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Efficient electron injection in organic light-emitting diodes using lithium quinolate/Mg:Ag/Al cathodes

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Abstract

A cathode structure of lithium quinolate (Liq)/Mg:Ag/Al was developed and device performances were investigated according to the thickness of Mg:Ag interlayer between Liq and Al. Device performances of Liq/Mg:Ag/Al were optimized at an interlayer thickness of 1.0 nm and power efficiency was enhanced by 50% by introducing Mg:Ag interlayer because of low driving voltage and high current efficiency.
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Keywords: Organic light emitting diodes; Cathode; Lithium quinolate

1. Introduction

Low power consumption is important in organic light-emitting diodes (OLEDs) and driving voltage as well as light-emitting efficiency have to be improved. There are many ways to get low driving voltage and to enhance electron injection from cathode to organic layer is one way to improve power consumption of OLEDs.

Typical cathode structure to get low driving voltage in OLEDs is LiF/Al [1–5]. LiF plays a role of electron injection layer to facilitate electron injection from Al to organic layer by lowering interfacial energy barrier between cathode and organic layer. CsF, MgF_2 and BaF_2 have also been useful to get low driving voltage and they were effective as electron injection materials [6,7]. In addition to metal halides, metal oxides were also efficient as electron injection layers and low driving voltage was obtained in metal oxide-based cathode systems [8,9]. Li_2O and Cs_2CO_3 were found to be effective to reduce driving voltage through interfacial energy barrier lowering.

Even though metal halides and metal oxides have been used as electron injection materials, organometallic complexes could also be used as an electron injection material. Lithium quinolate (Liq) is a representative organic-based electron injection material and it showed good electron injection properties [10].

In this work, a new electron injection structure of Liq/Mg:Ag/Al was developed and its performances as a cathode for OLEDs were compared with typical Liq/Al cathode. Mg:Ag thickness was controlled to monitor the effect of Mg:Ag interlayer thickness on device performances of OLEDs.

2. Experimental

A device configuration of indium tin oxide (ITO)/N,N′-diphenyl-N,N′-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (DNTPD, 60 nm)/N,N′-di(1-naphthyl)-N,N′-diphenylbenzidine (NPB, 30 nm)/tris(2-hydroxyquinoline) aluminium (Alq_3, 50 nm)/Liq (1 nm)/Mg:Ag (*x* nm)/Al (100 nm) was used to study the effect of metal interlayer thickness on device performances. The thickness of Mg:Ag was controlled from 0 to 10 nm to correlate Mg:Ag thickness with device performances. Relative ratio of Mg and Ag was 9 to 1 and deposition rate of Mg:Ag was 0.2 Å/s. Al was evaporated at a deposition rate of 2 Å/s. All organic materials except Liq were deposited at a rate of 1 Å/s and Liq was evaporated at a rate of 0.1 Å/s. DNTPD was supplied from Chemipro Kasei and all other organic materials were purchased from Gracel display Co. Ltd.

ITO substrates were sonicated in distilled water for 30 min and in isopropyl alcohol for additional 30 min. After sonication, the ITO substrate was cleaned in hot isopropyl alcohol to remove organic contaminants on ITO substrate. The ITO glass was dried in oven at 100 °C for 1 h and it was exposed to ultraviolet/O_3 for

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surface treatment. After 10 min exposure to ultraviolet/O_3, the substrate was transferred to vacuum chamber for organic material deposition. The substrate was encapsulated with glass lid to protect moisture and oxygen from outside. CaO-based dryer was inserted inside devices as a getter for oxygen and moisture.

Current–voltage–luminance (I–V–L) characteristics of Liq/Mg:Ag/Al devices were measured with Keithley 2400 source measurement unit and CS 1000 spectrophotometer.

3. Results and discussion

Liq is useful as an electron injection material as well as electron transport material. Binding energy between Li and quinolate unit is weaker than that of LiF and it can give better performances as an electron injection layer than LiF [10]. LiF has been known to dissociate into Li and F during deposition of Al on top of LiF and Al deposition on Liq can also induce effective dissociation of Liq into Li and quinolate unit. In particular, reactive metals such as Ca and Mg:Ag can activate Liq dissociation due to easy dissociation of Liq [11,12]. It was already reported that Ca activated LiF and Liq dissociation during deposition, resulting in improved electron injection [12]. Therefore, it is expected that Mg:Ag deposition on Liq can also induce efficient electron injection through interfacial energy barrier lowering. In this work, Mg:Ag was used instead of Mg because Mg could not be deposited on organic layer due to low sticking coefficient of Mg.

Current density of Liq/Mg:Ag/Al devices was measured according to the thickness of metal interlayer to investigate the effect of Mg:Ag thickness on device performances. Fig. 1 shows current density of Liq devices with different cathode structures. Current density was increased by introducing a metal interlayer between Liq and Al and it showed a maximum value at a metal interlayer thickness of 1 nm. Current density was decreased above 1 nm and it was almost constant above 3 nm even though it was higher than that of Liq/Al standard device. The high current density in Liq devices with a metal interlayer can be explained by effective liberation of Li by deposition of reactive metal on Liq [10]. Interfacial chemical reaction between Liq and Mg:Ag can be induced effectively because Gibbs energy of formation for the following reaction is negative from molecular orbital calculation.

$$2\mathrm{Liq} + \mathrm{Mg} + 2\mathrm{Alq3} \rightarrow 2\mathrm{Li}^{+}\mathrm{Alq3}^{-} + \mathrm{Mgq}_2$$

Negative value of Gibbs energy for the reaction of Mg indicates efficient dissociation of Liq by Mg, resulting in high current density through efficient electron injection. Other factors such as interface dipole can also affect the current density of Liq devices, but it cannot greatly contribute to current density because interface dipole of Liq would not be so different. Therefore, effective dissociation of Liq by reactive metals might be responsible for high current density in Liq/Mg:Ag/Al. Thickness dependence of current density can also be closely related with Liq dissociation. High current density at low metal interlayer thickness may be due to supply of additional thermal energy from high temperature Al deposition. Thick Mg:Ag layer protect Liq from thermal energy transfer during Al deposition and current density could not be increased.

Luminance of Liq/Mg:Ag/Al showed almost the same tendency as current density (Fig. 2) because luminance is generally depend on charge density in the device. High luminance was obtained in the device with 1 nm thick Mg:Ag interlayer between Liq and Al.

Luminance efficiency of Liq devices was calculated based on current density and luminance. Fig. 3 shows current efficiency of Liq devices according to metal interlayer thickness. Current efficiency of Liq devices was enhanced by metal interlayer and it showed the highest value at metal interlayer thickness of 1.0 nm. High current efficiency of Liq devices with metal interlayer can be explained by efficient hole and electron recombination in light-emitting layer. In general, hole is a majority carrier in organic devices and more electron injection from cathode to emitting layer or less hole injection can improve charge balance in light-emitting layer. In case of Liq/Mg:Ag/Al, electron injection was greatly improved by a metal interlayer and hole–electron balance in Alq_3 can be better after introduction of metal interlayer. High current efficiency in Liq devices with high current density supports the explanation. Current efficiency of Liq devices was enhanced from 3.1 to 3.8 cd/A by Mg:Ag interlayer.

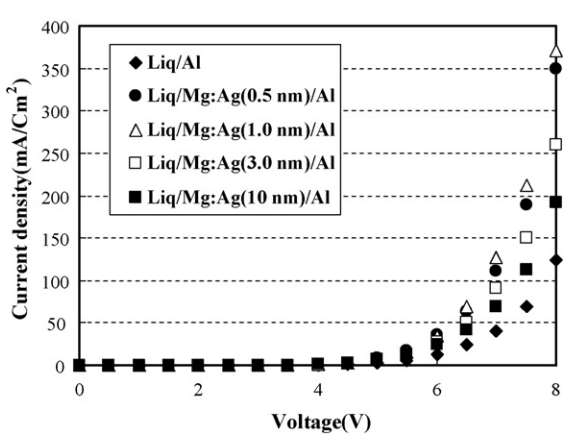

Fig. 1. Current density–voltage curves of Liq/Mg:Ag/Al devices according to metal interlayer thickness.

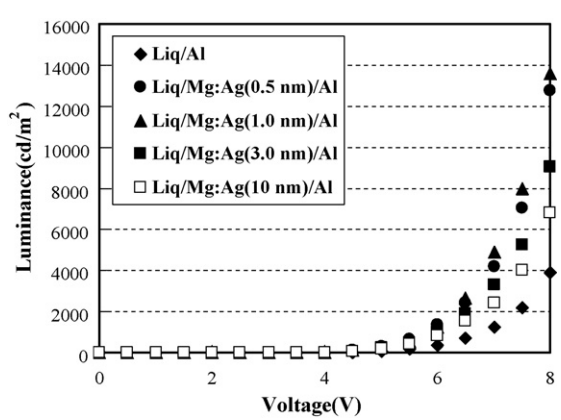

Fig. 2. Luminance–voltage curves of Liq/Mg:Ag/Al devices.

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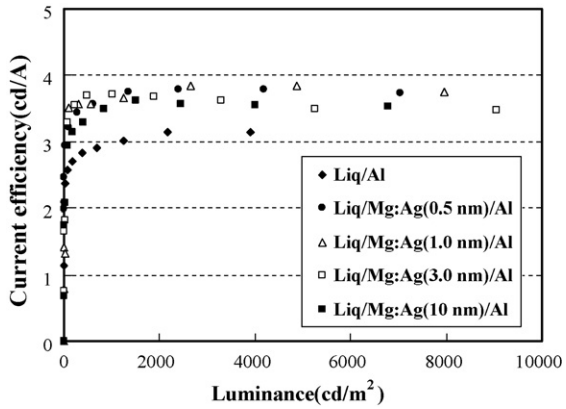

Fig. 3. Plot of current efficiency of Liq/Mg:Ag/Al devices according to metal interlayer thickness.

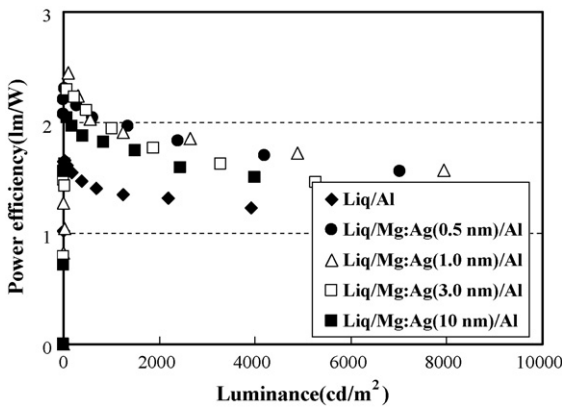

Fig. 4. Plot of power efficiency of Liq/Mg:Ag/Al devices according to metal interlayer thickness.

Power efficiency of Liq/Mg:Ag/Al devices is shown in Fig. 4. Power efficiency was even more improved than current efficiency and power efficiency of 2.0 lm/W could be obtained in Liq/Mg:Ag/Al devices compared with 1.37 lm/W of standard device. 50% improvement of power efficiency was observed in Liq/Mg:Ag/Al devices and high power efficiency of Mg:Ag devices is due to high current efficiency and low driving voltage of Liq/Mg:Ag/Al devices. Driving voltage was lowered by Mg:Ag interlayer and current efficiency was also improved by Mg:Ag interlayer. Combined effect of low driving voltage and high current efficiency contributed improved power efficiency in Mg:Ag interlayer devices.

Electroluminescence spectra of green devices with Mg:Ag interlayer in cathode structure are shown in Fig. 5. All devices showed typical EL spectra of Alq_3 with a peak maximum at 538 nm. The interlayer did not affect the luminance spectra because optical length may be the same irrespective of Mg:Ag interlayer thickness.

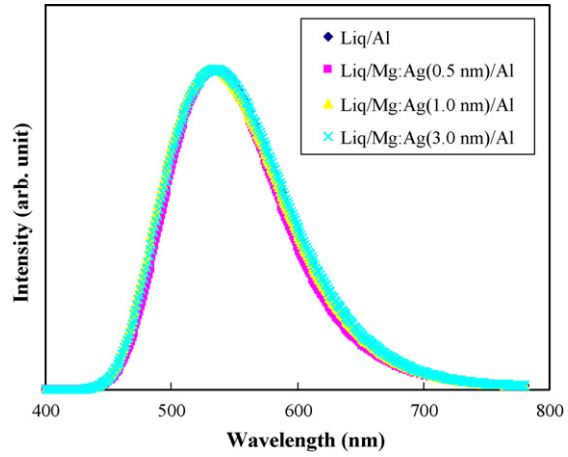

Fig. 5. Electroluminescence spectra of Liq/Mg:Ag/Al devices with different metal interlayer thickness.

4. Conclusions

In summary, introduction of Mg:Ag interlayer was effective to improve electron injection from cathode to Alq_3 and high current efficiency could be obtained. Power efficiency of Liq/Mg:Ag/Al devices was improved by 50% and it showed a maximum value at Mg:Ag thickness of 1 nm.

References

[1] L.S. Hung, C.W. Tang, M.G. Manson, Appl. Phys. Lett. 70 (1997) 152.
[2] S. Shi, D. Ma, Appl. Surf. Sci. 252 (2006) 6337.
[3] H. Heil, J. Steiger, S. Karg, M. Gastel, H. Ortner, H. von Seggern, M. Stoßel, J. Appl. Phys. 89 (2001) 420.
[4] M.G. Mason, C.W. Tang, L.-S. Hung, P. Raychaudhuri, J. Madathil, D.J. Giesen, L. Yan, Q.T. Le, Y. Gao, S.-T. Lee, L.S. Liao, L.F. Cheng, W.R. Salaneck, D.A. dos Santos, J.L. Brédas, J. Appl. Phys. 89 (2001 1756).
[5] S.Y. Oh, C.H. Lee, S.H. Ryu, H.S. Oh, J. Ind. Eng. Chem. 12 (2006) 69.
[6] Y. Park, J. Lee, S.K. Lee, D.Y. Kim, Appl. Phys. Lett. 79 (2001) 105.
[7] J. Lee, Y. Park, S.K. Lee, E.-J. Cho, D.Y. Kim, H.Y. Chu, H. Lee, L.M. Do, T. Zyung, Appl. Phys. Lett. 80 (2002) 3123.
[8] T. Wakimoto, Y. Fukuda, K. Nagayama, A. Yokoi, H. Nakada, M. Tschuida, IEEE Trans. Electron. Devices 44 (1997) 1245.
[9] J. Huang, G. Li, E. Wu, Q. Xu, Y. Yang, Adv. Mater. 18 (2006) 114.
[10] C. Schmitz, H. Schmidt, M. Thelakkat, Chem. Mater. 12 (2000) 3012.
[11] T.M. Brown, R.H. Friend, I.S. Millard, D.J. Lacey, T. Butler, J.H. Burroughes, F. Cacialli, J. Appl. Phys. 93 (2003) 6159.
[12] S.H. Kim, J. Jang, J.Y. Lee, Appl. Phys. Lett. 91 (2007) 103501.

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