

## Solvent-enhanced dye diffusion in polymer thin films for color tuning of organic light-emitting diodes

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A method of solvent-enhanced dye diffusion in polymer films for organic light-emitting diode (OLED) application is introduced. After an initial dye transfer from a dye source substrate into the top of the device polymer film, the device substrate is then exposed to solvent vapor. Due to solvent absorption by the polymer film, the glass transition temperature of the polymer is significantly decreased which leads to enhanced diffusion of the dye in the polymer film. Secondary ion mass spectroscopy and depth dependent photoluminescence show that the temperature for dye diffusion can be decreased by at least 100 °C, to room temperature. OLEDs with 0.6% external quantum efficiency have been demonstrated with this method using the polymer poly(9-vinylcarbazole) combined with electron transport molecules and the dyes coumarin 47 and coumarin 6. © 2001 American Institute of Physics. [DOI: 10.1063/1.1366368]

Recent progress in polymer-based organic light-emitting devices (OLEDs) demonstrates remarkable potential for commercial applications.<sup>1,2</sup> The ease of processing along with the ability to tune the emission color makes OLEDs a promising technology. Usually, the organic film is deposited on a substrate previously coated with a transparent conductor [e.g., indium tin oxide (ITO)]. Subsequently, a cathode is deposited onto the organic film. However, to fabricate a full color display, pixels emitting different colors (namely red, green, and blue) have to be placed next to one another on the same substrate, making patterning of the organic film inevitable. For OLEDs based on small molecules, these molecules are thermally evaporated through a shadow mask onto the substrate to obtain the desired pattern.<sup>3</sup> This method is not applicable for polymer based devices because it is not possible to evaporate polymers.

In our work, the polymer film is deposited by spin coating from solution forming a homogeneous layer on the substrate, which can emit only one color. Ink-jet printing of polymer solution,<sup>4-7</sup> or screen printing of the polymer<sup>8</sup> have been introduced to overcome this problem. The emission color of the OLED can easily be changed by adding a small amount of chromophores (dyes) into the polymer matrix. Other methods make use of this fact, for example ink-jet printing of a dye solution on a substrate previously coated with polymer,<sup>9</sup> or photobleaching of a dye.<sup>10</sup> In a previous letter,<sup>11</sup> we introduced a method to locally transfer dye from a dye source substrate into the polymer layer of the device. The patterning can either be achieved by simply placing a separate physical mask between the dye source substrate and the device substrate during the transfer process, by patterning a thin film as diffusion barrier on top of the dye source, or by patterning the dye source itself.<sup>12,13</sup> Local heating of the device substrate was also used to pattern the dye transfer.<sup>14</sup>

Polymers used for OLEDs have a relatively high glass transition temperature  $T_g$  for polymer stability. However,

diffusion of dye in polymer below  $T_g$  decreases rapidly.<sup>15-17</sup> Thus, diffusing the transferred dye throughout the polymer film requires a high process temperature, which can degrade the performance of the device. It is therefore desirable to temporarily lower  $T_g$  of the polymer film after the dye is transferred and thereby enhance the diffusion of the dye.

The OLED polymer film (90 nm thick) was deposited on a glass substrate coated with ITO (30  $\Omega/\square$ ). The polymer used was poly(9-vinylcarbazole) (PVK) (MW~1 100 000 g/mole, 71.5% by weight in the final solution) as the hole transport material and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (28.5% by weight in the final solution) as the electron transport material.<sup>18</sup> The polymer blend also contained the dye coumarin 47 (C47, emission peak at 440 nm). The dye diffused into the polymer film is coumarin 6 (C6, emission peak at 505 nm). The dye source was a glass substrate with a spun-on polymer film containing the dye to be diffused. The device substrate and the dye source substrate were then placed into intimate contact in a vacuum oven at 64 °C for 1 h for the initial dye transfer. After this step, the dye is located primarily on the top of the PVK layer. Further diffusion of dye requires substantially higher temperatures. Figure 1 shows secondary ion mass spectroscopy (SIMS) profiles of thermally annealed samples. Because only the C6 molecule contains sulfur (one atom per molecule), it can be used as a marker for C6. The increase of sulfur starting at a depth of 60 nm is an artifact due to oxygen interference from the substrate. In this case, the samples were prepared by evaporating a thin film of C6 on a sample with a previously spun-on PVK/PBD layer (85 nm thick). The samples were then annealed at 92 °C for 4 and 8 h. After annealing, the penetration of C6 into the PVK layer is still clearly limited.

To lower the temperature required for dopant diffusion, we then studied the dye diffusion in air saturated with acetone vapor. It is known that the presence of solvents lower the  $T_g$  of polymer films.<sup>19,20</sup> The initial transfer of C6 into the PVK/PBD/C47 film was carried out as described above

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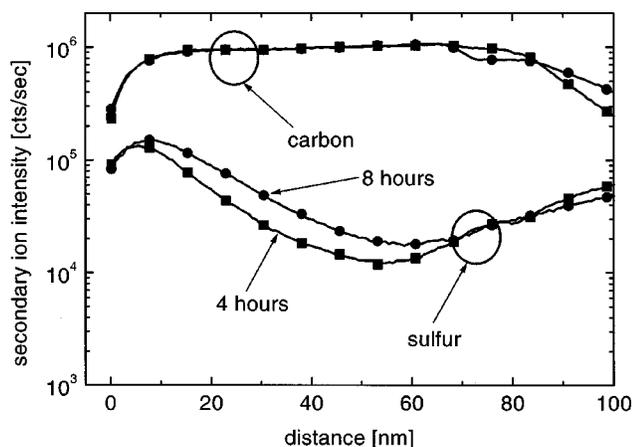


FIG. 1. SIMS profile of PVK film with C6 diffused and annealed for 4 h (squares) and 8 h (circles) at 92 °C in vacuum.

in vacuum at 64 °C for 1 h. A control sample was created in which the dye C6 was already contained in the PVK/PBD/C47 solution (0.2% by weight) before spin coating, and it was not subject to the dye transfer step. Figure 2 shows SIMS profiles of dye after the initial dye transfer and after the anneal in acetone vapor, along with the control sample to establish an absolute reference level for C6.

The polymer layer of the control samples shows a uniform sulfur profile. As expected, the sample with C6 diffused into the polymer film without the anneal process shows a high concentration of sulfur at the surface. The concentration exponentially decreases with depth, due to the low diffusivity of the polymer below  $T_g$ . The rise of the sulfur count at about 80 nm is due to O<sub>2</sub> interference from the ITO substrate. The sample with the dye on its surface was then annealed at 35 °C for 10 min in acetone vapor. In contrast to the profile shown in Fig. 1, after the anneal at 92 °C for many hours, the dye profile is now flat after only 10 min. To confirm the proposed diffusion enhancement mechanism, the polymer thickness was measured *in situ* during the anneal process by ellipsometry. The thickness increased by 27%. Combining this volume expansion with the initial measured  $T_g$  of the PVK/PBD blend of 125 °C (measured by Jiang and

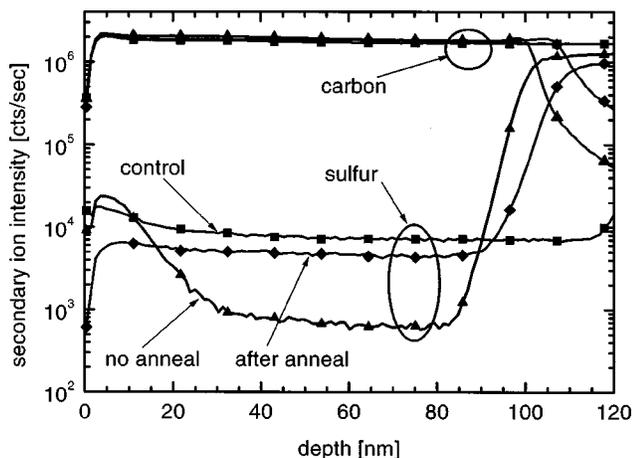


FIG. 2. SIMS profiles of dye in a sample exposed to acetone for 10 min (diamonds). The dye profile of the untreated sample (triangles) and of a sample with dye contained in the spun-on film (squares) are also shown.

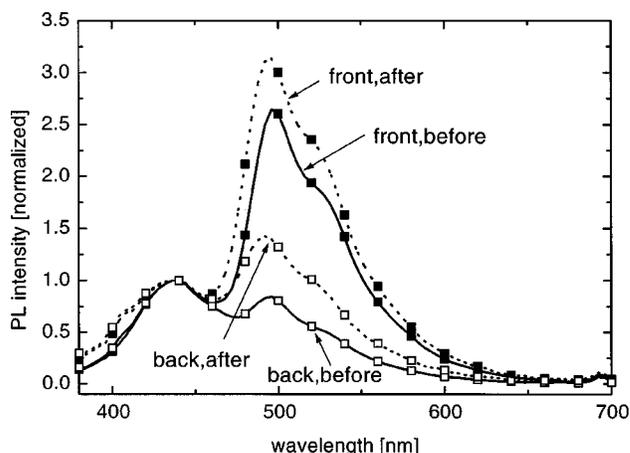


FIG. 3. Photoluminescence (PL) spectra of PVK/PBD/C47 film on sapphire substrate in which C6 was diffused. The backside (open squares) denotes the excitation and emission through the sapphire substrate, the front side (solid squares) denotes these of the polymer layer. PL measurements were recorded before (solid lines) and after (dotted lines) the anneal in an acetone atmosphere.

Register, Princeton University), standard polymer models<sup>20</sup> predict  $T_g$  to be reduced by ~150 °C to -25 °C.

Under UV excitation, the vapor-annealed sample showed a stronger C6 emission than the not annealed sample, suggesting less “inactive” dye piled up at the surface. To investigate this observation further, the PVK/PBD/C47 solution was spun on onto a sapphire substrate to enable UV excitation through the substrate. This allowed the UV fluorescence spectra to be recorded from the polymer surface (the front side) and from the back of the polymer film (i.e., the sapphire side).<sup>15</sup> Because of the relatively small absorption length of 50 nm at the excitation wavelength of 254 nm,<sup>21</sup> one can selectively probe the fluorescence (and thus the dye concentration)<sup>18</sup> of the front versus the back of the polymer film. To eliminate any attenuation effect due to the sapphire substrate, we chose a relative measurement of the emission intensity of C47 (which was contained in solution and therefore was homogeneously distributed throughout the polymer film) and the diffused dye C6. Figure 3 shows the spectra (normalized with respect to the C47 emission peak) from the front and the back after the initially transfer of C6 at 64 °C, and then again after an anneal in acetone vapor for 10 min at room temperature. After the dye transfer, the C6 emission is stronger from the front versus the back of the film because of the higher concentration of C6 at the polymer surface. After the solvent-enhanced diffusion, the C6 emission increased relative to the C47 emission for both sides. However, the increase is more pronounced for the emission from the sapphire side. This result shows that the dye diffusion is indeed drastically enhanced due to the presence of the acetone vapor, consistent with the SIMS data.

To quantify these results, a uniformity coefficient  $h$  was defined as

$$h = \frac{I_{C6,front}/I_{C47,front}}{I_{C6,back}/I_{C47,back}}$$

$I$  denotes the intensity at the emission peak of the respective dye. If  $h$  is 1, the C6/C47 ratio is uniform throughout the film. Figure 4 shows a comparison of  $h$  at different anneal

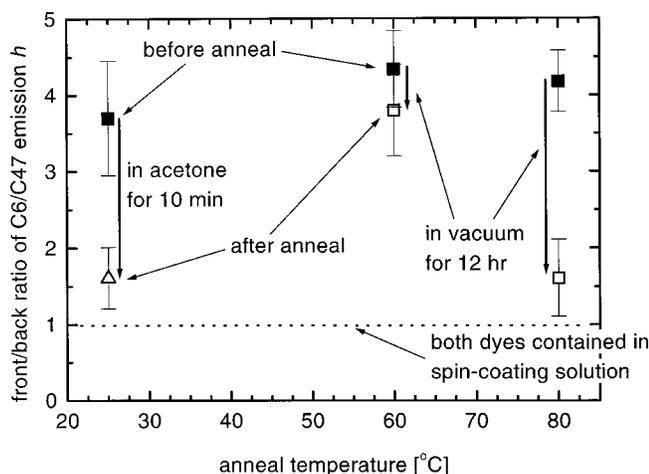


FIG. 4. Comparison of the ratio of back/front emission of C6 vs C47 for different anneal temperatures. The anneal in acetone vapor at room temperature for 10 min had approximately the same effect on the dye diffusion as a conventional anneal for 12 h at 80 °C in vacuum.

temperatures after the initial dye transfer and then after different diffusion processes. After the initial dye transfer  $h$  is about 4, indicating that the concentration of C6 is higher at the surface of the polymer film. Using conventional anneal for 12 h at 80 °C,  $h$  decreased to 1.6. However, solvent anneal at room temperature yielded the same  $h$  after only 10 min.

OLEDs were then fabricated with polymer films either subject to only the 64 °C dye transfer or with the additional solvent vapor diffusion step. Control samples with a spun-on PVK/PBD/C47/C6 solution served as a reference. A 100-nm-thick layer of Mg:Ag (10:1) was thermally evaporated as cathodes (2 mm<sup>2</sup>).

The untreated control sample shows a much lower leakage current than the solvent-treated sample. However, the amount of light emitted by the sample exposed to solvent vapor is only slightly lower than that of the unexposed one, indicating that the treatment does not damage the polymer film significantly. The external quantum efficiency (QE) dropped from 0.9% for the pristine device to 0.61% for the treated device.

The  $I$ - $V$  curves along with the measured photocurrent of the devices with C6 diffused are shown in Fig. 5. These samples were prepared in exactly the same way as for the SIMS analysis. Again, the solvent vapor processed sample shows a higher leakage current. But the photocurrent increased drastically for the treated sample, and the emission changed from blue to green. The QE rose from 0.07% for the device with C6 only diffused into the polymer film but without the subsequent anneal step to 0.54% for the annealed device. For comparison, results for C6 diffused devices with a thermal anneal for 4 h at 80 °C were 0.3%.

In summary, we have demonstrated the solvent-enhanced diffusion of dye in polymer films for OLED fabrication. The solvent treatment lowers the glass transition temperature  $T_g$  of the polymer film temporarily by as much as 150 °C, resulting in very low process temperatures required

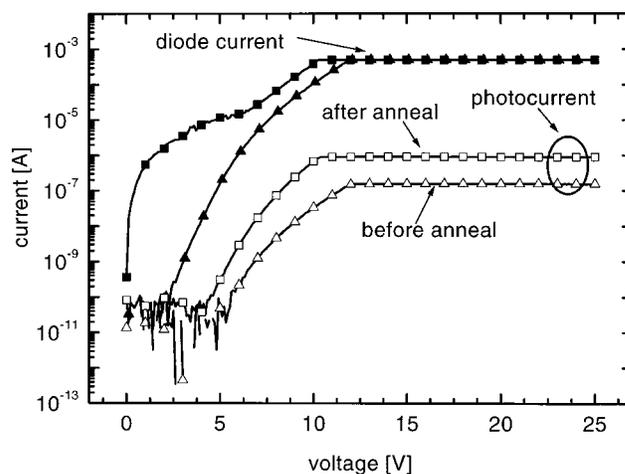


FIG. 5.  $I$ - $V$  curves and photocurrents of samples with C6 transferred by dye diffusion into the PVK film. The nonannealed sample (triangles) shows a very poor ext. quantum efficiency. It improved by nearly an order of magnitude after the sample was annealed in acetone vapor (squares) for 10 min at room temperature.

for the diffusion of the dye. OLEDs with efficiencies close to those of devices with the dye contained in solution during the spin-coating process were obtained. Future work will focus on the application of this process to full color OLED displays.

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