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Study on Electron Injection of Phosphorescent Polymer Light-Emitting Diodes Utilizing CsF/Metal Cathode

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The effect of electron injection in polymer light-emitting diodes based on the phosphorescent material of fac-tris(2-phenylpyridine) iridium ($\text{Ir}(\text{ppy})_3$) devices with CsF/MgAg/Ag cathodes were investigated. The device with MgAg (1 nm)/CsF (3 nm)/Ag cathode showed almost similar current density-voltage-luminance characteristics to that with CsF (3 nm)/MgAg (1 nm)/Ag cathode. The existence of interface between the organic layer and Cs or CsF results in low turn on voltage. To achieve the efficient electron injection and the low turn on voltage, it is necessary to exist MgAg and CsF interface at the position of about 1 nm from organic layer. To achieve the efficient electron injection, it is necessary to exist Cs layer just on the organic layer. The electron injection effects between devices with CsF and Cs are different. It is suggested that the dipole of CsF affect the efficient electron injection.

Keywords: CsF; electron injection; metal interface; organic light-emitting diode; phosphorescent materials

1. INTRODUCTION

Phosphorescent organic light-emitting diodes (PHOLEDs) fabricated using phosphorescent dyes have demonstrated high external quantum efficiencies [1]. In order to realize high device performance, it is necessary

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to achieve highly efficient of electron injection from cathode. To achieve the high efficient electron injection, it is well established that the employed low-work-function metals [2]. MgAg is a classical example of electron contact for most organic materials [3]. K. M. Vaeth *et al.* reported highly efficient injection cathodes by inserting thin lithium fluoride (LiF) or cesium fluoride (CsF) between organic layer and cathode metals [4]. In the case of the devices with LiF contained cathodes, there are some reports about mechanisms that proposed for enhanced electron injection, including tunneling effect [5], band bending at the interface between organic layer and metal layer [6], lowering the work function of metal [7], formation of dipoles at the interface between organic layer and metal layer [8], and LiF dissociation with Li atoms and subsequent and generate organic anions [9]. In the case of the devices with CsF contained cathodes, there are also some reports about electron injection mechanisms [10,11]. However, detailed electron injection mechanism is still unclear.

In this study, we fabricated polymer light-emitting diodes (PLEDs) based on phosphorescent material of Ir(ppy)₃, and focused on the interface between CsF and metals at the cathode, and investigated the effect of the electron injection in PLEDs.

2. EXPERIMENTAL

Organic layers were fabricated by spin coating onto a glass substrate coated with patterned indium-tin-oxide (ITO) electrode. The patterned ITO-coated glass substrates were pre-cleaned by deionized water, chloroform, ethanol, acetone and cleaned in a ultraviolet (UV)-ozone chamber. First, a poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) hole injection layer was spun over the ITO-coated glass substrate with a 35-nm-thick layer and baked in air at 120°C for 10 min. The emitting layer which consists of the host poly(n-vinylcarbazole) (PVK), a dopant *fac*-tris(2-phenylpyridine) iridium (Ir(ppy)₃) and an electron-transport material 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) were dissolved in 1,2-dichloroethane. We fixed the weight ratios of the various materials PVK:PBD:Ir(ppy)₃ = 50:30:2%. The emitting layer was spin-coated to 90-nm thickness. The cathode consisting of CsF/MgAg/Ag was deposited in vacuum at a chamber base pressure of $< 10^{-4}$ Pa. Finally, the device was covered with a glass plate and encapsulated by epoxy resin in an argon gas atmosphere to prevent oxidation of the cathode and the organic layer. The active device area of 4 mm² was obtained using shadow mask. The current-voltage-luminance (I-V-L) characteristics were obtained using a 2000 multimeter (Keithley) and a luminance meter (Minolta, LS-100).

The forward bias condition was a positive bias with respect to the cathode. All measurements were carried out at room temperature in an inert gas atmosphere.

3. RESULTS AND DISCUSSION

The maximum luminance and the maximum current efficiency of devices for different thickness of CsF layer deposited on the organic layer are shown in Figure 1. The cathode was composed of CsF (0 ~ 10 nm)/MgAg (150 nm)/Ag (50 nm). The maximum luminance and current efficiency of non-CsF layer device were about 4,400 cd/m^2 and 18 cd/A , respectively. On the other hand, CsF layer was inserted into the interface between the organic layer and the MgAg layer, the device performances were markedly increased. The highest luminance and current efficiency were observed at CsF thickness of 3 nm. The maximum luminance and current efficiency of the device with 3 nm-thick CsF layer were about 38,800 cd/m^2 and 24 cd/A , respectively. However, CsF thickness increased more than 3 nm, the luminance and the current efficiency were decreased. It was seemed that the efficient electron injection was achieved because of the formation of the alloy of CsF and MgAg at the interface between the organic layer and the cathode metal. When the CsF thickness was more than 5 nm, it was seemed that the layered structure of CsF and MgAg layer was existence at the interface between the organic layer and the cathode metal. Thus, it was clearly that the decreases of the luminance and the current efficiency were depended on the insulation of CsF.

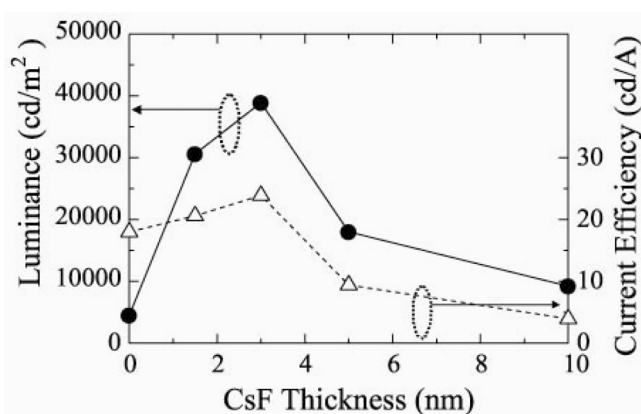


FIGURE 1 The maximum luminance and current efficiency of OLEDs for different thickness of CsF layer deposited on organic layer.

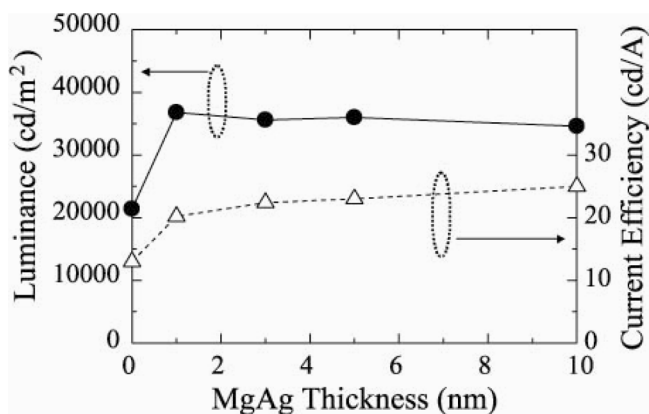


FIGURE 2 The maximum luminance and current efficiency of OLEDs for different thickness of MgAg deposited on 3 nm-thick CsF layer.

Figure 2 shows the maximum luminance and current efficiency of devices for different thickness of MgAg deposited on 3 nm-thick CsF layer. The cathode was composed of CsF (3 nm)/MgAg (0 ~ 150 nm)/Ag (150 nm). When the thickness of MgAg layer was more than 1 nm, the devices show almost the similar maximum luminance of 36,000 cd/m² and current efficiency of more than 20 cd/A. While, the non-MgAg layer device showed the maximum luminance of 21,400 cd/m² and current efficiency of 13 cd/A. From this result, we have confirmed that the efficient electron injection achieved when the thickness of MgAg deposited on CsF was more than 1 nm.

In order to understand the electron injection effects at the interface between CsF layer and MgAg layer, we investigated the devices with the cathode of variety deposition order of CsF and MgAg and compared with the device of Cs and MgAg cathodes. Figure 3 shows the I-V (a) and V-L (b) and I-current efficiency (E) (c) characteristics of devices with several cathode compositions. The compositions of cathode metals are following:

CsF (3 nm)/MgAg (1 nm)/Ag (150 nm) (device A); MgAg (1 nm)/CsF (3 nm)/Ag (150 nm) (device B); Cs (2 nm)/MgAg (1 nm)/Ag (150 nm) (device C); MgAg (1 nm)/Cs (2 nm)/Ag (150 nm) (device D); MgAg (1 nm)/Ag (150 nm) (device E).

Table 1 summarizes device performances of OLEDs with several cathode compositions. Compared with device A and B, both devices showed almost similar I-V, V-L and I-E characteristics. The maximum luminance of device A and B were 35,000 cd/m² and 32,000 cd/m² at

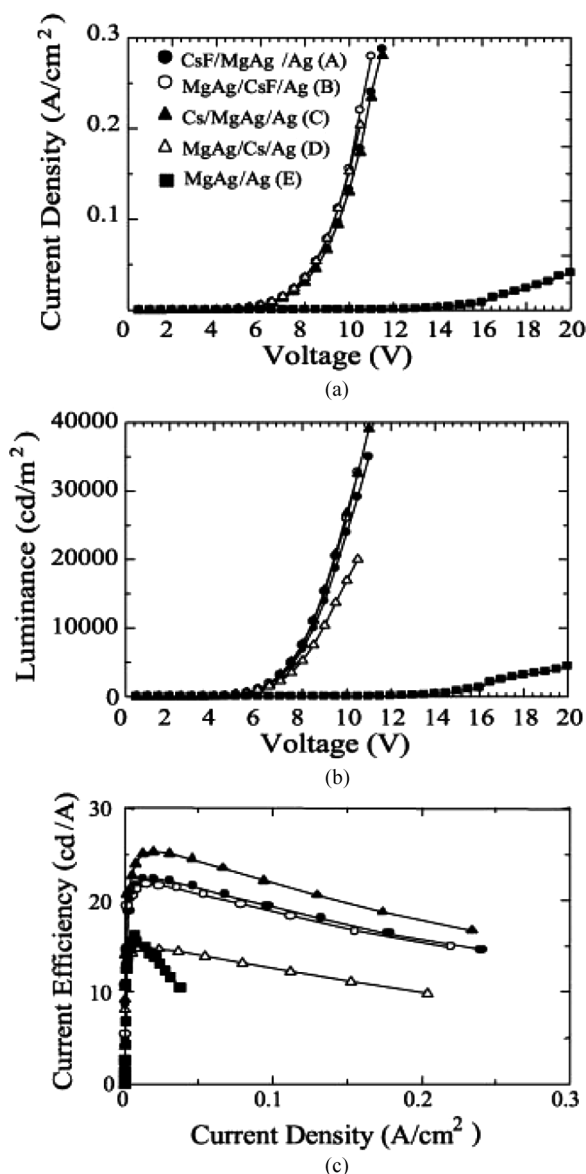


FIGURE 3 The voltage-current density (a) and voltage-luminance (b) current density-current efficiency (c) characteristics of the devices with several cathode compositions: CsF (3 nm)/MgAg (1 nm)/Ag (150 nm) (device A:●); MgAg (1 nm)/CsF (3 nm)/Ag (150 nm) (device B:○); Cs (2 nm)/MgAg (1 nm)/Ag (150 nm) (device C:▲); MgAg (1 nm)/Cs (2 nm)/Ag (150 nm) (device D:△); MgAg (1 nm)/Ag (150 nm) (device E:■).

TABLE 1 Device Performances of OLEDs with the Several Cathode Compositions, Including the Turn-on Voltage (Voltage at 0.01 cd/m^2) (V_{on}), the Maximum Luminance (L_{max}), Current Density (I) and Voltage (V) at L_{max} , the Maximum Current Efficiency (E_{max}), I and V at E_{max} and Current Efficiency (E) at 20 mA/cm^2

Device	Cathode composition	V_{on} (V)	L_{max} (cd/m^2)	(I, V)	E_{max} (cd/A)	(I, V) @	E @ 20 mA/cm^2 (cd/A)
				@ L_{max} (mA/cm^2 , V)		E_{max} (mA/cm^2 , V)	
A	CaF (3 nm)/ MgAg (1 nm)/Ag	3	35,000	(240, 11)	22.3	(13, 7)	21.8
B	MgAg (1 nm)/ CaF (3 nm)/Ag	3	32,700	(220, 10.5)	21.8	(14, 7)	19.3
C	Ca (2 nm)/ MgAg (1 nm)/Ag	3	39,000	(230, 11)	25.3	(20, 7.5)	25.3
D	MgAg (1 nm)/ Ca (2 nm)/Ag	3	20,000	(204, 10.5)	14.9	(15, 7)	14.6
E	MgAg (1 nm)/Ag	6.5	3,960	(37, 19.5)	16.2	(6, 15.5)	13.8

the current density of 240 and 220 mA/cm^2 , respectively. The maximum current efficiency of device A and B shows 23 and 22 cd/A at the current density of 15 and 20 mA/cm^2 , respectively. Both devices of A and B exhibited almost similar luminance and current efficiency. Compared with device E with non-CsF layer, the turn-on voltage (voltage at 0.01 cd/m^2) of both devices with CsF is markedly improved. This result suggests that the electron injection characteristics of both device A and B are improved by CsF effect. It is considered that the deposition order of CsF and 1 nm-thick MgAg is independent to achieve the efficient electron injection. And we have understood that to achieve the efficient electron injection and low turn-on voltage, it is necessary to exist MgAg and CsF interface at the position of about 1 nm from organic layer.

On the other hand, compared with device C and D, device D shows the obvious lower luminance and current efficiency than those of device C. While, compared with device D and E, the maximum luminance and the turn-on voltage of device D are improved, and the maximum current efficiency is almost same. It is known that the work function of Cs (1.9 eV) is much lower than that of both Ag (4.3 eV) and Mg (3.7 eV). The lower turn-on voltage of device C and D should be due to the reduction of the cathode work function. Four devices with Cs and CsF show same I-V characteristics. It is considered that lower current efficiency of device D results from the unbalance of the injected carrier. Taking the result of Table 1 into consideration, the electron

injection characteristics of device C is improved by Cs effect. In the case of device D, 1 nm-thick MgAg layer on the organic layer prevented electron from injecting from Cs layer to organic layer. That is, we found that to achieve the efficient electron injection, it is necessary to exist Cs layer just on organic layer. There are some reports that CsF deposited on organic layer is dissociated to free released Cs atoms [10,11]. And this released free Cs atoms behave as well as deposited Cs. However, from the result of Figure 3, it is considered that the behavior between deposited CsF and deposited Cs on organic layer is different. According to K. Seki *et al.*, for the deposition of LiF on organic layer, LiF do not dissociate and the dipole of LiF affect bending the band of organic layer leading to reduction of injection barrier [12,13]. These results suggest that the formed dipole of CsF on the organic leads to achieve the efficient electron injection.

4. CONCLUSION

We investigated the effect of electron injection in polymer light-emitting diodes based on the phosphorescent material of Ir(ppy)₃ devices with CsF/MgAg/Ag cathodes. When 3 nm-thick CsF were deposited on organic layer, highest device performances were achieved. When the thickness of MgAg layer deposited on 3 nm-thick CsF layer was more than 1 nm, the efficient electron injection was achieved. The device with MgAg (1 nm)/CsF (3 nm)/Ag cathode showed almost similar current density-voltage-luminance characteristics to that with CsF (3 nm)/MgAg (1 nm)/Ag cathode. The existence of interface between the organic layer and Cs or CsF results in low turn-on voltage. To achieve the efficient electron injection and the low turn-on voltage, it is necessary to exist MgAg and CsF interface at the position of about 1 nm from organic layer. To achieve the efficient electron injection, it is necessary to exist Cs layer just on the organic layer. The electron injection effects between devices with CsF and Cs are different. It is suggested that the dipole of CsF affect the efficient electron injection.

REFERENCES

- [1] Baldo, M. A., O'Brien, D. F., You, Y., Shoustikov, A., Sibely, S., Thompson, M. E., & Forrest, S. R. (1998). *Nature.*, 395, 151.
- [2] Brown, T. M., Friend, R. H., Millard, I. S., Lacey, D. J., Burroughes, J. H., & Cacialli, F. (2001). *Appl. Phys. Lett.*, 79, 174.
- [3] Tang, C. W. & VanSlyke, S. A. (1987). *Appl. Phys. Lett.*, 51, 913.
- [4] Vaeth, K. M. & Dicillo, J. (2003). *J. Polym. Sci. Part B.*, 41, 2715.
- [5] Hung, L. S. Tang, C. W., & Mason, M. G. (1997). *Appl. Phys. Lett.*, 70, 152.

- [6] Ihm, K., Kang, T. H., Kim, K. J., Hwang, C. C., Park, Y. J., Lee, K. B., Kim, B., Jeon, C. H., Park, C. Y., Kim, K., & Tak, Y. H. (2003). *Appl. Phys. Lett.*, *83*, 2949.
- [7] Shaheen, S. E., Jabbour, G. E., Morrell, M. M., Kawabe, Y., Kippelen, B., Peyghambarian, N., Nabor, M. F., Schlaf, R., Mash, E. A., & Armstrong, N. R. (1998). *J. Appl. Phys.*, *84*, 2324.
- [8] Baldo, M. A. & Forrest, S. R. (2001). *Phys. Rev. B*, *64*, 085201-1-085201-17.
- [9] Hung, L. S., Zhang, R. Q., He, P., & Mason, G. (2002). *J. Phys. D.*, *35*, 103.
- [10] Chan, M. Y., Lai, S. L., Fung, M. K., Tong, S. W., Lee, C. S., & Lee, S. T. (2003). *Appl. Phys. Lett.*, *82*, 1784.
- [11] Chan, M. Y., Lai, S. L., Fung, M. K., Tong, S. W., Lee, C. S., & Lee, S. T. (2004). *J. Appl. Phys.*, *95*, 5397.
- [12] Seki, K., Ito, E., & Ishii, H. (1997). *Synthetic. Metals.*, *91*, 137.
- [13] Yokoyama, T., Yoshimura, D., Ito, E., Ishii, H., Ouchi, Y., & Seki, K. (2003). *Jpn. J. Appl. Phys.*, *42*, 3666.