Three-color organic light-emitting diodes patterned by masked dye diffusion

Florian Pschenitzka and J. C. Sturm[a)]

*Department of Electrical Engineering, Center for Photonic and Optoelectronic Materials (POEM),
Princeton University, Princeton, New Jersey 08544*

A method of masked dye diffusion to locally pattern the emissive color of organic light-emitting devices (OLEDs) over a large area is introduced. By using a large-area diffusion source, which may be a spin-coated doped polymer film, the entire process of masked diffusion of dye into a polymer film of an OLED to create an integrated three-color device has been demonstrated at atmospheric pressure. The materials used to demonstrate this method are the polymer poly(9-vinylcarbazole) combined with electron transport molecules, and the dyes bimane, coumarin 6, and Nile red. © *1999 American Institute of Physics.* [S0003-6951(99)02913-7]

Organic light-emitting diodes (OLEDs) have demonstrated a remarkable potential for flat-panel display applications because of their relatively simple structure and the use of noncrystalline materials.[1,2] However, the fabrication of color displays, which requires red, green, and blue emitters, is a current research challenge. So far, several methods to achieve three colors with a single uniform organic layer have been introduced: a white emitter and color filters,[3,4] a blue emitter and down-converter for the green and the red emitters,[5,6] and microcavities.[7] Other approaches which actually pattern the organic layer by etching and/or shadowing include: the locally defined deposition of organic material using dry etching,[8,9] direct printing of the organic material onto the substrate,[10] and a stacked structure where the three different OLEDs are deposited on top of each other.[11] All of these methods suffer from drawbacks related to power efficiency, manufacturability, or other reasons.

The emission color of OLEDs, both those based on polymers or those based on small molecules, can be changed through the addition of small amounts ($\sim$ wt. 1%) of dyes into the host material.[12,13] Thus the color can be locally tuned by just patterning the dye material in some way without disturbing the host material. This concept has been demonstrated using the local photo-oxidation of dyes by ultraviolet (UV) radiation.[14] Alternatively, it has recently been shown that the dyes may be locally added by ink-jet printing onto a previously spin-coated polymer film.[15,16] However, this method has the possible shortcoming that for each pixel a separate dye droplet has to be applied and therefore the throughput of substrates might be limited.

In this letter, we present a method of introducing a dye pattern into an organic thin film over a large area in one step by dye diffusion. We also demonstrate a method of using a large area dye-doped polymer layer as a diffusion source and the combination of both methods to integrate red, green, and blue OLEDs on a single substrate. To obtain a large-area uniform diffusion, we used a flat plate as a diffusion source which was as large as our device substrate. The experimental

arrangement is shown in Fig. 1. The diffusion source consists of a flat plate with a deposited layer of dye. A patterned masking layer is sandwiched between a dye source plate and the substrate containing the film for later OLED fabrication. Initial experiments were done with a conventional vacuum-evaporated dye layer on a glass plate as a diffusion source. However, because the evaporation to form this layer was hard to control and because we wanted to eliminate vacuum processes, we then used a highly doped polymer film as the dye source, which was deposited by spin coating. Much better results were obtained with such a dye source. The shadow masks were made from glass slides (100 μm thick) with holes as small as 160 μm.

The organic layers to be doped were deposited on a glass substrate coated with sputtered indium–tin–oxide (ITO) (30 Ω/sq). A polymer blend layer with poly(9-vinylcarbazole) [(PVK) $M_w \sim 1\,100\,000$ g/mole; 71.5% by weight in the final film] as a hole transport polymer and 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole [(PBD) 28.5% by weight] as an electron transport molecule was created by spin coating.[17] Some blends also contained 9,10-dioxa-*syn*-dimethylbimane[18,19] (bimane; wt 0.2%) as an emissive dye (emission peak at $\lambda = 435$ nm). The resulting thickness of the organic film after spin coating was approximately 100 nm. The dye used during the diffusion process was either coumarin 6 (C6, green) or Nile red. The doped polymer diffusion source layer was deposited by spin coating using a solution of equal amounts by weight of PVK and C6 or Nile Red dissolved in chloroform. The diffusion source
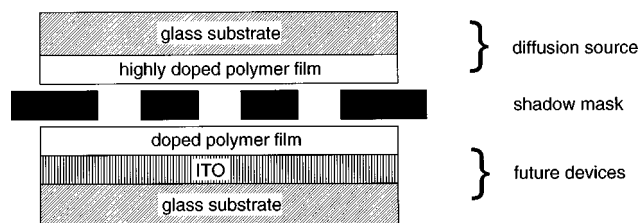

FIG. 1. Experimental arrangement: a patterned masking layer is sandwiched between the diffusion source and the device substrate.

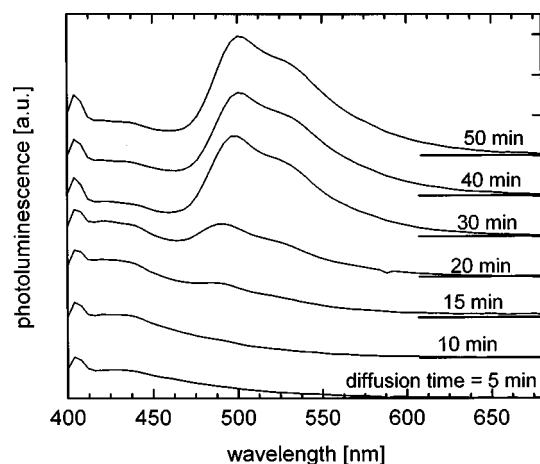[a)]Electronic mail: sturm@princeton.edu

FIG. 2. Photoluminescence spectra of a PVK film after different diffusion times. The diffused dye was C6 (emission peak at ~500 nm).

FIG. 4. Electroluminescence spectra of integrated blue, green, and red device. Blue devices contain bimane from spin-coated film, green devices contain C6 from diffusion and bimane, and red devices contain Nile red from diffusion and bimane.

layer, the shadow mask, and the polymer film of the device substrate were then placed in close contact as shown in Fig. 1 to perform the diffusion.

Figure 2 shows the photoluminescence (PL) spectra after different diffusion times in which C6 was diffused into a layer of pure PVK (i.e., the film does not contain PBD or binane) in an oven at 100 °C in air. The PL excitation source was an ultraviolet lamp. Before the diffusion, one only observes the emission of PVK with a peak at 407 nm. After 15 min, the C6 emission peak at ~500 nm can be detected. After about 50 min the C6 peak dominated the spectrum.

The process of introducing a dye molecule into the target film consists basically of three steps: the dye must desorb from the source film, travel to the surface of the target film, and then diffuse into this film. If the diffusion is slow compared to the desorption and transfer process, the transferred dye might pile up on top of or very near to the surface of the target polymer film. Thus annealing of the sample after the dye source plate and the mask are removed might increase the photoluminescence as more dye diffuses into the film. Figure 3 shows the effect of annealing a sample of PVK film, originally doped in solution with bimane, after C6 was transferred into it by the described process for 60 min at 90 °C.
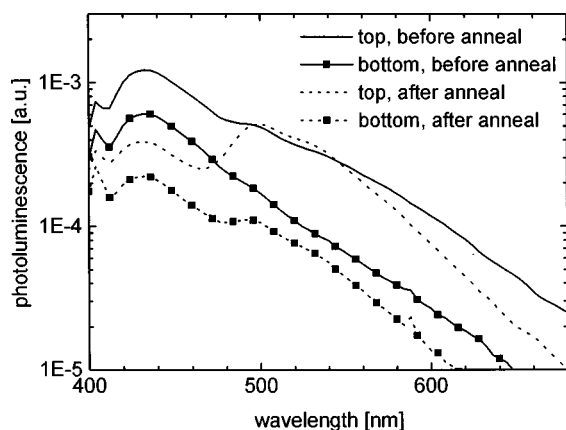

FIG. 3. Photoluminescence spectrum (before and after annealing) of a PVK film containing bimane in which C6 was diffused. The film was spun-on on a sapphire substrate to allow for probing the top and the bottom of the PVK film separately. The C6 peak is more pronounced after the substrate was annealed at elevated temperatures.
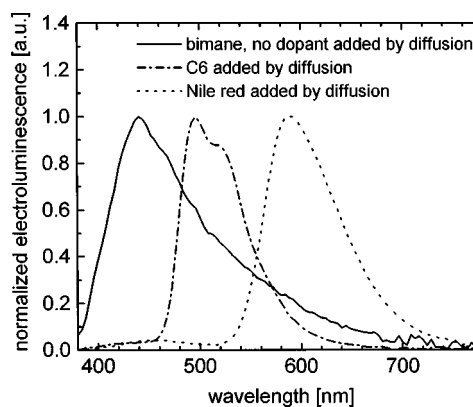
The film was deposited by spin coating on a transparent sapphire substrate to enable PL measurements to be performed by exciting the organic film from the top surface or from the back side. The absorption length at the excitation wavelength of 254 nm is about 50 nm in PVK, less than the 100 nm thickness of the PVK film.[20] This allows us to probe the top or the bottom of the PVK film separately. Before the anneal, the PL spectrum of the surface (excited from the top) shows a shoulder at about 500 nm corresponding to the emission of C6. However, the emission peak of bimane at 435 nm is still much more pronounced. The PL spectrum from the back side does not exhibit any emission from C6 at all. This shows that the C6 diffused only into the top of the organic film. After the sample was annealed at 90 °C for 6 h, the C6 peak becomes stronger. On the top surface, C6 emission now surpasses the intensity of bimane, whereas on the back side only a small shoulder due to the C6 emission emerged. From this we conclude that the dye indeed diffuses deeper into the PVK layer during annealing, but that the C6 concentration is still higher at the top of the film compared to the back. No lateral diffusion could be detected for moderate doping levels usually used in devices. So far, the feature size is entirely limited by the resolution of the shadow mask. Feature sizes down to ~160 μm could be obtained.

By repeating this previously described process for both dyes (i.e., C6 and Nile red) with different mask patterns, it was possible to demonstrate the integration of red, green, and blue OLEDs. The diffusion of Nile red was carried out first at 110 °C for 5 min in air followed by the diffusion of C6 at 90 °C for 1 h. The sample was then annealed without any dye source for 100 min at 90 °C. After evaporation of the cathode metal (Mg:Ag, 10:1; Ag), the region without any diffused dopant emitted blue light (due to the bimane dye already contained in the spun-on film). The regions with C6 added by diffusion emitted green light and those treated with Nile red emitted orange/red light as shown in Fig. 4.

Note that the PL spectra of the film doped by diffusion with a background bimane dopant from the spin coating showed a combination of both the bimane (blue) and the diffused dopant (green or red) emission as shown in Fig. 3. However, the electroluminescent (EL) spectra of the same films showed emission from the diffused dopant only (C6 or Nile red) and not from bimane (Fig. 4). It is not known if this

TABLE I. External quantum efficiencies of integrated RGB devices and control devices.

	Control device	Integrated RGB device
Blue (bimane)	0.25%	0.10%
Green (C6)	0.9%	0.45%
Red (Nile red)	0.6%	0.13%

effect is due to a nonuniform dye distribution coupled with a different location for exiton formation in the EL vs PL, a fundamental different nature for the process leading to the creation of exitons on the dye in EL vs PL, or other reasons. Further investigation is underway. But this fortuitous effect allows the fabrication of a three-color display with only two diffusion steps instead of three since the blue dopant can be uniformly incorporated into film deposited by spin coating.

Shown in Table I are the external quantum efficiencies of the integrated red, green, blue (RGB) devices fabricated by masked dye diffusion. Also shown are the external quantum efficiencies of ''control'' devices where the dyes were added to the previously described polymer blend solution before spin coating (C6: wt 0.003% in solution, Nile red: wt 0.002%). The external quantum efficiencies of all three color devices are in the percent range and not much lower than those of the control devices. This makes this diffusion process a very promising patterning technique. Improved results might be expected when performing the diffusion process in dry nitrogen instead of air. The method should be extendable to other dyes and polymers and perhaps to devices based on small molecules as well.

In conclusion, we have demonstrated a method for patterning the color of organic light-emitting devices using a masked large-area diffusion technique. The dye is transferred from a large-area diffusion source into the organic layer of the device where it changes the emission color accordingly. The diffusion source may be a heavily doped polymer layer deposited by spin coating and the whole process may be carried out in air. Using this process, RGB devices of reasonable efficiencies have been achieved. It appears feasible to fabricate devices with feature sizes smaller than 100 μm.

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