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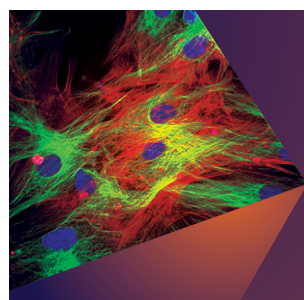


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Graded doping profiles for reduction of carrier trapping in organic light-emitting devices incorporating doped polymers

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Dispersing emissive dopants into luminescent polymers is an effective approach to enhance luminescence and to tune emission color in organic light-emitting devices incorporating polymer films. However, the carrier trapping effect due to emissive dopants often causes deterioration of electrical characteristics. In this letter, we show that, by introducing a graded doping profile to match the carrier recombination zone in the doped polymer, the carrier trapping, and the deterioration of electrical characteristics can be minimized while the enhancement in efficiency maintains. The finite-source dye-diffusion thermal transfer is used to produce graded doping profiles into a luminescent polymer. The effectiveness of this approach has been demonstrated in both single-layer and heterostructure devices incorporating doped polymers. © 2001 American Institute of Physics. [DOI: 10.1063/1.1344223]

Emissive doping, either fluorescent or phosphorescent, is an important technology for organic light-emitting devices (OLEDs) based on molecular or polymeric materials, for tuning emission colors and for enhancing device efficiency.^{1–7} Emissive dopants, however, can also function as carrier traps and degrade the transport properties of carriers, leading to the increase of the operation voltage of devices.^{1,6–10} In molecular OLEDs fabricated by vacuum deposition, the effect of carrier trapping due to emissive dopants can be reduced by doping only in the necessary region, i.e., the carrier recombination zone.¹ In OLEDs incorporating molecularly doped polymers (MDPs), the conventional blending process can only produce uniform dispersion of dyes throughout the polymer layer, providing no spatial selectivity. Alternatively, the doping of polymer films can be performed after the film formation using the recently proposed and demonstrated thermal transfer processes.^{11–13} Such thermal transfer processes have been applied to produce lateral dye patterns into polymer films for color integration in OLED devices or displays. Beyond the lateral modulation of dopant distribution, the capability of the thermal transfer process to produce graded doping profiles has not been explored for different designs of device architectures. In this letter, we report that with properly graded doping profiles produced by the thermal transfer process, it is possible to confine the dopant distribution mostly around the carrier recombination zone in the MDPs. As a result, the effect of carrier trapping due to emissive dopants is minimized in OLEDs incorporating MDPs.

Two types of device structures studied are shown in Fig. 1. Both have the structure of glass/indium–tin–oxide (ITO) anode/hole-injection layer/active organic layer(s)/Mg:Ag cathode/Ag protection layer, where the conducting polymer

polyethylene dioxythiophene/polystyrene sulphonate (PEDT/PSS, Bayer Corp.) was used as the hole-injection layer. In the single-layer structure [Fig. 1(a)], the thermally stable, hole-transport, and deep-blue-emitting polymer poly(N-vinylcarbazole) (PVK) was used as the host polymer in the MDP.^{14,15} Coumarin 6 (C6, green) was used as dye dopants. The shades in the MDP layer indicate the graded concentration of dopants, decreasing from the top of the MDP layer. Since PVK is mainly hole-transport, owning very limited electron-transport capabilities,^{14,15} it is expected that in the single-layer structure, the carrier recombination zone be closer to the cathode due to the highly unbalanced transport properties of holes and electrons. Thus, only dopants near the cathode would contribute to emission, while dopants away from the cathode may solely function as carrier traps. It is therefore speculated that with properly graded doping profiles, a compromise may be achieved between the emission efficiency and the electrical characteristics. Even so, the device efficiency may still be limited by the quenching effect of the cathode on neighboring excitons. The mitigation of this possible problem requires moving the recombination zone away from the cathode by forming a heterostructure as shown in Fig. 1(b), where a layer of 3-(4'-tert-butylphenyl)-

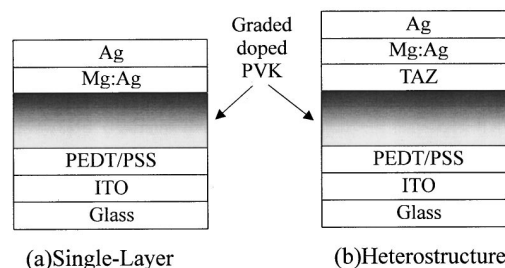


FIG. 1. Configurations of OLEDs incorporating doped PVK with graded doping profiles: (a) single-layer structure: ITO||PEDT:PSS (300 Å)||doped PVK (1000 Å)||Mg:Ag||Ag; (b) heterostructure device: ITO||PEDT:PSS (300 Å)||doped PVK (1000 Å)||TAZ (450 Å)||Mg:Ag||Ag.

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4-phenyl-5-(4''-biphenyl)-1,2,4-triazole (TAZ) is deposited on top of PVK as the electron-transport and hole-blocking layer.¹⁶ In all these structures, the PEDT/PSS layer and the PVK layer were prepared by spin coating and the thicknesses were kept at ~ 300 and ~ 1000 Å, respectively. The ~ 450 Å TAZ was deposited at a rate of ~ 4 Å/s by thermal evaporation in a vacuum of $\sim 10^{-6}$ Torr. All the thermal transfer experiments, device fabrication, and characterization were performed in air.

The graded doping profile into the PVK layer was introduced by the finite-source dye-diffusion thermal transfer (FS-D2T2) process,¹² prior to the deposition of following layers. In this process, the pure PVK receiver film (~ 1000 Å) is placed in direct contact with the dye-dispersed PVK donor film (also ~ 1000 Å) to permit direct dye-diffusion thermal transfer at elevated temperatures. Previous theoretical and experimental studies indicate that this doping process can be modeled by Fick's diffusion theory and that a desired dopant distribution from shallow to flat profiles may be obtained in a single transfer step by adjusting the diffusion conditions, i.e., time and temperature.¹² In this study, an initial C6 concentration of 3 wt. % in the source was used. It would give the maximum concentration in the doping profile of 1.5 wt. %. Four conditions for preparing the PVK layers in both device structures were used to produce different doping profiles in the receiver PVK film: (I) purely annealing at 240 °C, 4 min, (II) annealing at 240 °C, 4 min, followed by FS-D2T2 at 220 °C, 30 s, (III) annealing at 240 °C, 4 min, followed by FS-D2T2 at 220 °C, 1 min, and (IV) FS-D2T2 at 240 °C, 4 min. Condition (I) is used for the undoped sample, (II) and (III) for shallow doping profiles, and (IV) for a flat doping profile. The devices made from these films are correspondingly labeled as S-I to S-IV for single-layer devices, and H-I to H-IV for heterostructure devices. These temperatures were chosen to obtain practical transfer rates in high- T_g (glass transition temperature) polymer PVK.¹² The 4 min annealing at 240 °C prior to the FS-D2T2 process for the undoped and shallow doped samples was introduced to minimize the difference in thermal budgets received by different samples. It was carefully examined to ensure that pure PVK films undergoing purely thermal treatments as in (I)–(IV) all give the same electrical characteristics and that these thermal treatments do not degrade the fluorescence intensities of PVK and dyes in PVK within our experimental variation. Therefore differences in the characteristics of device (I)–(IV) of both structures can be clearly attributed to the variation in doping profiles. Figure 2 shows the dye profiles in the PVK films doped under conditions (II)–(IV), calculated from Fick's diffusion theory using diffusion coefficients extracted from the measured ratio of dyes transferred. The ratio of dye transferred was determined from the absorption intensities of dyes in receiver films.¹² The extraction of diffusion coefficients was then carried out by the least-square fitting of the experimentally measured ratios of dyes transferred versus diffusion time at different diffusion temperatures, as shown in the inset of Fig. 2.

Figure 3 compares the spectral, current–voltage (I – V) and brightness–current (L – I) characteristics of undoped, shallow and fully doped single-layer devices. The electroluminescence (EL) spectrum of device S-I is purely PVK

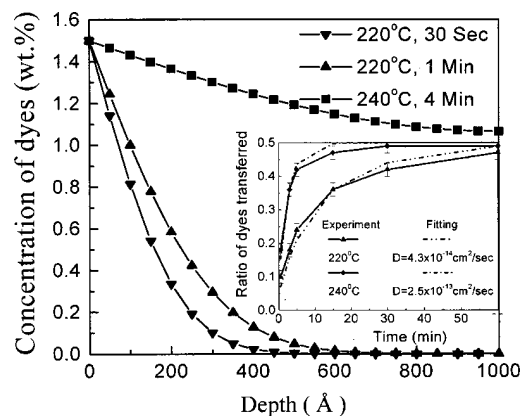


FIG. 2. Dye profiles calculated from Fick's diffusion theory using diffusion coefficients extracted from the thermal transfer data shown in the inset. The inset: the ratio of dyes transferred vs diffusion time at different diffusion temperatures, along with the least-square theoretical fitting.

emission. EL of S-II exhibits contributions from both PVK and C6. EL of S-III and S-IV show only dye emission, the same as the conventional blending device containing 1.5 wt. % of C6. It indicates that the doping profile in S-II is not yet deep enough to cover the whole carrier recombination zone and therefore there is still emission from PVK. In contrast, the profile in S-III is deep enough for C6 to dominate the emission. These data also confirm that the carrier recombination in the single-layer structure is indeed close to the cathode side. Compared to the undoped device, the I – V char-

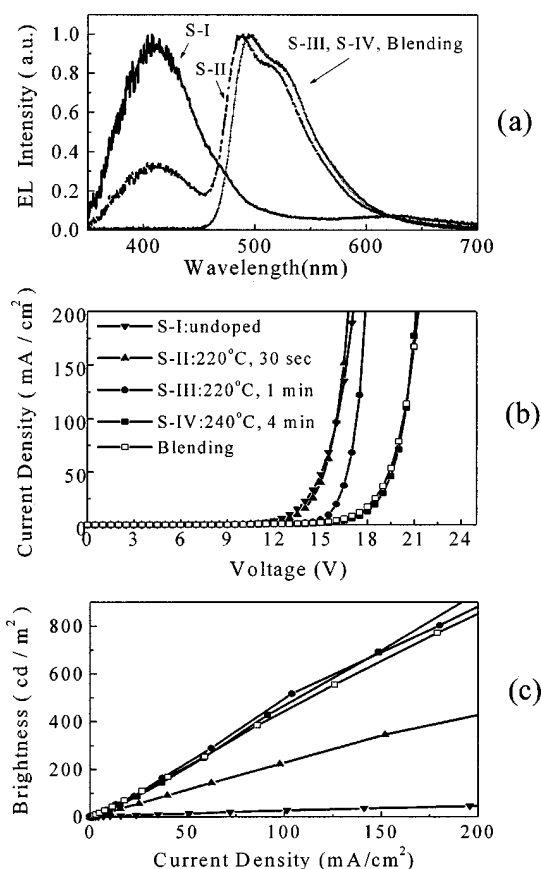


FIG. 3. Comparison of device characteristics of single-layer devices with various doping profiles: (a) EL spectra; (b) I – V characteristics; and (c) L – I characteristics.

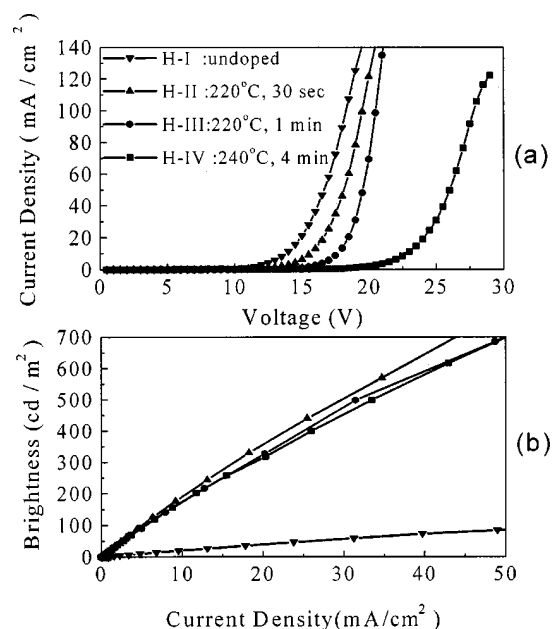


FIG. 4. Comparison of device characteristics of heterostructure devices with various doping profiles: (a) I - V characteristics and (b) L - I characteristics.

acteristics of the fully doped device shifts to a substantially higher voltage, similar to the conventional dye-blended device. In contrast, the I - V characteristics of the shallow doped devices only show a slight shift. These verify that the carrier trapping is serious in the fully doped device and that it can be largely reduced by graded doping. The external quantum efficiencies are 0.05% for device S-I, 0.1% for device S-II, and 0.2% for the S-III, S-IV, and dye-blended devices, respectively. The efficiencies of device S-III and S-IV are higher than that of device S-II, consistent with the picture that the more emission from the efficient dopants the higher the efficiency. In summary, by optimizing the graded doping profiles to match the recombination zone in the hole-transport PVK layer, the luminescence in devices is enhanced, while the voltage shift due to the carrier trapping effect of dye dopants can be minimized. In addition to optimizing device performance, the graded doping may also be used to probe the behaviors of carriers in doped polymers. The transition of EL characteristics from S-II to S-III, as shown in Fig. 3(a), provides a good example of using the depth of the graded doping to sense or to estimate the recombination or emission zone in doped polymers.

Figure 4 compares the I - V , L - I characteristics of heterostructure devices containing undoped, shallow and fully doped PVK layers. In I - V characteristics, an increase in the voltage shift with the depth of doping profiles as in the single-layer devices is observed. In the L - I characteristics, all the shallow and fully doped devices show nearly the same L - I characteristics and the same efficiency of $\sim 0.8\%$ – 0.9% . The insertion of the electron-transport and hole-blocking layer TAZ largely enhances the efficiency, presumably due to the enhancement of electron injection and the suppression of the cathode quenching. Interestingly, unlike single-layer devices, the shallowest doped device (H-II) also gives nearly the same L - I characteristics and efficiency as H-III

and H-IV. It suggests that the recombination zone in the heterostructure be narrower than that in the single-layer structure, so that a shallower doping profile is enough for covering the whole recombination zone. It is consistent with the fact that all H-II, H-III, and H-IV devices actually show the same C6-dominated EL spectra.

Since the introduction of graded doping relies on thermal diffusion of dopant molecules, one may be concerned about diffusion of dyes during device operation and consequent change or degradation of device characteristics. While such concerns need further examination, one usual strategy of “freezing” dopants during device operation would be to have the required diffusion temperatures far apart from the operation temperatures and to make the diffusion a highly thermally activated process. This may be realized by combining host polymers owning very high T_g 's and dopant molecules of proper sizes and structures.^{17,18}

In conclusion, we have used the thermal transfer process to introduce graded doping profiles into luminescent polymers. By matching the graded doping profiles with the carrier recombination zone in OLEDs incorporating doped polymer, the carrier trapping and the deterioration of electrical characteristics due to emissive dopants can be minimized. Meanwhile, the enhancement of device efficiency due to emissive dopants maintains. Furthermore, graded doping may provide a means for sensing the behaviors of carriers in OLEDs containing doped polymers.

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