Effects of PEDOT:PSS Buffer Layer in a Device Structure of ITO/PEDOT:PSS/TPD/Alq_3/Cathode

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(Received January 4 2005, Accepted February 5 2005)

We have investigated the effects of hole-injection buffer layer in organic light-emitting diodes using poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate)(PEDOT:PSS) in a device structure of ITO/PEDOT:PSS/TPD/Alq_3/cathode. Polymer PEDOT:PSS buffer layer was made by spin casting method. Current-voltage, luminance-voltage characteristics and efficiency of device were measured at room temperature with a variation of cathode materials ; Al, LiF/Al, LiAl, and Ca/Al. The device with LiF/Al cathode shows an improvement of external quantum efficiency approximately by a factor of ten compared to that of Al cathode only device. Our observation shows that cathode is important in improving the efficiency of the organic light-emitting diodes.

Keywords : Organic light-emitting diodes, Hole-injection buffer layer, External quantum efficiency.

1. INTRODUCTION

Organic light-emitting diodes(OLEDs) based on organic thin layers are a little bit different from similar to conventional semiconductor-based light-emitting diodes, and today they are considered to be one of the possible flat-panel displays of the next generation[1]. For vapor-deposited organic light-emitting diodes, the best performming devices are usually bilayer structures, in which a hole-transport layer is used to transport holes and an electron-transport layer to transport electrons. By optimizing electron and hole mobility and making recombination zone away from the electrode, we can make efficient organic light-emitting diodes with low turn-on voltage[2].

Essential improvement of the operational stability is desired for applications in information displays. Operational stability is insufficient with the fundamental bilayer structure. A contact problem between hole transport layer and indium-tin-oxide(ITO) anode can be considered as one of the causes of degradation. In order to enhance a performance of the organic light-emitting diodes, some organic materials are adopted for hole-injection buffer layer inserted between ITO anode and the emissive layer. The buffer layer is used to improve the performance of organic light-emitting diodes in several aspects, such as a good mechanical contact, energy-band adjustment, suppressing noisy leakage current, reducing the operating voltage, and enhancing the thermal stability and quantum efficiency. However, a unique buffer layer that can efficiently provide all the above mentioned functions is yet to be found.

Polymeric anodes, such as polyaniline and PEDOT:PSS have proved to be successful in spite of smaller conductivity than that of ITO[3]. The ITO/PEDOT:PSS combination has given the most promising results yielding an increase in device efficiency and lifetime and a reduction in the operating voltage[4].

Also, cathodes play an essential role in OLEDs, influencing strongly the current-voltage characteristics [5-7]. Using low work-function metals or alloys[7], the onset voltage of light emission is lowered. In addition to a reduction of operation voltage, the emission luminous efficiency(l m/W) and current efficiency[cd/A] are also improved[8]. This effect is related to a distribution of the electron-hole recombination zone, which is strongly dependent on the electron injection characteristics of the cathodes[8]. Among the cathodes so far reported, double-layer cathode consisting of a very thin LiF layer and Al layer are very attractive, because they are prepared using chemically stable starting materials and the operation voltage of the light-emitting diodes can be drastically lowered[8,9]. Matsumura and Jinde[8] have attributed the lowering of the operation voltages to the low work-function of the cathode, which is probably caused by the formation of the topmost layer consisting of a mixture of Li and Al. On the other hand, Hung et al explained that it forms an insulating layer and assists the tunneling of electrons from the Al electrode into the Alq_3 layer.

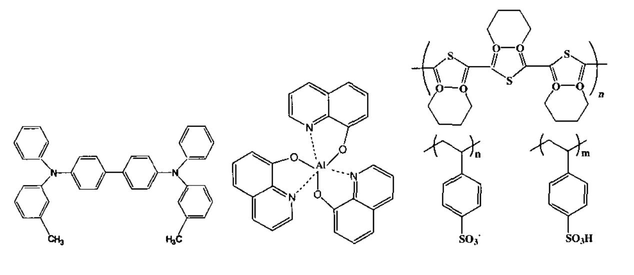
In this paper, we are presenting the effects of PEDOT:PSS hole-injection buffer layer and cathode in OLEDs based on Alq_3 thin films by investigating current-voltage characteristics, luminance-voltage characteristics and luminous efficiency.

2. EXPERIMENTAL

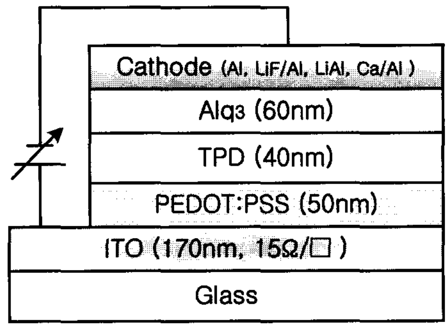
We have fabricated the OLEDs with a use of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine(TPD) as a hole-transport and 8-hydroxyquinoline aluminum(Alq_3) as an electron transport and emissive material. The ITO glass, having a sheet resistance of 15 Ω/□ and 170 nm thick, was received from Samsung Corning Co. A 5 mm wide ITO strip line was formed by selective etching in solution made with hydrochloric acid(HCl) and nitric acid(HNO_3) with a volume ratio of 3 : 1 for 10 ~ 20 minutes at room temperature. And then the patterned ITO glass was cleaned by sonicating it in chloroform for 20 minutes at 50 °C. And then the ITO glass was heated at 80 °C for 1 hour in solution made with second distilled deionized water, ammonia water and hydrogen peroxide with a volume ratio of 5 : 1 : 1. We sonicated the substrate again in chloroform solution at 50 °C for 20 minutes and in deionized water at 50 °C for 20 minutes. After sonication, the substrate was dried with N_2 gas stream and stored it under vacuum.

Figure 1 shows molecular structures of TPD, Alq_3, PEDOT:PSS, and device structure. The organic materials were successively evaporated under 1×10^{-6} torr with a rate of about 0.5 ~ 1 Å/s. The film thickness of TPD and Alq_3 was made to be 40 nm and 60 nm, respectively. And cathodes(Al(150 nm), LiF(0.5 nm)/Al(150 nm), LiAl(150 nm), Ca(50 nm)/Al(150 nm)) were deposited at 1.0×10^{-5} torr. Light-emitting area was defined by using a shadow mask to be 3×5 mm^2.

Current-voltage characteristics and luminance-voltage characteristics of OLEDs were measured using Keithley



(a) TPD (b) Alq_3 (c) PEDOT:PSS



(d) Device structure

Fig. 1. Molecular structures of (a) TPD, (b) Alq_3, (c) PEDOT:PSS, and (d) device structure.

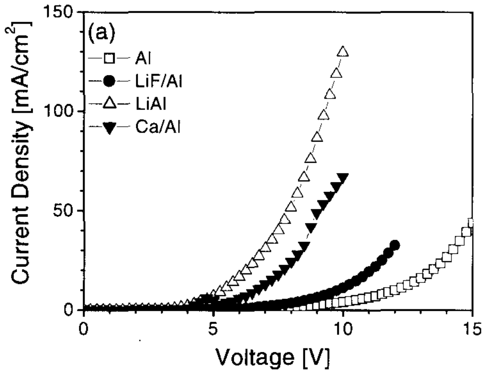
236 source-measure unit, 617 electrometer and Si-photodiode. Luminance-voltage characteristics and luminous efficiency were also measured at the same time when the current-voltage characteristics were measured. Luminous efficiency was calculated based on the luminance, EL spectra and current densities.

3. RESULTS AND DISCUSSION

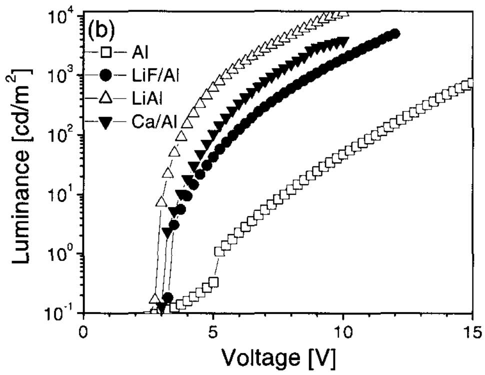
Figure 2(a) shows typical nonlinear current-voltage characteristics of ITO/PEDOT:PSS/TPD/Alq_3/cathode devices for several different cathodes such as Al, LiF/Al, LiAl and Ca/Al. Figure 2(b) is a corresponding luminance of device depending on the applied voltage. As the voltage increases, the current density and the luminance also increase as well. The current density and the luminance in the device of LiAl cathode is higher than the others. As the voltage increases above 3 V, the current density and luminance start to increase and there

Table 1. Work-function of metal cathode and barrier height between Alq_3 and cathode[10,11].

Cathode	**Al**	**LiF/Al**	**LiAl**	**Ca/Al**
Work-function [eV]	4.3	3.1	3.0	2.9
Barrier height (Alq_3/cathode) [eV]	1.2	0	-0.1	-0.2

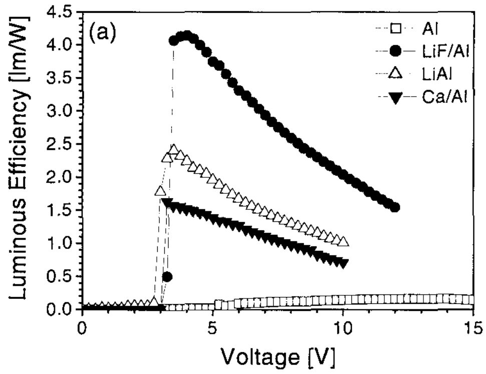


(a)

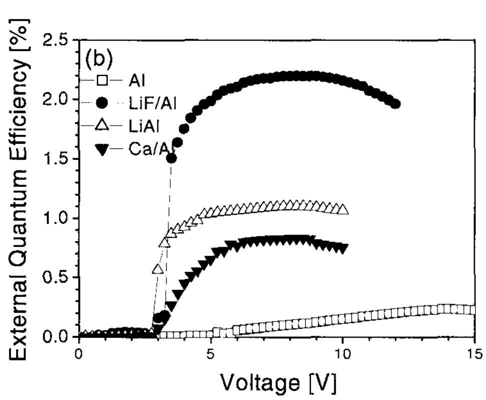


(b)

Fig. 2. (a) Current density and (b) luminance-voltage characteristics with a variation of cathode in ITO/ PEDOT:PSS/TPD/Alq_3/Cathode devices.



(a)



(b)

Fig. 3. (a) Luminous efficiency and (b) external quantum efficiency-voltage characteristics with a variation of cathode ITO/PEDOT:PSS/TPD/Alq_3/Cathode devices.

occurs a light emission. However, the luminance in Al cathode starts to increase near 5 V. This may be due to a reduction of energy barrier height between Alq_3/cathode with a use of low value of work-function, so that the charge injection becomes easier. Table 1 shows literature values of work-function of metal cathodes and energy-barrier height between Alq_3/cathode[10,11].

To see how the electrical current affects on the luminance, the efficiency of device was calculated using Figs. 2(a) and 2(b). Figure 3(a) shows the luminous efficiency as a function of the applied voltage. For Al cathode, the maximum luminous efficiency is 0.17 lm/W at 13 V. However, the device with low work-function cathodes shows the maximum luminous efficiency of 4.14 lm/W at 4 V for LiF/Al, 2.41 lm/W at 3.5 V for LiAl, and 1.64 lm/W at 3.25 V for Ca/Al, respectively. There is an improvement of efficiency by a factor twenty with a use of LiF/Al cathode compared to the one with Al cathode. Even though the current and the luminance are higher in the device with LiAl cathode, the efficiency is more than two times higher in the device with LiF/Al cathode. Since the energy band diagram in the device with LiAl and LiF/Al cathodes are similar, the difference in the current density, luminance, and efficiency cannot be explained by the energy band diagram in these devices. We can speculate that there might be an associated effect of adhesion between Alq_3 and the cathodes. In the device with Al cathode, the luminous efficiency increases gradually and reaches a maximum near 13 V. However, when the low work-function cathodes are used, the luminous efficiency rapidly increases near 3 ~ 4 V and then decreases again.

Figure 3(b) shows the external quantum efficiency as a function of the applied voltage. For Al cathode, the maximum external quantum efficiency is 0.24 % at 14 V. However, the devices with low work-function cathode shows the maximum luminous efficiency of 2.2 % at 8.25 V for LiF/Al, 1.1 % at 8 V for LiAl, and 0.836 % at 8.5 V for Ca/Al, respectively. There is an improvement of external quantum efficiency by a factor of ten with the use of LiF/Al cathode compared to the one with Al cathode. From these results, we can expect the improvement of efficiency and reduction of operation value by using low-value work-function cathode.

4. CONCLUSION

We have fabricated the efficient organic light-emitting diodes using the PEDOT:PSS hole-injection buffer layer and low work-function cathode in a device structure of ITO/PEDOT:PSS/TPD/Alq_3/cathode. By using the cathode with the low work-function, we have achieved the improvement of efficiency and the reduction of operation voltage. We need further study on the effect of adhesion between Alq_3 and cathode to the efficiency of device.

REFERENCES

[1] R. F. Service, "Organic light emitters gain longevity", Science, Vol. 273, Iss. 5277, p. 878, 1996.
[2] C. W. Tang and S. A. VanSlyke, "Organic electroluminescent diodes", Appl. Phys. Lett., Vol. 51, No. 12, p. 913, 1987.
[3] G. Gustafsson, Y. Gao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, "Flexible light-emitting diodes made from soluble conducting", Nature, Vol. 357, Iss. 6378, p. 477, 1992.
[4] J. S. Kim, R. H. Friend, and F. Cacialli, "Improved operational stability of polyfluorene-based organic light-emitting diodes with plasma-treated indium-tin-oxide anodes", Appl. Phys. Lett., Vol. 74, No. 21, p. 3084, 1999.
[5] I. D. Parker, "Carrier tunneling and device characteristics in polymer light-emitting diodes", J. Appl. Phys., Vol. 75, No. 3, p. 1658, 1994.
[6] M. Matsummura, T. Akai, M. Saito, and T. Kimura, "Height of the energy barrier existing between cathodes and hydroxyquinoline–aluminum complex of organic electroluminescence devices", J. Appl. Phys., Vol. 79, No. 1, p. 264, 1996.
[7] E. I. Haskal, A. Curioni, P. F. Seidler, and W. Anderoni, "Lithium–aluminum contacts for organic light-emitting devices", Appl. Phys. Lett., Vol. 71, No. 9, p. 1151, 1997.
[8] M. Matsumura and Y. Jinde, "Analysis of current–voltage characteristics of organic light emitting diodes having a LiF/Al cathode and an Al–hydroxyquinoline/diamine junction", Appl. Phys. Lett., Vol. 73, No. 20, p. 2872, 1998.
[9] L. S. Hung, C. W. Tang, and M. G. Mason, "Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode", Appl. Phys. Lett., Vol. 70, No. 2, p. 152, 1997.
[10] S. W. Pyo, S. P. Lee, H. S. Lee, O. K. Kwon, H. S. Hoe, S. H. Lee, Y.-K. Ha, Y. K. Kim, and J. S. Kim, "White-light-emitting organic electrolumine-scent devices using new chelate metal complex-es", Thin Solid Films, Vol. 363, No. 1-2, p. 232, 2002.
[11] I. D. Parker, "Carrier tunneling and device characteristics in polymer light-emitting diodes", J. Appl. Phys., Vol. 75, No. 3, p. 1657, 1994.