Fabrication of highly efficient polymeric phosphorescent light-emitting devices with Laser Induced Thermal Imaging (LITI) technique

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Abstract

We report highly efficient phosphorescent-dye-doped polymeric light-emitting devices. The devices consist of a polymeric light-emitting layer comprising the phosphorescent dye, host, and matrix polymers. We patterned the phosphorescent-dye-doped polymeric layer with the LITI technique. The devices showed high efficiencies and good pattern quality to adapt to the development of full-color electroluminescent (EL) devices.

1. Introduction

The report of highly efficient phosphorescent organic light-emitting diodes (OLED) has been attracted much interests to realize a large area display with the organic electroluminescent devices [1]. The phosphorescent devices with thermal evaporation showed very high efficiencies, which utilize both singlet and triplet states. Recently, highly efficient polymeric light emitting diodes (PLED) doped with the phosphorescent dye were also reported [2,3]. The polymeric electro-luminescent materials have potentials to adapt to fabricate the light-emitting devices owing to their good processability, which can be coated on the large substrate by spin coating process. Although the materials have good processabilities, it is not easy to pattern each colors of red, green, blue onto pixelized substrate. Conventional ink-jet technology has been applied to pattern the polymeric layers in fabricating the polymeric light-emitting device [4]. Recently, we developed a unique technique to transfer polymeric layers onto patterned indium tin oxide (ITO) substrates. We have succeeded in fabricating a full color polymeric light-emitting device with the LITI technique [5]. Here, we report the formulation of the laser-patternable phosphorescent-dye-doped polymeric light-emitting layers, the structure of the devices and the characteristics of the devices.

2. Experiment

Poly(vinyl carbazole) (PVK) purchased from Sigma-Aldrich was used as a matrix polymer. 4,4'-*N,N'*-dicarbazole-biphenyl(CBP) and tris(2-phenylpyridine) iridium [$Ir(ppy)_3$] were supplied by Universal Display Corporation (UDC) and used as the triplet host/guest materials. Toluene was used as a solvent to make a solution of the CBP and PVK. Dichloroethane(DCE) was used as a solvent in the $Ir(ppy)_3$ solution. All the solvents were also purchased from Sigma-Aldrich and used as received. Each solution was stirred at a temperature of 60°C for at least 24 hours. The blendings of the matrix polymer, triplet host, and dopant were mixed in an appropriate mass ratio. This blended solution was sufficiently stirred at a room temperature (25°C) for at least three hours to make a homogeneous blending.

ITO with $4mm^2$ of active area for the conventional spin-coated test devices and patterned ITO (80μm width, 0.56 aperture ratio) with $4.6mm^2$ of active area for the LITI devices were imaged with photo-lithography process. The ITO substrates were cleaned by ultrasonication dipped into acetone and isopropylalcohol. A hole transporting layer made of a "PEDOT/PSS" from Bayer AG is coated on the substrate. The PEDOT layer was spin-coated on a UV-O_3 treated ITO with a thickness of 60nm. The light-emitting polymeric composition containing the phosphorescent dye was spin coated on the PEDOT-coated ITO substrate to make a conventional spin-coated device to a thickness of 25 ~ 40nm. The thickness of the PEDOT and the light-emitting layer were measured by a surface profiler ("α-step", Tenco Instrument Co.). In case of fabricating the LITI devices, the light-emitting polymeric layers were spin-coated on a transfer film, so called "donor film", and transferred to the patterned ITO substrates using the laser transfer technique. The LITI process are

described elsewhere [5]. The donor film converts laser energy to heat, which makes it possible to pattern the polymeric layers to the ITO substrates. After annealing the light-emitting layer on the hot plate, bis-(2-methyl-8-quinolinolato)-4-(phenyl-phenolato)-aluminium-(III) ($BAlq_3$) and tris-(8-hydroxy-quinoline)-aluminium (Alq_3) layers were deposited sequentially by thermal sublimation in a vacuum of $\sim 1\times10^{-6}$ Torr and used as a hole-blocking and electron transporting layers, respectively. LiF and Al were deposited by thermal evaporation and used as the cathode of the device. The device structure consists of ITO / PEDOT (60nm) / CBP:PVK: $Ir(ppy)_3$ (25~40nm) / $BAlq_3$ (5nm) / Alq_3 (5~20nm) / LiF(1nm) / Al (300nm) as shown in Figure 1. Finally, an encapsulation process was performed to protect the devices from the penetration of moisture and oxygen. The luminance-current-voltage (L-I-V) characteristics of the devices were measured using a spectrophotometer (Photo Research, PR 650) and a high current source measure unit (Kiethly 238).

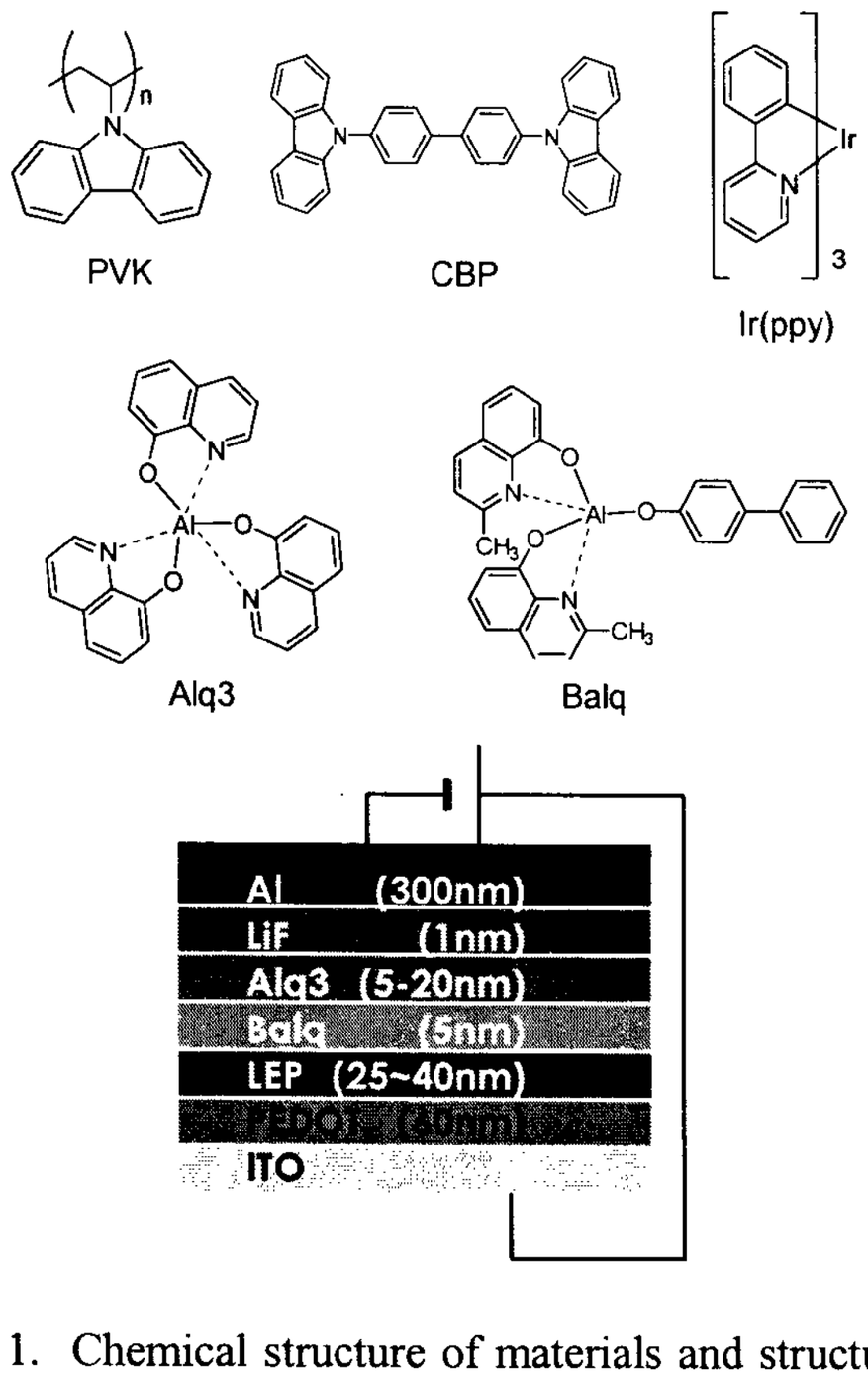


Fig. 1. Chemical structure of materials and structure of the PLED device.

3. Results and Discussion

First we determined the optimal weight ratio of the dopant in the matrix to get an efficient energy transfer from the host and chose a matrix polymer to give a uniform coating quality. Then, the selection of a process window that resulted in a good pattern quality was followed. Finally, we optimized the process of device fabrication and the structure of the devices with high efficiency.

3.1 Energy transfer from the host

CBP has been chosen as a host material that can be dissolved in organic solvents. Optically inert polymers such as polystyrene, poly(methyl methacrylate), polyacenaphthylene, and poly(vinyl carbazole) were used as a matrix polymer which bound the low molecular weight material in the light-emitting layer and gave a good quality of the spin-coating process. Among the optically inert, we used a PVK as the matrix polymer because of its good hole transporting ability and compatibility with the low molecular weight materials. By increasing the weight ratio of $Ir(ppy)_3$ in a fixed host material, we determined the process window for the spin-coating process to show a uniform film quality and optimized the ratio of the dopant for the sufficient energy transfer of $Ir(ppy)_3$ from CBP. Fig. 2 illustrates the emission spectrum of PVK, CBP, and blended film of CBP/PVK/$Ir(ppy)_3$, which proves a complete "Dexter" energy transfer of the dopant from the host [3]. The optimal weight ratio of the dopant was 3~10% to the CBP weight as reported elsewhere [6].

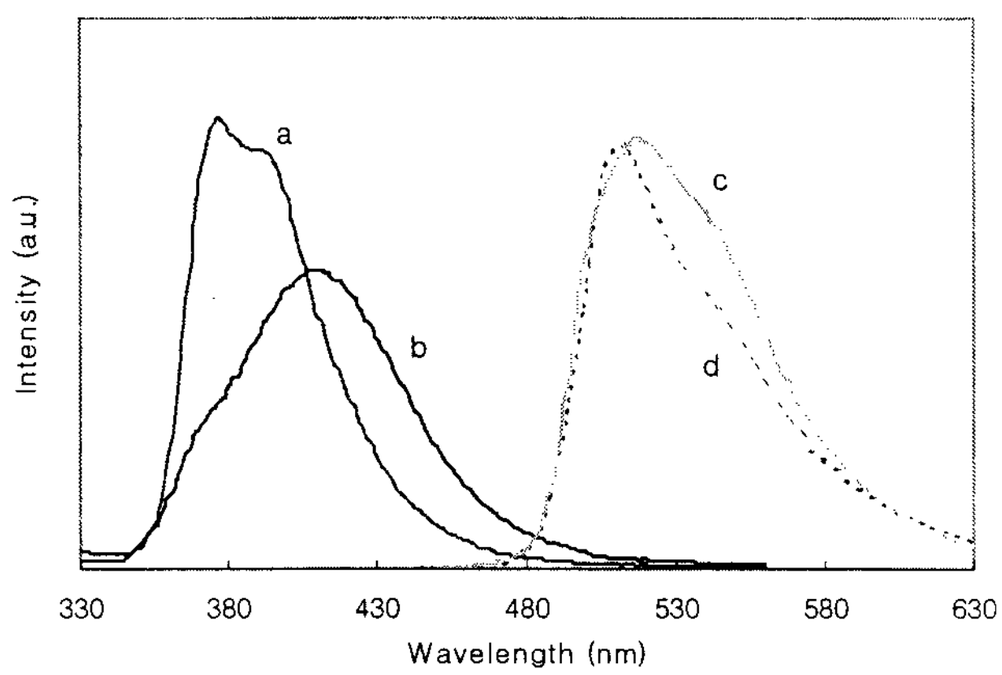


Fig. 2. The emission spectrum of the materials (a: PL spectra of CBP, b: PL spectra of PVK, c: PL spectra of blended films of CBP/PVK/$Ir(ppy)_3$, d: EL spectra of blended films of CBP/PVK/$Ir(ppy)_3$.

3.2 Pattern quality by the LITI process

The formulation of the laser-patternable phosphorescent-dye-doped polymeric light-emitting layers includes three components; an optically inert matrix polymer, a host material having a low molecular weight, and a triplet dopant. It is necessary for the spin-coating process to incorporate the polymeric moiety, because most of the low molecular weight materials show poor solubility and coating quality. But, in terms of the pattern quality of the layers by the LITI process, we need an optimization of the components in the light-emitting layer. Fig. 3 is a schematic view illustrating a laser transfer process for patterning a light-emitting layer. Referring to Fig. 3, an organic film is formed on a donor film, a laser beam is irradiated to the film, so that the organic film separated from the film and transferred to a patterned ITO. Here, parameters that determine a transfer characteristic include an adhesion between the donor film and the organic film, a cohesion between elements of the organic films, and an adhesion between the organic film and the patterned ITO. As the cohesion between the elements of the organic film becomes smaller than the adhesion between the respective substrates and the organic film, the better pattern quality we can get. Since the polymer film has a high molecular weight, the cohesion between elements of the polymer film is relatively large. However, the transfer characteristic of the polymer film can be improved by lowering the cohesion between the polymeric film and/or raising the adhesion between the substrate and the polymer film. The incorporation of the materials having a low molecular weight lowers the cohesion between elements of the polymer film without greatly lowering the adhesion between the substrate and the polymer film. Consequently, the transfer characteristic of the polymer film can be improved.

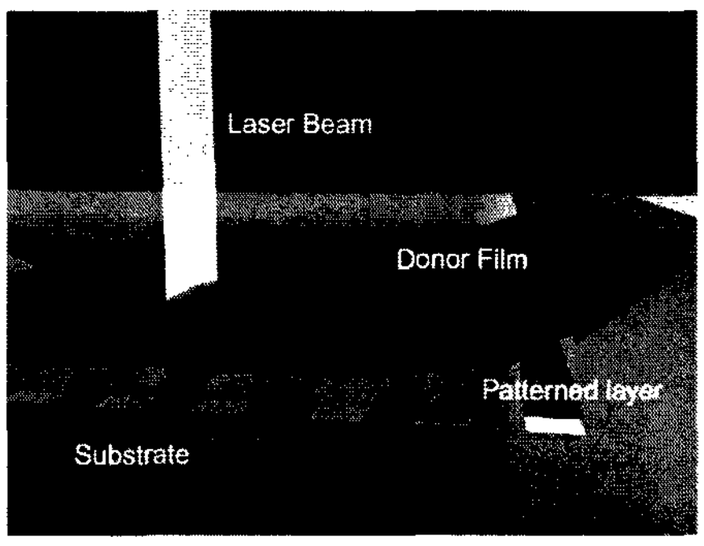
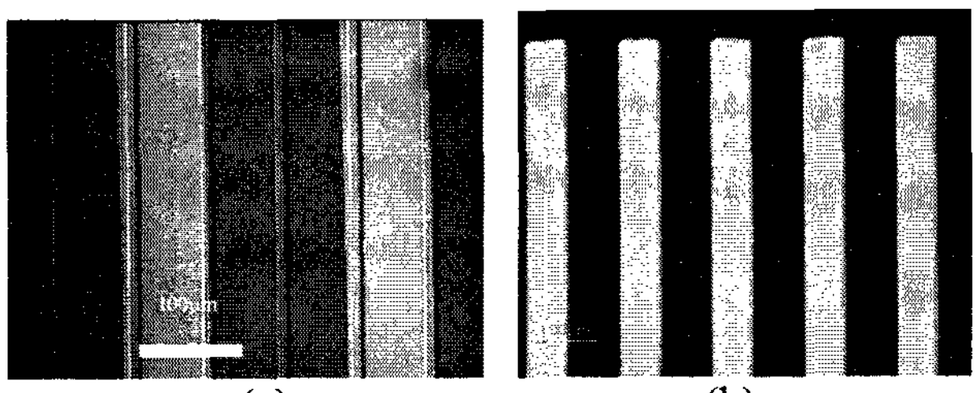


Fig. 3. Schematic diagram of the LITI process.

By varying the weight ratio of the CBP, PVK, and $Ir(ppy)_3$, we determined the process window for the LITI process and optimized the device structure for the EL performances. We fixed the ratio of the dopant as 5% of $Ir(ppy)_3$ to CBP, because the composition showed a sufficient energy transfer from the host. The spin-coated layer of the optimized solution with (CBP:PVK:$Ir(ppy)_3$ showed a good film quality. The spin-coated layer of the phosphorescent-dye-doped polymer on the donor film was transferred to the patterned ITO with the scanning of the laser. The image pattern of the light-emitting layer on the patterned ITO coated with PEDOT was excellent as shown in Figure 4. The edge roughness of the imaged line, which is defined as the difference between the maximum line width and minimum line width, is less than 5 μm. A large amount of the CBP and $Ir(ppy)_3$ in the mixture resulted in a bad coating quality because of low solubility. The optimal blending ratio of CBP for the edge roughness and good coating uniformity was in the range of 50% ~ 70% to the PVK matrix for the CBP amount when the relative ratio of the dopant in CBP was 5%.



(a) (b)

Figure 4. Microscope image of the patterned light-emitting layer on the ITO coated with PEDOT by the LITI process (a), and the light-emitting image of the devices (b).

3.3 Device characteristics

The structure of the LITI device was quite identical with the spin-coated device except the shape of the ITO pattern. The characteristics of the LITI devices were almost same as the spin-coated device. Therefore, we optimized the blending ratio of the light-emitting layers using the spin-coated devices with the same structure. For an organized analysis of experiments, we used a design of experiments (DOE). The annealing temperature was one of the main factors to determine the performance of the devices. At a high temperature above 130°C, there showed a crystallized region in the films because of the low T_g

of CBP. The optimal thickness of the light-emitting layer is very similar to that of the conventional devices with a thermal evaporation method [7]. The blending ratio of CBP/PVK was the main factor for the driving voltage and the thickness of Alq3 was the main factor for the efficiency. At the optimal condition of the device, the performance of the spin coated devices showed very high efficiencies compared to a conventional polymeric green emitter. Fig. 5 is a graph illustrating the luminance-current-voltage (L-I-V) characteristics of the optimized devices. The efficiency of the devices reached 25 Cd/A (9 lm/W) at 500 Cd/m^2 (CIE x=0.28, y=0.63).

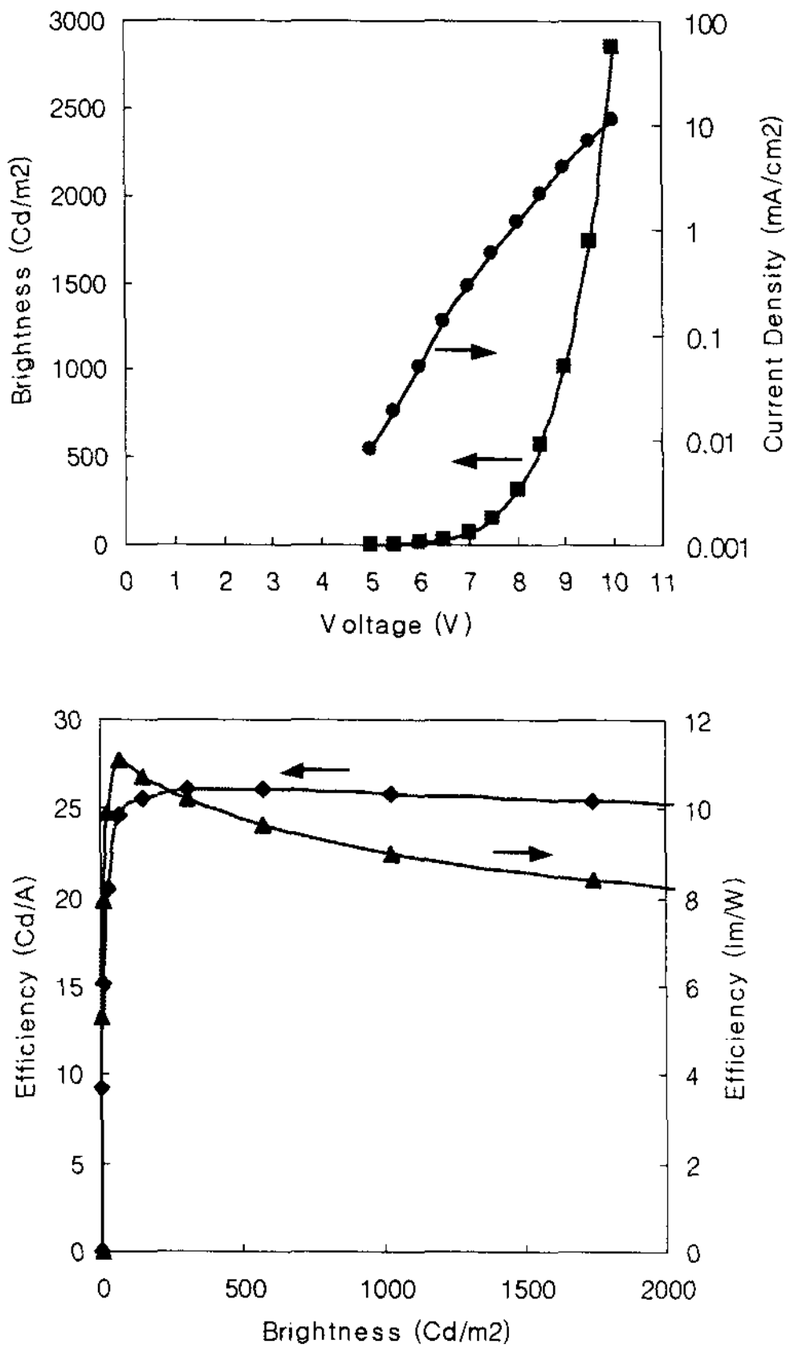


Fig. 5. Luminance-current-voltage (L-I-V) characteristics of the optimized devices.

4. Conclusions

We fabricated highly efficient phosphorescent EL devices by the spin-coating process. The performances of the devices including efficiency and working voltage were much better than other polymeric light-emitting device doped with the phosphorescent dye. The efficiency of the optimized devices reached 25 Cd/A (9 lm/W) at 500 Cd/m^2 (CIE x=0.28, y=0.63). The adaptation of the phosphorescent material into polymeric devices with the spin-coating process showed a possibility to fabricate an efficient EL device of large size. Furthermore, the LITI technique enables us to achieve full color EL devices with high resolution.

5. References

[1] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, and S.F. Forrest, *Nature*, **395**, 151(1998).

[2] S. Lamansky, R.C. Kwong, M. Nugent, P.I. Djurovich, and M.E. Thompson, *Organic Electronics*, **2**, 53 (2001).

[3] C.L. Lee, K.B. Lee, and J.J. Kim, *Materials Science and Engineering*, **B85**, 228 (2001)

[4] T. Shimoda, et al., *SID 1999 DIGEST*, p. 372 (1999).

[5] S.T. Lee, J. Y. Lee, M.H. Kim, M.C. Suh, T.M. Kang, Y.J. Choi, J.Y. Park, J.H. Kwon, and H. K. Chung, J. Baetzold, E. Bellmann, V. Savvateev, M. Wolk, and S. Webster, *SID 2002 DIGEST,* p.784 (2002).

[6] M.A. Baldo, S. Lamansky, P.E. Burrow, M.E. Thompson, and S.R. Forrest, *Applied Physics Letters*, **75**, 4 (1999)

[7] T. Watanave, K. Nakamura, S. Kawami, Y. Fukuda, T. Tsuji, T. Wakimoto, S. Miyaguchi, M. Yahiro, M. J. Yang, and T. Tsutsui, *Synthetic Metals*, **122**, 203 (2001).