Local tuning of organic light-emitting diode color by dye droplet application

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We have demonstrated that fluorescent dyes may be introduced into previously fabricated polymer thin films by local application of a dye-containing droplet. The UV fluorescence spectra of the films and the spectra of organic light-emitting diodes made from these films can be successfully tuned by this method. The technique has been implemented by ink-jet printing of the dye droplet. © *1998 American Institute of Physics.* [S0003-6951(98)01339-4]

A main goal of the field of organic light-emitting diodes (OLEDs) is the realization of full color flat panel displays. OLEDs are attractive because of their potential to be used for large area displays and potential low cost and because they do not have the inherent viewing angle problem associated with liquid crystals. One of the difficulties in realizing this goal has been the integration of red, green, and blue devices on the same substrate. Integration has been difficult because standard deposition techniques, such as spin-on for polymers and evaporation for small molecules, both create blanket films of one organic layer, and patterned layers are clearly attractive for multicolor integration. Patterning and etching of organics is difficult using photoresist and standard semiconductor wet etching techniques because of their sensitivity to aqueous and solvent solutions. Therefore, much attention has been focused on various alternatives for color displays. These methods include: (i) integrating organic white emitters with pixelated red, green, and blue color filters;¹ (ii) integrating organic blue emitters with pixelated red and green downconversion materials;^{2,3} (iii) adjusting the emission of a single type of broadband organic emitter by integrating with pixelated microcavities;⁴ (iv) stacking of red, green, and blue emitters on top of one another; 5,6 (v) laterally patterning red, green, and blue emitters using etching;^{7,8} (vi) selective photo-oxidation of dopants by patterned UV exposure;9 and (vii) using an ink-jet printer to directly deposit patterned organic layers.¹⁰

The above methods have potential drawbacks. Color filters and down converters have inherent energy inefficiencies. Microcavities have a direction-dependent resonance frequency which causes angular color and brightness variations. Stacked structures require transparent contacts and contacts to intermediate electrodes. The reported dry etching work,⁷ in principle, applicable to all classes of organics, required a metal cathode etch mask by shadow masking, and the devices patterned directly by photoresist required special polymers and had low demonstrated efficiencies.⁸

The direct deposition of patterned red, green, and blue fluorescent polymers by ink-jet printer and the fabrication of OLEDs in these layers was recently reported.¹⁰ Thickness and morphology nonuniformities led to a substantial variation in OLED threshold voltage, however. Recently, the patterning of hole transport layers by ink-jet printing, followed by spin coating of a polymer has been used to demonstrate patterned OLEDs if indium tin oxide (ITO) with a low work function surface is used.¹¹ This method of ink-jet patterning cannot be directly extended to realizing color displays, however. In this letter, we report a technique in which the emissive color of a thin organic film can be adjusted by the local application of a wet dye droplet *after* a uniform organic film has already been deposited by conventional techniques (i.e., spin coating in our case), and the application of such dyecontaining droplets by ink-jet printing. This overcomes the previous drawbacks of thickness nonuniformity¹⁰ or only single color capability¹¹ of the previous ink-jet printing work.

This initial work was based on molecular doped polymers, using coumarin 6 (C6, green) and other dyes to adjust the emission of poly(9-vinylcarbazole) (PVK) films in single-layer devices.¹² As a first experiment, a solution of 100 mg of PVK in 7.5 ml of chloroform was spin coated onto two glass substrates and the solvent was given time to evaporate. Onto one of these films, a droplet of a solution of 0.3 mg of C6 dissolved in 7.5 ml of acetone was applied using a pipette with a droplet volume of \sim .011 ml. To isolate the dye without any possible PVK interaction, another drop of the same C6 solution was applied by the same method to a bare glass substrate. A control sample of C6 blended in solution with PVK before spin coating was also fabricated (referred to as a "blend" film). UV fluorescence spectra of all four samples are shown in Fig. 1. Note that pure PVK has a deep blue luminescence, and the PVK/C6 blend film and the film with C6 applied through a droplet had identical green luminescence, which was clearly visible by eye. The dye on top of glass had a red luminescence, suggesting that the dye applied on top of the PVK was not remaining isolated on top of the PVK, but was interacting with it in some way.

To confirm the location of dye, similar samples of blend films and droplet doped films were prepared as above, except ITO-coated glass substrates were used. Secondary ion mass spectroscopy (SIMS) was then used to profile sulfur using a PHI 6300 quadrupole-based SIMS instrument. C6 contains sulfur which is not present in PVK, so that sulfur profiles

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FIG. 1. PL spectra of PVK film, PVK/C6 blend film, PVK film with C6 deposited after spinning, and C6 deposited on glass.

will indicate the C6 profile. The concentration of sulfur is constant throughout the depth of the film for the film which had C6 deposited with a dye droplet after spin-coating PVK, just as in the blend device (Fig. 2), indicating that not only does the C6 diffuse into the PVK, but it diffuses in such a way that its profile is identical to that of a blend film. This was most surprising since no high temperature steps were done after the dye dopant application to promote diffusion. The large sulfur signal in the ITO is a SIMS artifact due to mass interference from O_2 . The different absolute levels of sulfur (and C6) in the two samples are due to the concentration of dye used in our experiment and are not thought to be significant.



FIG. 2. SIMS profiles of carbon and sulfur in (a) a blend film of PVK/C6 and (b) a PVK film with C6 deposited via a dye droplet. The background sulfur signal in an undoped PVK film was ~ 100 cts/s.



FIG. 3. (a) I-V curve of a PVK:C6 blend device (control) and a device with C6 deposited after spinning and (b) the EL spectra of PVK film, PVK/C6 blend film, and PVK film with C6 deposited after spinning.

OLEDs were then made by depositing a 30 nm thick magnesium:silver (Mg:Ag) (10:1) cathode with a 170 nm thick Ag cap on top of the above samples on ITO. These devices were then tested and an electroluminescent (EL) spectra was taken using a Photo Research PR 650 Colorimeter. Figure 3(a) shows the current versus voltage curve of spin-coated blend (control) and a dye-doped device and Fig. 3(b) shows EL spectra of three devices, one with undoped PVK, one with C6 applied via a droplet onto PVK, and one device made from a blend film. The reason for the differences in the turn-on voltages of the blend device and the dye-doped device is unknown at this time. The blend device and the device with C6 deposited after spinning have the same EL peak wavelength, which is redshifted from the pure PVK device consistent with the UV fluorescence results. To the best of our knowledge, this is the first OLED reported by such a local dye diffusion technique.

The introduction of dyes into polymers is not a new problem; it has been around in the textile industry for many years, but not on a local scale.¹³ There are two models describing the diffusion of dyes into polymers: the pore model and the free volume model. In the pore model, dye molecules infiltrate the polymer matrix by way of open pores in the surface of the polymer layer. In the free volume model, the polymer absorbs the solvent, which lowers the glass transition temperature of the polymer, creating a larger free volume in which the dye molecules can diffuse. To determine which of these models most closely describes C6 diffusion into PVK, the following experiment was conducted. A blend film was prepared by spinning a solution of 100 mg PVK and 0.3 mg of C6 dissolved in 7.5 ml of chloroform onto a glass substrate. Next, the surface was washed with acetone, which does not dissolve or remove the PVK film. Under UV expo-

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FIG. 4. UV fluorescence image of ink-jet printed C6 dyed lines on a PVK film. The true colors are green lines on a deep blue background.

sure, the area which had not come into contact with the acetone fluoresced green, while the area that had come into contact with the acetone fluoresced deep blue, indicating that the C6 was "washed out" of the PVK by the acetone. EL experiments of such washing (before cathode deposition) had similar results. Although we have no independent data on the microstructure of our PVK, if we assume that the active dye in spin-coated blend films sits throughout the PVK network and not just on pore walls, if any, these results indicate that C6 can move throughout the entire polymer matrix, not just to and from pore walls. This suggests that diffusion of the dopant is described by the free volume model.

To apply smaller dye droplets and demonstrate a route towards manufacturing, we then applied droplets using an Epson Stylus 400 ink-jet printer. The printer was modified by removing the commercial inks in the ink cartridge, and replacing them with a solution of 3 mg of C6 dissolved in 7.5 ml of acetone. Unlike chloroform, acetone does not rapidly degrade the printer. This solution was then printed onto a film spun cast from a solution of 100 mg of PVK dissolved in 7.5 ml of chloroform on an ITO-coated glass substrate. Figure 4 shows a UV fluorescence image of some lines which were printed by this method, demonstrating the successful introduction of dye into the polymer. The extension towards multiple colors using such a printer and multiple dyes should be straightforward. The minimum widths of the dyed lines in Fig. 4 are ~400 μ m. However, we expect to achieve ~100 μ m resolution, consistent with the small pixel size in high information content displays, in the near future.

In conclusion, we have demonstrated that fluorescent dyes may be introduced into polymer thin films by local application of a dye-containing droplet. The UV fluorescence and spectra of the film can be successfully tuned, and the method can be implemented by ink-jet printing of the dye droplet. The method should be applicable to the realization of full color OLED displays.

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