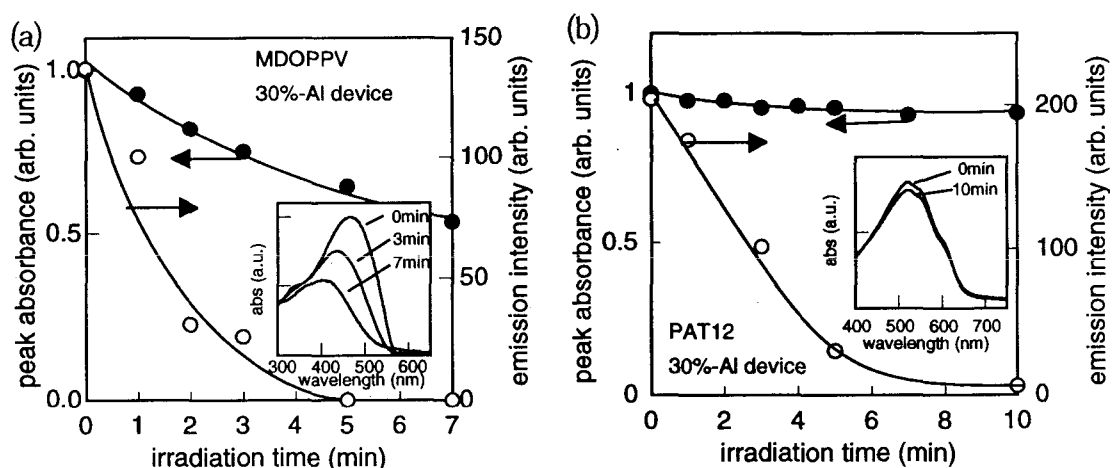


Fig. 2 Dependence of emission intensity of the optically patternable devices based on (a)MDOPPV and (b)PAT12. Dependence of optical absorption peak is also shown. Insets show the modification of optical absorption spectrum of the bare film upon photo-irradiation.

The device with an ITO/polymer/semitransparent-Al structure as shown in Fig. 1 was used in this study. Either poly(2-methoxy-5-dodecyloxy-p-phenylene vinylene) (MDOPPV) or poly(3-dodecylthiophene) (PAT12) was used as a polymer layer in this structure. Photo-irradiation was carried out in air by using a slide projector with a 150W-halogen lamp and an IR-cut filter. Optical transmittance of the Al cathode at 500 nm in wavelength was measured and was used as a reference of the thickness.

As shown in Fig. 2(a), emission from the MDOPPV device was rapidly quenched upon photo-irradiation. The emission intensity of device became under the measurement limit within 10 min of irradiation. It is also noted that the optical absorption corresponding to the interband transition of the polymer was considerably bleached by irradiation. This clearly indicates correlation of the suppressed emission with the broken conjugation system.

Similar photoinduced quenching of emission was also observed in the PAT12 device, as shown in Fig. 2(b). The patterning time was found to be almost the same to the MDOPPV device, several min. However, in this case, change in the optical absorption spectrum of the polymer was quite small,

unlike the MDOPPV device. This difference indicates that the mechanism of patterning is considerably different between MDOPPV device and PAT12 device.

Figure 3 indicates some examples of patterned emission from MDOPPV devices.

3. Maskless Dye Diffusion

Figure 4 schematically illustrates the maskless dye diffusion technique proposed here. A receiver film of polymer, poly(N-vinylcarbazole) (PVK) was spin-coated onto a prepatterned ITO coated glass plate from a chloroform solution. Typical shape of the electrode was strip with 3 mm in width and 20 mm in long. A diffusion source film was prepared on another glass plate by spin-coating from a chloroform solution of PVK containing a dye (1:1 by weight). The dyes used in this study were 1,1,4,4-tetraphenyl-1,3-butadiene (TPB), coumarin 6 (C6) and Nile red (NR). These materials are typically used as dopants for the PLEDs based on dye-doped polymers.[6] The thickness of the films is of the order of 100 nm.

After preparation of the films, both glass plates were placed so that the diffusion source and receiver films were brought into close contact as shown in the center of Fig.4. It is noted that there is no shadow mask between the polymer films. The ITO was heated by means of Joule heating and the dye molecules in the source film near the ITO electrode were activated and diffused into the receiver film. These process was carried out in air. Typical condition for this step is application of 10 V between two points 17 mm apart each other for 1.5 min. Under this condition, the current is initially about 0.18 A as expected by the Ohm's law and gradually drops. The driving force of the diffusion should be difference in dye concentration between the two PVK films contacted. After this diffusion step, an Al electrode is vacuum deposited onto the receiver polymer film.

One of the most important feature of the present

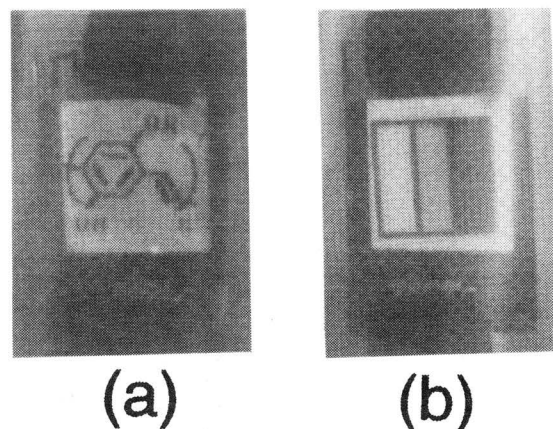


Fig. 3 Examples of patterned emission from optically patternable device based on MDOPPV. (a) A molecular structure of PPV derivative and (b) stripe.

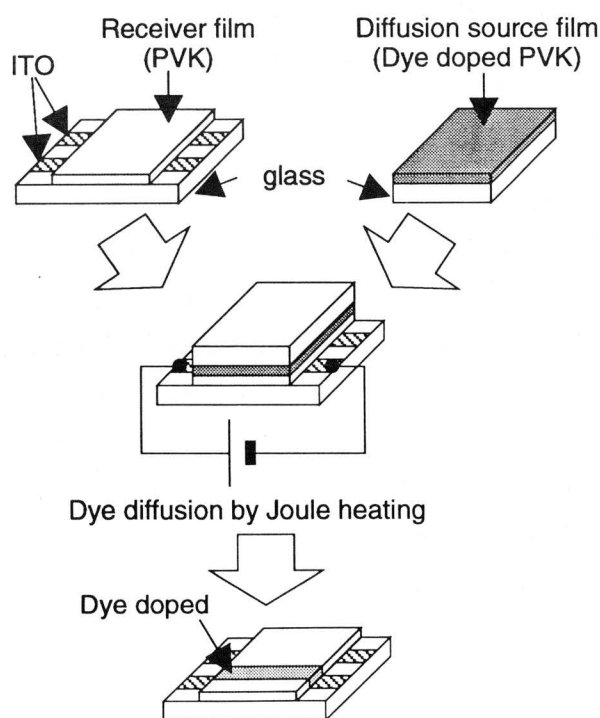


Fig. 4 A scheme of the maskless dye diffusion technique proposed here.

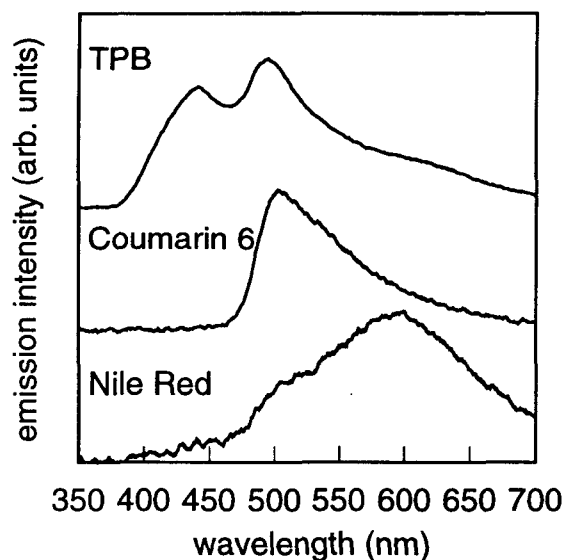


Fig. 5 Emission spectra of the PLEDs fabricated through the maskless dye diffusion technique proposed here.

method is that this technique is capable to doping dye only in a region determined by a selected electrode without mask. Although the shape of electrode should be limited to rectangular, this method possibly opens a way to fabricate low-cost full-color display panel based on PLEDs.

As shown in Fig. 5, by using above three dyes, blue, green and red emission devices were realized. Moreover, by repeating this technique, RGB devices were integrated on a glass plate.

It should be noted that the local dye doping technique proposed here is applicable not only to PLEDs but also to other devices such as photovoltaic devices. For example, photovoltaic devices with different spectral response can be integrated in a glass plate, the integrated devices can be used as a color sensing device.

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