ITO/PEDOT:PSS/TPD/Alq_3/Cathode 소자 구조에서 PEDOT:PSS 층과 음전극의 영향

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

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Abstract

We have investigated the effect of hole-injection buffer layer and cathodes 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 using spin casting method. Current-voltage, luminance-voltage characteristics and efficiency of device were measured at room temperature with a variation of cathode materials. 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 the energy barrier-height in cathode side is important in improving the efficiency of the organic light-emitting diodes.

Key Words : Organic light-emitting diodes, Hole-injection buffer layer, external quantum efficiency

1. Introduction

Organic light-emitting diodes(OLEDs) based on organic thin layers are 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 performing 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 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[3]. 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[4]. 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[5].

Also, cathodes play an essential role in OLEDs, influencing strongly the current-voltage characteristics[6-8]. Using low work function metals or alloys[8], the onset voltage of light emission is lowered. In addition to a reduction of operation voltage, the emission power efficiency (lm/W) is also improved. Futhermore, an adoption of low work function cathode is effective in raising the current efficiency, which is defined as luminance per ampere(cd/A), of the LEDs having an aluminum-hydroxyquinoline (Alq) layer[9]. This effect is related to the distribution of the electron-hole recombination zone, which is strongly dependent on the electron injection characteristics of the cathodes[9]. 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 operational voltage of the LEDs can be drastically lowered[9,10]. Matsumura and Jinde[9] have attributed the lowering of the operational voltages to the low work function of the cathode, wihch 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 LiF forms an insulating layer and assists the tunneling of electrons from the Al electrode into the Alq layer.

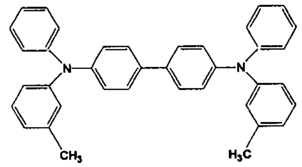
In this paper, we have studied the effects of PEDOT:PSS hole-injection buffer layer and cathode in OLEDs based on Alq_3 thin films by investigating current-voltage characteristics, luminance-voltage characteristics and luminous efficiency.

2. Experiments

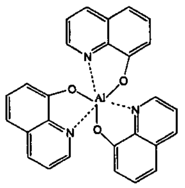
We have fabricated the OLEDs with a use of N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) as a hole-transport and 8-hydroxyquinoline aluminum (Alq_3) as an electron transport and emissive material. The ITO glass, having a sheet resistance of 15Ω/□ and 170nm thick, was received from Samsung Corning Co. A 5mm 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℃. And then the ITO glass was heated for 1 hour at 80℃ 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 for 20 minutes at 50℃ and in deionized water for 20 minutes at 50℃. After sonication, the substrate was dried with N_2 gas stream and stored it under vaccum.

Fig. 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 0.5~1Å/s. The film thickness of TPD and Alq_3 was made to be 40nm and 60nm, respectively. And cathodes (Al(150nm), LiF(0.5nm)/Al(150nm), LiAl(150nm), Ca(50nm)/Al(150nm)) were deposited at 1.0×10^{-5} torr. Light-emitting area was defined by using a shadow mask to be 0.3×0.5 cm^2.

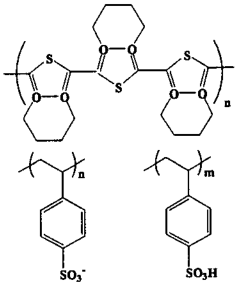
Current-voltage characteristics and luminance-voltage characteristics of OLEDs were measured using Keithley 236 source-measure unit, 617 electrometer and Si-photodiode. Luminance-voltage characteristics and luminous efficiency were also measured at the same time when the current-voltage characteristics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



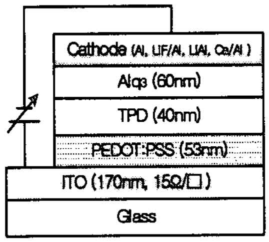
(a) TPD



(b) Alq_3



(c) PEDOT:PSS



(d) Device sturcture

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

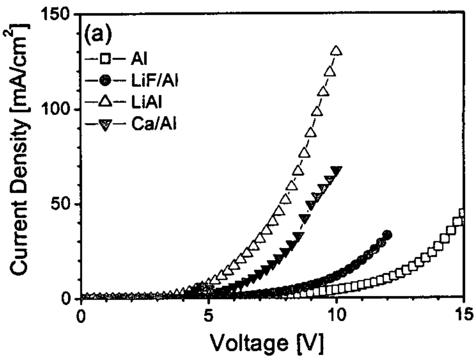
3. Results and discussions

Fig. 2(a) shows typical nonlinear current-voltage characteristics of ITO/PEDOT:PSS/TPD/Alq_3/Cathode devices with several different cathodes such as Al, LiF/Al, LiAl, Ca/Al, respectively. Fig. 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. For Current density, as the voltage increases above 3V, the current density and luminance start to increase and there occurs a light emission. However, the luminance in Al cathode starts to increase near 5V.

This is due to a reduction of barrier height between Alq_3/cathode with a use of low value of work function. Thus the charge injection is easier. Table 1 shows a work function of metal cathode and barrier height between Alq_3/cathode.

To see how the electrical current affects on the luminance, the efficiency of device was calculated using Figs. 2(a) and 2(b).



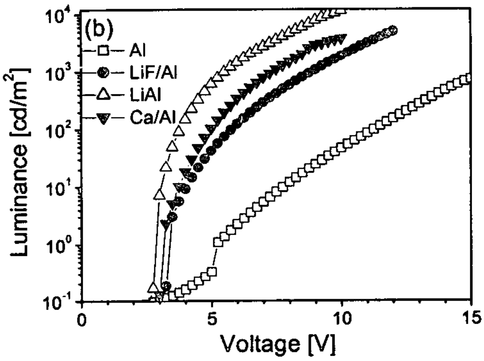


Fig. 2. (a) Current density and (b) luminance-voltage characteristics with a variation of cathode in ITO/PEDOT:PSS/TPD/Alq_3/Cathode devices.

Table 1. Work function of metal cathode and barrier height between Alq_3 and cathode.

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

Fig. 3(a) shows the luminous efficiency as a function of the applied voltage. For Al cathode, the maximum luminous efficiency is 0.165[lm/W] at 13V. However, the devices with low work function cathode shows the maximum luminous efficiency of 4.14[lm/W] at 4V for LiF/Al, 2.41[lm/W] at 3.5V for LiAl, and 1.64[lm/W] at

3.25V for Ca/Al, respectively. There is an improvement of efficiency by an order of two. In the device with Al cathode, the luminous efficiency increases gradually and reaches a maximum near 13V. However, when the low work function cathodes are used, the luminous efficiency increases rapidly near 3V and 4V. And it decreases again.

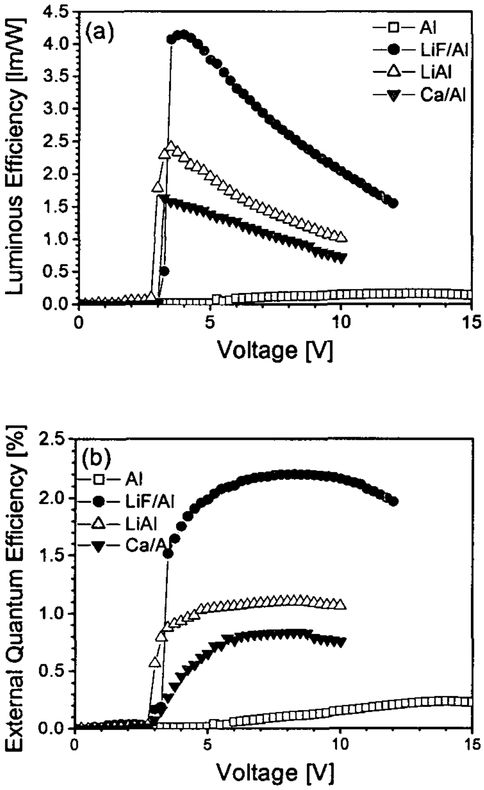


Fig. 3. (a) Luminous efficiency and (b) external quantum efficiency-voltage characteristics with a variation of cathode in ITO/PEDOT:PSS/TPD/Alq_3/Cathode devices.

Fig. 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 14V. However, the devices with low work function cathode shows the maximum luminous efficiency of 2.2[%] at 8.25V for LiF/Al, 1.1[%] at 8V for LiAl, and 0.836[%] at 8.5V for Ca/Al, respectively. There is an improvement of efficiency by a factor of ten. From these results, we can expect the improvement of efficiency by controlling the barrier height in cathode side.

4. Conclusion

We have fabricated the efficient OLEDs using the PEDOT:PSS hole-injection buffer layer and cathode with the low work function in a device structure of ITO/PEDOT:PSS/TPD/Alq_3/Cathode.

By using the cathode with the low work function, the luminous efficiency and the external quantum efficiency of device has improved by an order of two, and by a factor of ten respectively. This improvement is due to a reduction of energy barrier-height in cathode side.

Acknowledgement

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