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Abstract:

The alkali and alkali-earth metals doping were widely investigated to improve the electroluminescence characteristics of organic light-emitting diodes (OLED). We study the effects of magnesium (Mg) incorporation in the transport layer, and also the emission layer of the OLED. A thermally deposited Mg has been inserted into the various positions, and the thickness was varied either. By the position and the thickness, the Mg made partially an electronic channel and made a leakage path ways. Resulted difference of initial maximum luminance distribution was observed. On the other hand, with the optimized inserting position and thickness of Mg, the OLED showed the improved EL characteristics.

Keywords: ORGANIC LIGHT EMITTING DIODES; ALKALI EARTH METAL; MAGNESIUM; INITIAL RESISTANCE; MAXIMUM LUMINANCE
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RESEARCH ARTICLE

Diffusion Characteristics and Induced Electronic Channels of Magnesium in Organic Light-Emitting Diodes

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The alkali and alkali-earth metals doping were widely investigated to improve the electroluminescence characteristics of organic light-emitting diodes (OLED). We study the effects of magnesium (Mg) incorporation in the transport layer, and also the emission layer of the OLED. A thermally deposited Mg has been inserted into the various positions, and the thickness was varied either. By the position and the thickness, the Mg made partially an electronic channel and made a leakage path ways. Resulted difference of initial maximum luminance distribution was observed. On the other hand, with the optimized inserting position and thickness of Mg, the OLED showed the improved EL characteristics.

Keywords: Organic Light Emitting Diodes, Alkali Earth Metal, Magnesium, Initial Resistance, Maximum Luminance.

1. INTRODUCTION

Since the first report of efficient organic electroluminescent device by Tang et al.,[1] the organic light emitting diodes (OLEDs) were widely investigated for its potential abilities which suffice to be the no. 1 candidate for the next generation flat panel display.[2] Recently, the remarkable achievements[3–4] were carried out followed by the historical research developments which improved the electroluminescent (EL) characteristics like the luminance, luminous efficiency, power efficiency, color purity, device life time, operating voltage, and etc.[5–6] The alkali or alkali-earth metal were used as the one of the key technique for improving the EL characteristics of OLEDs, such as lithium (Li) incorporated monolayer thin films for efficient charge transport,[7] lithium-fluoride (LiF) doped organic semiconductors for donated n-type charge carrier,[8] cesium doped organic thin films for manifesting gap states and saturation of the energy level shift,[9] these kinds of developments lowered the injection barriers and realized the efficient OLEDs.

However, the Li-doping method has a weakness which is due to the diffusion problems. The Li diffuses into organic thin films and react with some metal-centered molecular like tris-(8-hydroxyquionline) aluminum (Alq_3), and results the un-emissive islands, the low efficiency. We used magnesium (Mg) instead of Li. The Mg, which has work function of 3.82 eV,[10,11] is heavier than Li and it is not easy to be diffused into the organic thin films. We characterize the Mg diffusion and the related device characteristics by inserting the Mg thin layers into the various positions like EML and HTL, and also the thickness of Mg was varied. The analysis of the current density–voltage (J–V) characteristics and electroluminescence (EL) characteristics such as maximum luminance, luminous efficiency, power efficiency, EL spectra, and especially the relation between initial resistance and maximum luminance were used for the characterization.

2. EXPERIMENTAL DETAILS

The OLEDs having the structures of: in Figure 1, the glass substrate/indium-tin-oxide (ITO) transparent anode/Hole injection layer (HIL)/Hole transport layer (HTL)/Emissive

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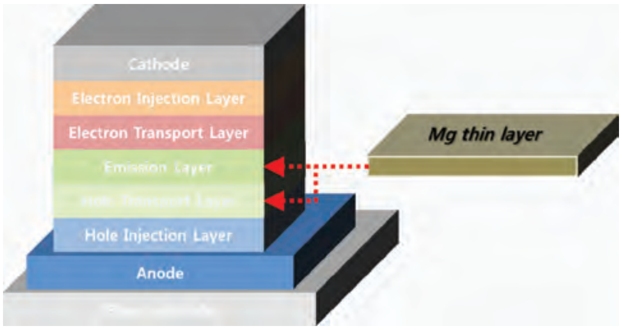

Fig. 1. Schematic structure of the fabricated devices. Mg thin layer was inserted into the EML and the HTL, respectively.

layer (EML)/Electron transport layer (ETL)/Electron injection layer (EIL)/Cathode were fabricated with the insertion of Mg thin layer. The thicknesses and positions of Mg thin layer were varied between 1 nm to 6 nm from EML to HTL. The *N*,*N*′-Bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine (α-NPB) was used as a HIL and also as a HTL, the thickness was 60 nm. The Alq_3 was used as an EML and also as an ETL. The thicknesses of those Alq_3 layers were 30 nm, respectively. The 1 nm of LiF was used as an EIL, and 150 nm of aluminum (Al) was used as a cathode.

For the fabrication of the OLEDs, the ITO coated glass ($\approx$30 $\Omega/\square$) was patterned by the photolithography, finely cleaned with solvents and de-ionized water with ultrasonication, blown dry in N_2, and oven-baked for dehydration. And the AZ1505 photo resist was patterned on it as an insulating layer by the photolithography to prevent the unwanted electrical short between the metal cathode electrode and the ITO anode electrode. The active emission area was defined by the insulating layer and the overlaying of two electrodes, 5 mm by 5 mm. All of the organic materials were deposited in vapor phase on the ITO coated glass substrate with the thermal evaporator. The organic materials were deposited at room temperature in high vacuum ($\sim 2 \times 10^{-6}$ Torr) with an evaporation rate of around 1.0 Å/s, and the metal electrode was deposited at the rate of around 10 Å/s. The film thickness and deposition rate were controlled by a programmable SID-242 thin film co-deposition controller (Sigma Instruments).

In total, 4 different devices were fabricated. One has no Mg inserted layer is control device, one other has double hetero structure of Mg inserted emissive layer (EML: Alq_3(5 nm)/Mg(1 nm)/Alq_3(5 nm)/Mg(1 nm)/Alq_3(20 nm)), and one another has single thick Mg inserted emissive layer (EML: Alq_3(5 nm)/Mg(6 nm)/Alq_3(20 nm)), and the last one has single thin Mg inserted HTL (HTL: α-NPB(5 nm)/Mg(1 nm)/α-NPB(55 nm)).

The current–voltage-luminance characteristics and the EL spectra of the OLEDs were measured with a Topcon BM-9 luminance meter and Keithely 237 source meter, and the EL spectra were measured by the Hitachi F-7000 spectrometer and general source meter.

3. RESULTS AND DISCUSSION

Figure 2 shows current density and luminance versus voltage characteristics of one control device and three Mg thin layer inserted devices. The Mg thin layer inserted device with inserting profile of double hetero structure shows highly improved luminance of 23,040 cd/m^2 at 400 mA/cm^2, which is about twice higher than that of the control device. This increased EL efficiency could be explained by the improved carrier transport by increased conductance and efficient recombination at quantum well made by double hetero structure of Mg. The Mg thin layer improves the electron transport by lowering the energy band and partially blocks the hole and as a result, the electron–hole recombination could be done effectively. The large improvement in current density after the device is turned on[12] and improved maximum luminance support above assumptions.

On the other hand, as the thickness of Mg increased or when the Mg thin layers were inserted into the HTL, the current density and luminance characteristics were decreased. The Mg affected on the operating voltage by increasing more than 5 V. This could be derived from the hole blocking property of Mg thin layer, just as other hole blocking material like 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), the hole injection barrier is high and the thickness of Mg is too thick to tunnel it, at the end the operating voltage has been increased.[13,14] In Figure 3, simplified diagram of hole blocking is illustrated.

In Figure 4, the EL spectra, the hole blocking property of Mg could be seen clearly. As the Mg insertion profile changed, the spectrum shifted into the region of

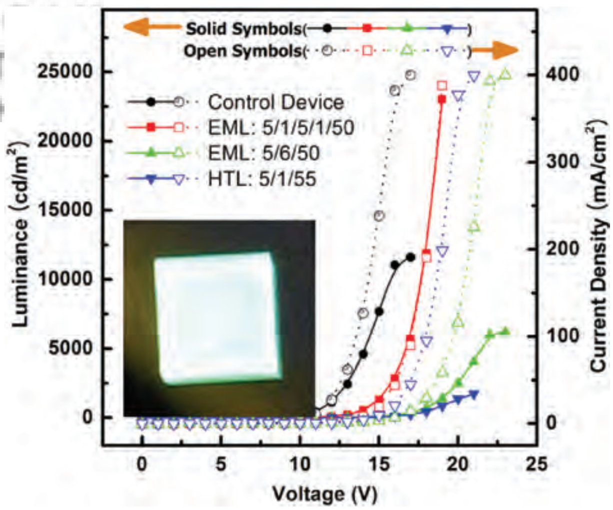

Fig. 2. Luminance and current density versus applied voltage characteristics. Solid symbols and solid lines represent the luminance and open symbols and dot lines represent the current density, (●○) control device, (■□) device with double hetero Mg inserted EML, (▲△) device with single thick Mg inserted EML, (▼▽) device with single thin Mg inserted HTL, respectively. Inset: emission image of the device with double hetero structure of Mg inserted EML at 100 cd/m^2.

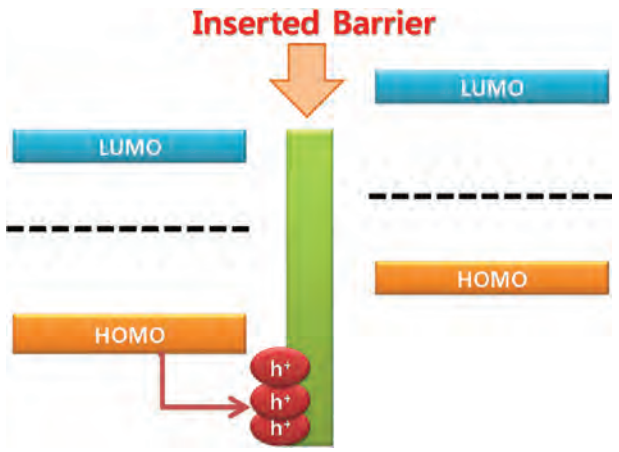

Fig. 3. Simplified diagram of hole blocking. Carrier accumulates at the interface of barrier.

shorter wavelength (blue-shift). When the Mg thin layer was inserted into the EML, the thicker Mg layer showed the larger shift. However, when the Mg thin layer inserted into the HTL, the EL spectrum shifted a lot more than the others. While the HTL has wider band gap, this spectrum shift must be oriented from the emission of HTL, which comes from accumulated carriers at the Mg interface. This blue-shifting truly shows the carrier blocking properties of Mg thin layer, which observed previously as increased operating voltage.

Figure 5 shows luminance efficiency and power efficiency versus luminance. The double hetero structure of Mg-thin layer inserted OLED showed highest EL efficiency of 6.61 cd/A, which is more than 50% higher

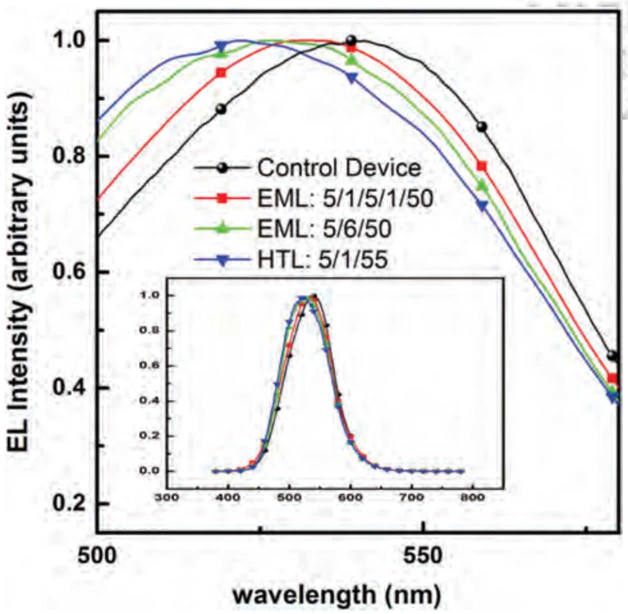

Fig. 4. Normalized EL spectra near peak wavelength range of fabricated devices. The symbols and lines represent same devices as in Figure 2. Inset: Normalized EL spectra in whole visible wavelength range.

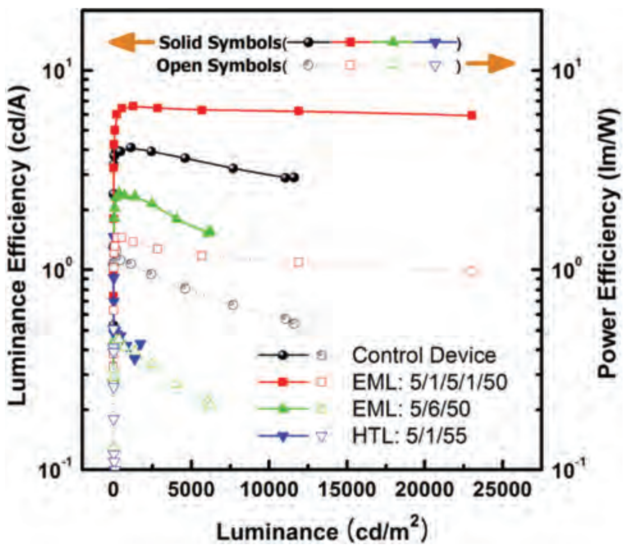

Fig. 5. Luminance efficiency and power efficiency versus luminance characteristics. The symbols and lines represent same devices as in Figure 2.

than control device. As the thickness of Mg thin layer increased in EML, the EL efficiency decreased. The thick Mg resulted the energy band banding and as a result, carrier and exciton accumulated at Mg interface, and non-radiative quenching of them occurs. This quenching at Mg is similar to the un-emissive quenching at the cathode electrode of some OLEDs.[5] When the Mg thin layer was inserted into HTL, the hard quenching was occurred and the EL efficiency was significantly decreased. This low EL efficiency could be explained by the carrier blocking property of Mg and resulted exciton accumulation between HTL/Mg interfaces. In this case, the HTL work as a dissociation layer of exciton rather than work as a carrier balancing layer.[15]

The Table I shows the comparison of EL characteristics of fabricated devices. Figure 6 shows the relation between the normalized maximum luminance by that of maximum versus normalized initial resistance by that of maximum, and the inset shows the un-normalized distributions of them. The distribution changed with thickness and position of Mg thin layer. The thicker Mg thin

Table I. Comparison of Mg thin layer inserted devices.

	EL characteristics		
Device structure	Maximum luminance (cd/m^2)	Maximum efficiency (cd/A)	Turn on voltage (V)
Control device	11,600	4.10	6.0
EML: Double hetero (5/1/5/1/50)	23,040	6.61	7.0
EML: Single thick (5/6/50)	6,190	2.42	10.0
HTL: Single thin (5/1/55)	1,730	1.47	8.0

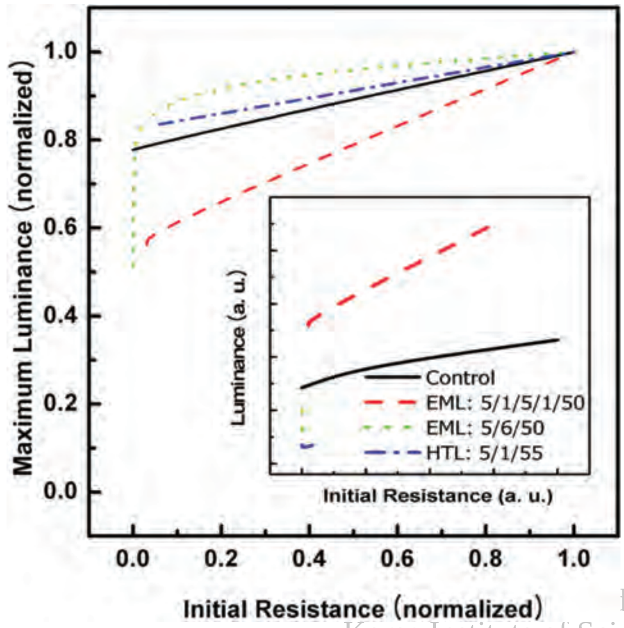

Fig. 6. Relation of normalized initial resistance and normalized maximum luminance. Each lines represent fabricated devices like, (solid line) control device, (dash) device with double hetero Mg inserted EML, (dot) device with single thick Mg inserted EML, (dash-dot) device with single thin Mg inserted HTL, respectively. Inset: relation in un-normalized units.

layer induced the lower initial resistance and narrow region of initial resistance. The inserted Mg, the diffusion of Mg induced the electrical path ways, the leakage path ways. This path ways reduces the device performance but could be treatable.[16] The reduced range of initial resistance means that the diffused Mg made partial islands of them and it became hard to diffuse further. The wide initial resistance range of double hetero structure of Mg thin layer becomes the strong evidence for mentioned theory. Due to the diffusion of Mg, not much that of Li but still exists, the appropriate amount of Mg insertion is becoming important.

4. CONCLUSION

The Mg thin layer insertion showed that it could be an effective way to improving the EL characteristics of OLED. The double hetero structured Mg thin layer insertion into the EML improved the maximum luminance about 98%, and luminance efficiency about 61%. On the other hand, when the Mg insertion was overdosed, the OLED performance decreased and EL characteristics were not anymore its own. The blue-shift of EL spectra and the increased operating voltage strongly back-upping that Mg thin layer is a hole blocking layer. Also the un-emissive metallic quenching could be derived from thick Mg layer. Also the Mg still could diffuse into the organic materials, the induced electrical path ways revealed. When the optimized thin layer insertion was accomplished, the Mg showed its potential ability for improving the EL characteristics of OLED.

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References and Notes

1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* 51, 913 (**1987**).
2. J. N. Bardsley, *IEEE J. Sel. Top. Quantum Electron.* 10, 3 (**2004**).
3. Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, *Nature* 440, 908 (**2006**).
4. Y. M. Kim, Y. W. Park, J. H. Choi, B. K. Ju, J. H. Jung, and J. K. Kim, *Appl. Phys. Lett.* 90, 033506 (**2007**).
5. L. S. Hung and C. H. Chen, *Mat. Sci. Eng. R* 39, 143 (**2002**).
6. B. Geffroy, P. L. Roy, and C. Prat, *Polym. Int.* 55, 572 (**2006**).
7. G. Parthasarathy, C. Shen, A. Kahn, and S. R. Forrest, *J. Appl. Phys.* 89, 4986 (**2001**).
8. Y. Yuan, D. Grozea, S. Han, and Z. H. Lu, *Appl. Phys. Lett.* 85, 4959 (**2004**).
9. H. Ding and Y. Gao, *Appl. Phys. Lett.* 86, 213508 (**2005**).
10. A. Kiejna, *Phys. Rev. B* 47, 7361 (**1993**).
11. K. F. Wojciechowski, *Europhys. Lett.* 38, 135 (**1997**).
12. W. Gao and A. Kahn, *Org. Electron.* 3, 53 (**2002**).
13. H. Tang, H. Liao, and L. Zhu, *Chem. Phys. Lett.* 381, 605 (**2003**).
14. M. E. Thompson, X. Ren, V. Adamovich, S. R. Cordero, B. W. D'Andrade, W. Brian, B. Alleyne, and S. R. Forrest, US Patent, 7261954 (**2007**).
15. Q. L. Song, C. M. Li, M. B. Chan-Park, M. Lu, H. Yang, and X. Y. Hou, *Phys. Rev. Lett.* 98, 176403 (**2007**).
16. F. L. Wong, H. Y. Sun, S. W. Tong, M. Y. Chan, C. S. Lee, and S. T. Lee, *J. Cryst. Growth.* 288, 110 (**2006**).

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