Solvent-enhanced Dye Diffusion in Polymer This-Films for OLED Application

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ABSTRACT

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 electractive 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 greatly enhanced diffusion of the dye in the polymer film. Secondary ion mass spectroscopy shows that the temperature for dye diffusion can be decreased by 150 °C. OLEDs with 0.4% external quantum efficiency were demonstrated. The materials used are the polymer poly(9-vinylcarbazole) (PVK) combined with electron transport molecules (PBD), and the dyes coumarin 47, coumarin 6 and Nile red.

INTRODUCTION

Polymer based organic light-emitting diodes (OLEDs) have demonstrated remarkable potential for commercial display applications [1]. Efficiencies of OLEDs are now comparable to those based on conventional crystalline semiconductors [2]. In addition, the fabrication process for OLEDs is possibly simpler, promising lower fabrication costs. Usually, the electroactive polymer film is deposited onto the substrate by spin-coating from solution. While spin-coating is a very low-cost process, it forms a uniform polymer layer which can generally only emit one color. For a full color display, however, devices emitting different colors (red, green and blue, RGB) have to be fabricated next to each other on the same substrate. Therefore, the need to pattern the polymer film is evident. Alternative approaches such as a white emitter with color filters or blue emitter with down-converter are inherently less efficient.

Several methods have been introduced to overcome this problem: ink-jet printing of polymer solution [3-5], and screen printing of the polymer [6]. Adding a small amount of chromophores (dyes) (usually less than 1% by weight for fluorescent dyes) into the polymer matrix can change emission color of the OLED. Other methods to pattern the color emission from polymers make use of this fact, for example ink-jet printing of a dye-solution on a substrate previously coated with polymer [7], or photobleaching of a dye [8]. In a previous paper [9], 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 [10,11]. Local heating of the device substrate to pattern the dye transfer has also been reported [12].
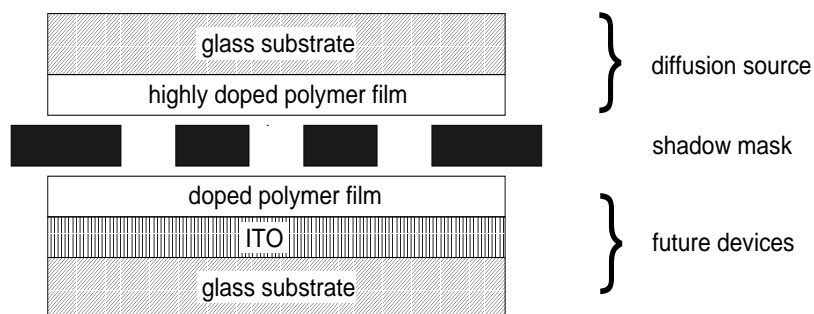
EXPERIMENTAL BACKGROUND

Figure 1. Experimental set-up: a shadow mask is sandwiched between the diffusion source that provides the dye and the device substrate with the polymer film [9].

A schematic diagram of our original approach to patterned dye diffusion is shown in Fig. 1. The device consists of an ITO substrate (30 $\Omega/\square$) on which the polymer is deposited by spin-coating from solution to form a 90 nm thick film. The solution contained poly(9-vinylcarbazole) (PVK; M_W ca. 1,100,000 g/mole; 71.3 % 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 electron transport molecule and the dye coumarin 47 (C47, 0.2% by weight, emission peak at ~ 440 nm) [13]. The diffusion source consists of a flat plate with a doped polymer layer as the dye source. The solution for the dye source layer contained the polymer Vylon 103 (obtained from Toyoba) and the dyes C6 (obtained from Lambda Physik, emission peak at ~ 505 nm, ~2% by weight in the final film) or Nile red (obtained from Aldrich, emission peak at ~ 600 nm, ~2% by weight in the final film). The diffusion process was carried out at 70 ^{o}C for 1 hour in vacuum.

Fig. 2 compares the IV-curves of devices with C6 diffused in to the PVK film to those where the same dye was already contained in solution. Also shown is the photocurrent of a silicon diode placed in close proximity to the OLED. To determine if the observed characteristics is due to thermal damage to the device during the diffusion process, we also included a sample where the dye C6 was contained in solution but was exposed to the same heat treatment as the device with diffused dye. The IV-characteristics are very similar for all devices. However, the photocurrents are strikingly different: Whereas the curves of the pristine device and the heat-treated device are about the same (indicating that the polymer film was not severely damaged during the heat treatment), the device with dye diffused into the film demonstrated a much lower photocurrent and thus a much lower external quantum efficiency (η_{ext}).

To investigate the reason for the low efficiency of the diffused devices, we performed secondary ion mass spectroscopy (SIMS) on the polymer films using the sulfur atom in the C6 molecule as the tracer. Fig. 3 shows the SIMS profiles for a PVK film in which the dye was diffused at 73 ^{o}C for different times. As expected, the concentration of dye increases with time, but the dye is only accumulating at the surface. The increase of the sulfur signal at the substrate interface is due to oxygen interference ($^{16}O_2^+$ is detected as $^{32}S^+$). Since the profile is limited by the SIMS resolution, the actual profile is probably much narrower than the one shown.
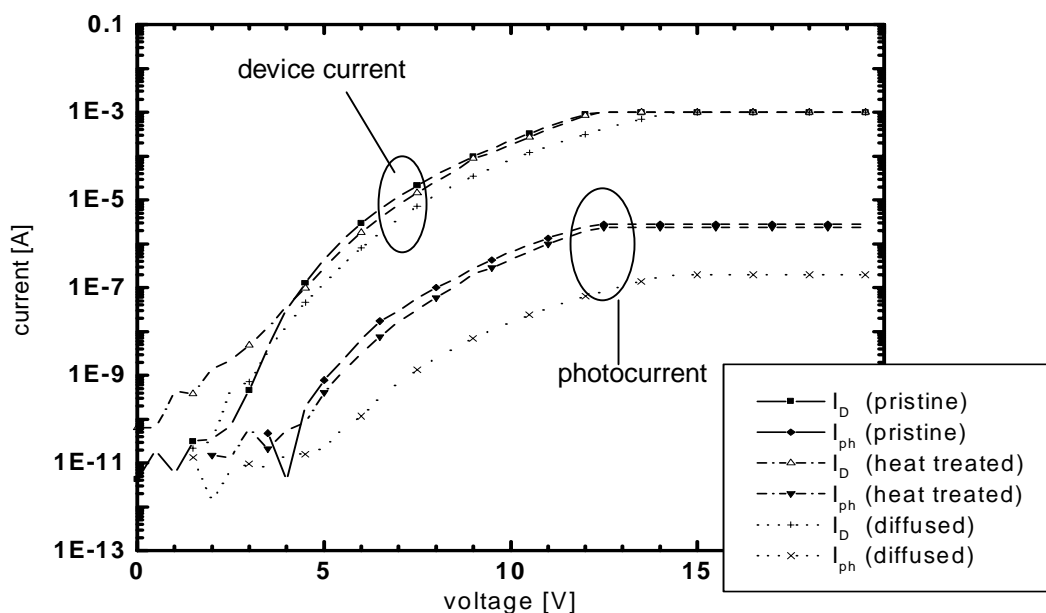
Figure 2. IV-characteristics and photocurrents of different devices: (a) a device (PVK/PBD/C6) which was not exposed to heat at all, (b) a device (PVK/PBD/C6) which was kept at 70 °C for 1 hour in vacuum, and (c) a device (PVK/PBD only) with diffused C6 at 70 °C for 1 hour in vacuum [10].
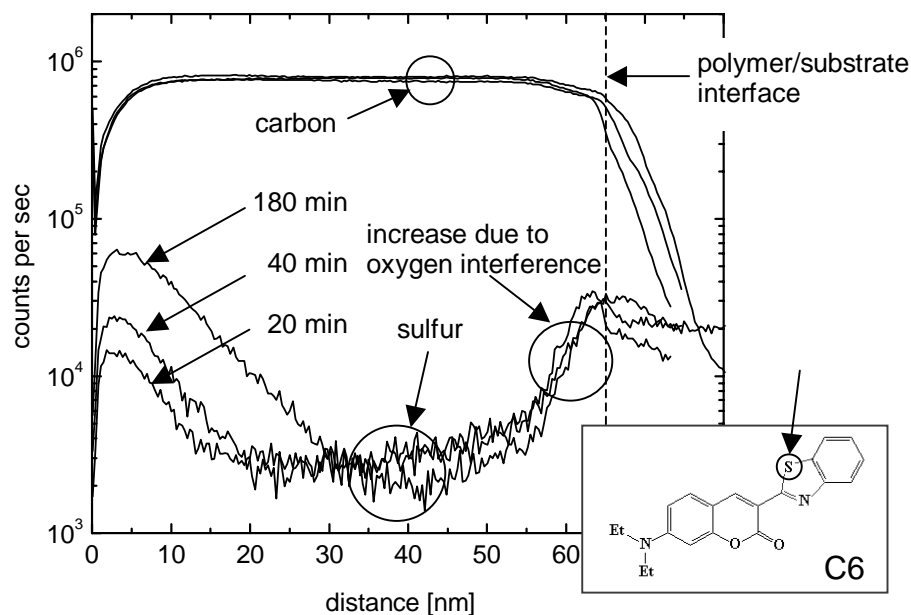

Figure 3. SIMS profiles of a PVK/PBD film with C6 diffused into a PVK film. The diffusion was carried out at 73 °C in vacuum.

To obtain efficient devices, the dye should be distributed in the polymer layer in a fashion that the optimal amount of dye is located in the recombination zone of the OLED. The easiest

approach is to distribute a well-defined amount of dye uniformly throughout the polymer film. We therefore added an anneal step after the initial dye transfer step (and removal of the dye source) to drive the dopant into the polymer film. Polymers for OLED application have a fairly high glass transition temperature T_g for stability reasons. The diffusion of molecules below this temperature is exceedingly slow. For the PVK/PBD blend T_g was determined to be 125 ^{o}C (measured by X. Jiang and R. Register, Princeton University). At a anneal temperature of 92 ^{o}C, the diffusion coefficient was measured to be about $\sim 10^{-17}$ cm^2/s [14], leading to unacceptable processing times. Further increase in process temperature, however, has a negative impact on the electrical characteristics of the device.

SOLVENT-VAPOR ASSISTED DIFFUSION

If a polymer is exposed to a solvent, the solvent diffuses into the polymer matrix and thereby causing the polymer to swell. The addition of small solvent molecules into the polymer film increases the average interchain distance and weakens the molecular interaction between the polymer molecules, allowing the polymer molecule to move more freely. When diffusing into glassy polymers at temperatures well below T_g, a sharp penetration boundary is often observed [15,16]. This penetration boundary moves into the pristine polymer and leaves the swollen polymer behind. We expect that the diffusion coefficient of this polymer-solvent system is increasing with increasing solvent concentration [17]. Because of the high mobility and small concentration of dye in the solvent, it can be assumed that the dye diffusivity can be scaled quantitatively to the solvent diffusivity [18]. After the exposure to solvent vapor, the film is dried in pure nitrogen and regains its original T_g and film thickness before the exposure to the solvent.
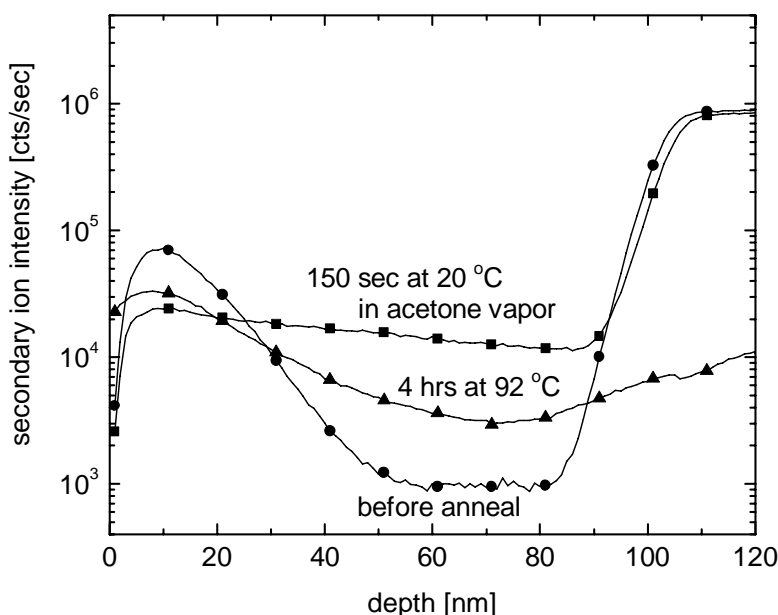

Figure 4. SIMS profile of a sample with C6 transferred into a PVK film before (squares) and after (circles) acetone anneal. The sample was annealed in acetone vapor for 150 sec at room temperature. For comparison, a thermally annealed sample (4 hours at 92 ^{o}C) after the same initial transfer is also shown (triangles).

A tube reactor was constructed where we could adjust the solvent-vapor pressure. Fig. 4 shows the SIMS profile of a sample (with C6 previously transferred) before and after the solvent anneal for 150 sec at room temperature in a nitrogen atmosphere with 130 ml gaseous acetone per liter of gaseous N_2. For comparison, the dye profile of a sample thermally annealed sample for 4 hours at 92 ^{o}C is also shown. Before the anneal we observed a dye profile mainly governed by the SIMS resolution limit. After the anneal process, the dye distribution was essentially flat throughout the film. The diffusion coefficient during the anneal process was 10^{-11} cm^2/s, higher than the diffusion coefficient at 135 ^{o}C in vacuum as shown in Fig. 5. In agreement with this observation is the estimated T_g derived from *in situ* thickness measurements of the polymer film by ellipsometry: From the volume change of the polymer film in air saturated with acetone (observed to be 28%), we estimated T_g to be -30 ^{o}C [19]. This is a drop of 150 ^{o}C from its initial value.
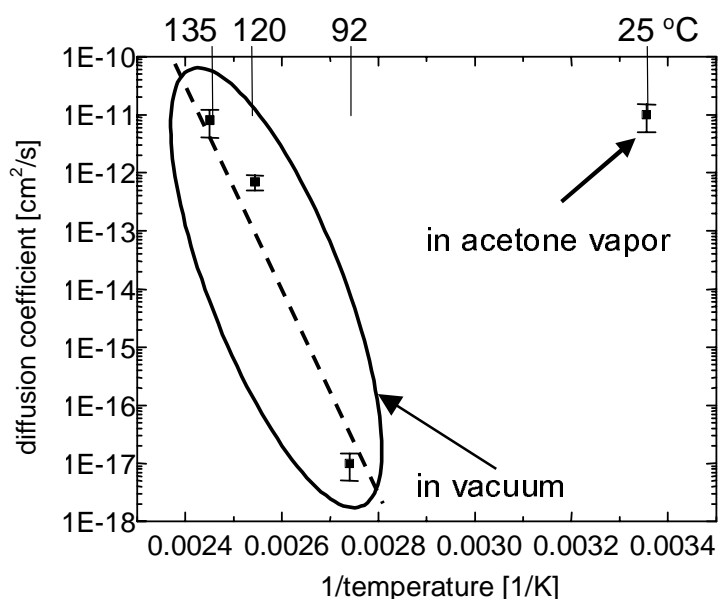

Figure 5. Diffusion coefficient of C6 in PVK in vacuum and in acetone vapor. The diffusion coefficient increases by many orders of magnitude in solvent vapor.

To investigate the effect of the solvent anneal on the electrical characteristics, we fabricated devices with a Mg:Ag (10:1) cathode (2 mm^2) thermally evaporated on top of the polymer film after the solvent anneal. The IV-characteristics along with the photocurrents of devices with the dye C6 already contained in the spin-on solution are shown in Fig. 6. These devices were subjected to the anneal in acetone vapor at room temperature without dye being added by the dye transfer step. The forward bias characteristics of the devices do not change significantly even after a 10 min anneal in acetone vapor (130 ml gaseous acetone per liter of gaseous N_2). However, the reverse current increased by roughly one order of magnitude.
For devices with dye transferred by dye diffusion we obtained very promising results, which is shown in Fig.7. As expected, the non-treated sample showed a very low photocurrent and thus a low quantum efficiency because the dye is still accumulated at the surface of the polymer film and is not active in the emission process. This is supported by the electroluminescence (EL)
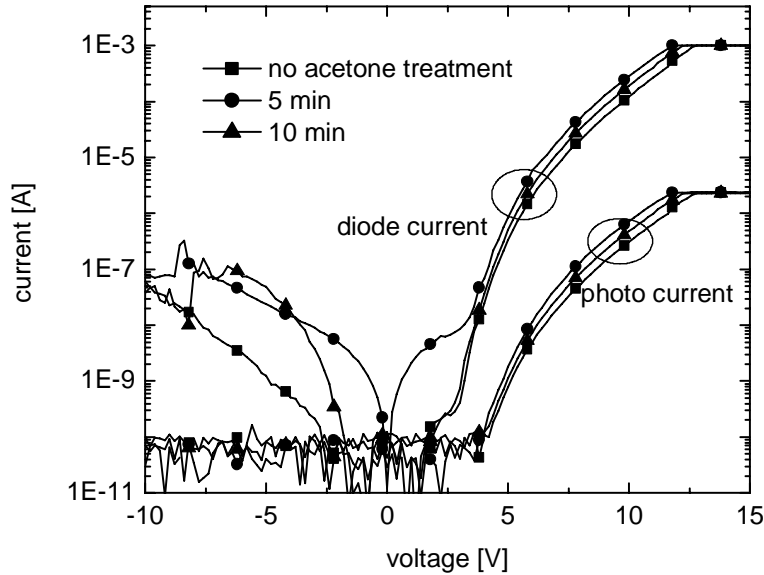
Figure 6. IV-characteristics of devices with C6 contained in the spun-on solution treated in acetone vapor for different times.

spectrum, which only shows emission from C47 (which was contained in the spin-on solution). After 60 sec acetone anneal, the ext. QE increases and the EL emission is shifted to green, indicating that C6 is moving into the polymer film. However, a small C47 peak is still observed in the EL spectrum due to insufficient dye in the recombination zone of the device. After a 4 min anneal, the dye is now homogeneously distributed throughout the polymer film. The EL emission originates now entirely from C6 and the ext. QE improved by nearly an order of magnitude. The ext. QE of these devices is comparable to those of devices with dye contained in the spin-on solution. Additional optimization of the dye transfer is necessary to raise the ext. QE further. Similar results were obtained using Nile red as the transferred dopant.
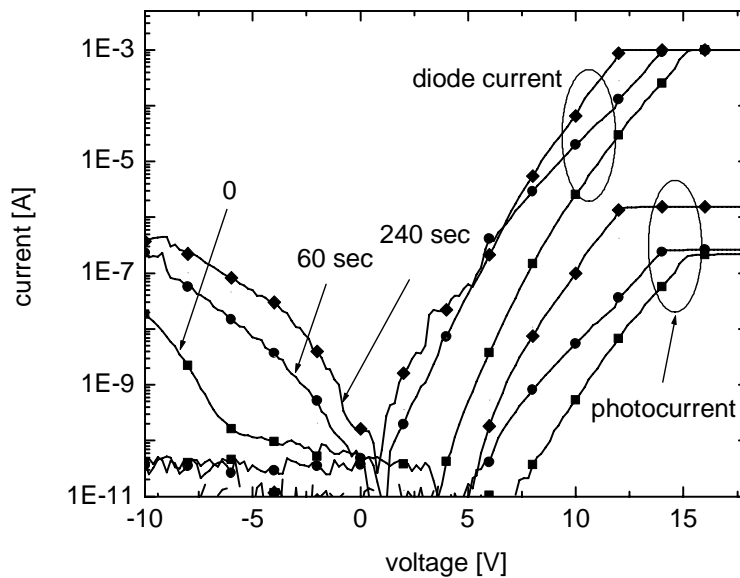

Figure 7. IV-characteristic of devices with C6 diffused into the polymer film. The photo-current of the device exposed to acetone vapor increased by nearly one order of magnitude.

SUMMARY

In conclusion, we have fabricated dye-doped OLEDs by a two-step process of 1) a dye transfer at 70 ^{o}C and 2) an anneal in solvent vapor at room temperature. During the solvent-vapor treatment, the diffusion coefficient of the polymer film increases by many orders of magnitude. This enables rapid redistribution of dye throughout the polymer film. No deterioration of turn-on voltage or efficiency due to the solvent anneal process was observed. The dye-doped devices show comparable efficiencies compared to devices fabricated using a spin-on polymer solution containing the same dye.

ACKNOWLEDGEMENT

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