

Stability of ITO/Buffer Layer/TPD/Alq₃/Cathode Organic Light-emitting Diode

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We have studied stability in organic light-emitting diode depending on buffer layer and cathode. A transparent electrode of indium-tin-oxide(ITO) was used as an anode. An electron injection energy barrier into organic material is different depending on a work function of cathodes. Theoretically, the energy barriers for the electron injection are 1.2 eV, -0.1 eV, and 0.0 eV for Al, LiAl, and LiF/Al at 300 K, respectively. We considered the cases that holes are injected to organic light-emitting diode. The hole injection energy barrier is about 0.7 eV between ITO and TPD without buffer layer. For hole-injection buffer layers of CuPc and PEDOT:PSS, the hole injection energy barriers are 0.4 eV and 0.5 eV, respectively. When the buffer layer of CuPc and PEDOT:PSS is existed, we observed the effects of hole injection energy barrier, and a reduction of operating-voltage. However, in case of PVK buffer layer, the hole injection energy barrier becomes high (1.0 eV). Even though the operating voltage becomes high, the efficiency is improved. A device structure for optimal lifetime condition is ITO/ PEDOT:PSS/TPD/Alq₃/LiAl at an initial luminance of 300 cd/m².

Keywords : Organic light-emitting diode, Buffer layer, Energy barrier, Lifetime, Stability

1. INTRODUCTION

Recently, there is a rapid development of information technology. Information display is one of concerns in the technology field. Organic light-emitting diode is rapidly commercialized in display market after the first report in 1983 by Tang and Vanslyke. There are currently available other displays such as CRT, LCD, and PDP. However, it is needed in display having a special function due to a development of high-density television and three-dimensional image processing technology.

In 1987, Tang and VanSlyke observed green light emission at low voltage using low molecule aromatic

diamine and 8-hydroxyquinolinato aluminum (Alq₃)[1]. In 1990, Friend et al., in Cambridge University reported the first green light-emitting polymer diode using poly (phenylenevinylene) (PPV). Since then, lots of progresses have been done to obtain highly efficient and stable light-emitting diodes[2-4]. The most suitable display devices which have self-light emitting type, fast response time, low drive voltage, flexible display, large emitting area, high efficiency, and low cost etc. are required[5]. To satisfy these conditions, understanding of an electrical conduction mechanism is important in improving the efficiency of the devices[6,7]. In this paper, we report stability in organic light-emitting diode depending on buffer layer and cathode.

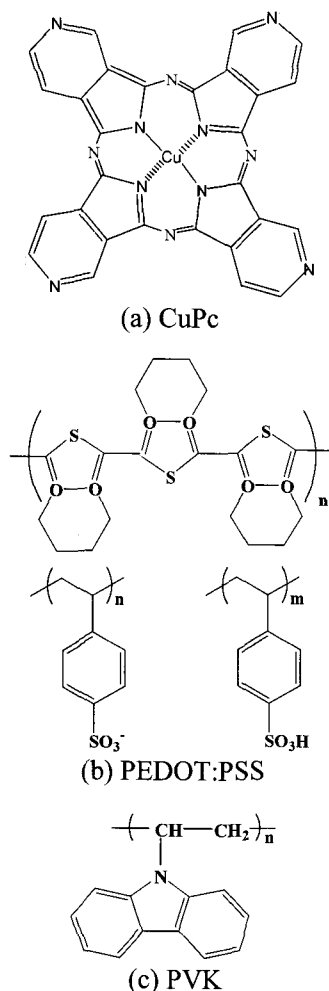


Fig. 1. Molecular structure of buffer materials.

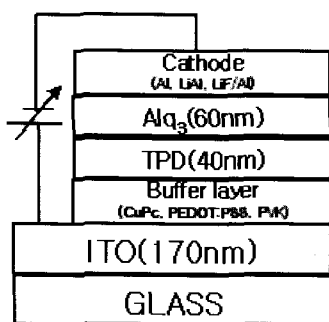


Fig. 2. Device structure of organic light-emitting diodes.

2. EXPERIMENTAL

To study stability in organic light-emitting diode, a device structure of ITO/Buffer layer/TPD/Alq₃/Cathode was fabricated. Figure 1 is a molecular structure of buffer materials we have used. Figure 2 is a device structure of organic light-emitting diodes used in our study.

A transparent electrode of indium-tin-oxide (ITO) was used as an anode, which has a surface resistance of 15 Ω/\square and a thickness of 170 nm. It was manufactured by Samsung Corning Co. The ITO was patterned to make a width of 5 mm.

In organic light-emitting diodes, N,N'-Diphenyl-N,N'-di(m-tolyl)-benzidine (TPD) material was used as a hole-transport layer, which was purchased from TCI. It was used as received from the company. A thermal evaporation was performed to make a thickness of 40 nm of TPD layer at a rate of 0.5~1 $\text{\AA}/\text{s}$ under a base pressure of 5×10^{-6} torr.

A material of tris (8-hydroxyquinolate) Aluminum (Alq₃) was used as an electron transport and emission layer. It was purchased from TCI and used as it is. A thermal evaporation of Alq₃ was done at a deposition rate of 0.7~0.8 $\text{\AA}/\text{s}$ under a base pressure of 5×10^{-6} torr. And the thickness of Alq₃ was made to be 60 nm.

For hole-injection buffer layers, several organic materials were used ; copper phthalocyanine (CuPc), poly (3,4-ethylenedioxythiophene) : poly (styrenesulfonate) (PEDOT:PSS), and poly(9-vinyl carbazole) (PVK). The CuPc layer was made by thermal evaporation at a deposition rate of 0.7~0.8 $\text{\AA}/\text{s}$ under a base pressure of 5×10^{-6} torr. The optimal thickness of CuPc layer was identified to be 35 nm in the earlier measurement of efficiency[8]. It was purchased from TCI and used as it is.

The PEDOT:PSS layer was made by spin casting at 6000 rpm for 60 s with a material from Vistorm Co. A measured thickness of PEDOT:PSS layer was 35.2 nm using ellipsometer (PLASMOS Co.). A PVK solution of 0.1 wt% was made with a solvent of dichloroethane. And it was spin-casted at 6000 rpm for 60 s (8.6 nm)[8].

Several cathodes for electron injection were used; Al, LiAl, and LiF/Al, which were purchased from TCI. The Al and LiAl (Al 99 wt%, Lithium 1 wt%) were thermally evaporated to make an electrode of 150 nm thick and 3 mm wide under a base pressure of 5×10^{-6} torr. A deposition rate was 0.5 $\text{\AA}/\text{s}$ upto 10 nm thick, and 15 $\text{\AA}/\text{s}$ for 10~150 nm thick. For LiF/Al electrode, 0.5 nm thick LiF was made at a deposition rate of 0.1 $\text{\AA}/\text{s}$, and then 150 nm thick Al was successively evaporated. An emissive area of all devices was made to be 15 mm² (5 mm ITO \times 3 mm cathode).

Current-Voltage-Luminance characteristics were measured using Keithley 236 source-measure unit, 617 electrometer and Si-photo diode (Centronics Co. OSD 100-5T) under a base pressure of 10^{-2} torr.

3. RESULTS AND DISCUSSION

Figure 3 shows the energy levels of the materials used in this study. The ionization potential of ITO used as an anode is 4.8 eV. The work functions of the cathode materials are 4.3 eV, 3.0 eV and 3.1 eV for Al, LiAl and LiF/Al, respectively. And ionization potential and electron affinity are different depending on the kinds of materials.

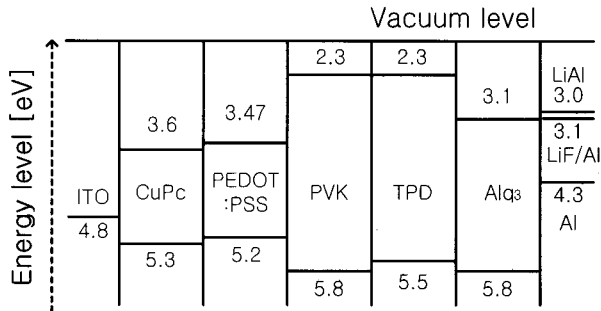


Fig. 3. Energy levels of several cathodes and organic materials.

We considered the cases that holes are injected to organic light-emitting diodes. The hole injection energy barrier is about 0.7 eV between ITO and TPD without buffer layer. For hole-injection buffer layers of CuPc and PEDOT:PSS, the hole injection energy barriers are 0.4 eV and 0.5 eV, respectively. When the buffer layer of CuPc or PEDOT:PSS is existed, we observed the effects of hole injection energy barrier, and a reduction of operating voltage. However, in case of PVK buffer layer, the hole injection energy barrier becomes high (1.0 eV). Even though the operating voltage becomes high, the efficiency is improved[9].

In consideration of the electron injection from the cathode into the organic materials, the electron injection energy barrier between LUMO level and Al work function is 1.2 eV. But the work functions of LiAl and LiF/Al are almost the same as the electron affinity of Alq₃. In cathodes of LiAl and LiF/Al, the electron injection energy barrier is about -0.1~0.0 eV. The effects due to the low electron injection energy barrier are little quenching phenomena and reduction of the operating voltage.

If there is a significant difference in the energy barrier, the small barrier controls the current-voltage characteristics, while the large barrier determines the device efficiency[9].

3.1 Luminance and voltage

Lifetime measurements were carried out in a continuous operation of current density 5 mA/cm² from an initial luminance of 300 cd/m². Figures 4, 5 and 6 represent the lifetime of device for three different cathodes. To have a stress on the device to be uniform, a constant current density of 5 mA/cm² was applied.

Figure 4 shows a luminance and voltage in ITO/TPD/Alq₃/Al device structure. The operating voltage increases rapidly in short-term behavior and slowly in long-term behavior. The luminance decreases rapidly in the former and slowly in the latter. Therefore, the luminance characteristics and the operating voltage

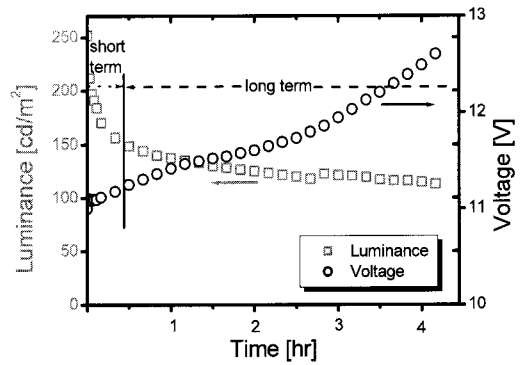


Fig. 4. Luminance(□) and a corresponding operating voltage(○) as a function of elapsed time for ITO/TPD/Alq₃/Al organic light-emitting diodes.

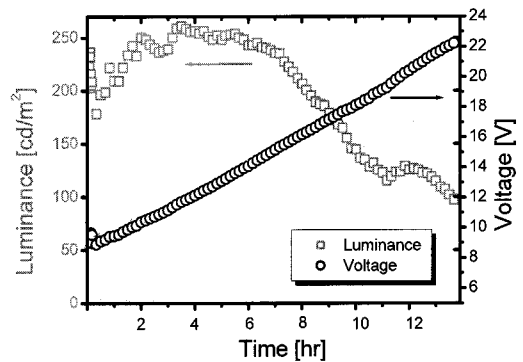


Fig. 5. Luminance-voltage of ITO/TPD/Alq₃/LiAl structure.

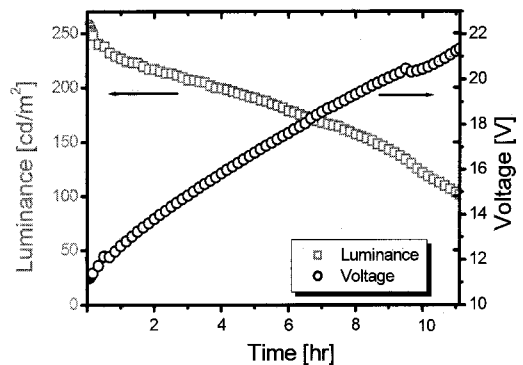


Fig. 6. Luminance-voltage of ITO/TPD/Alq₃/LiF/Al structure.

characteristics are more or less symmetric to each other.

In general, the short-term behavior is affected by an environmental condition, and the long-term behavior by a cathode condition[10].

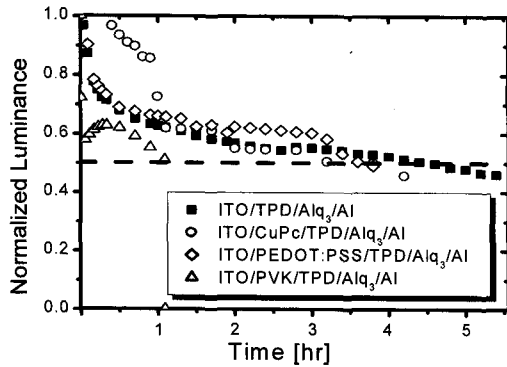


Fig 7. Normalized luminance as a function of elapsed time to investigate a lifetime for ITO/Buffer layer/TPD/Alq₃/Al organic light-emitting diodes.

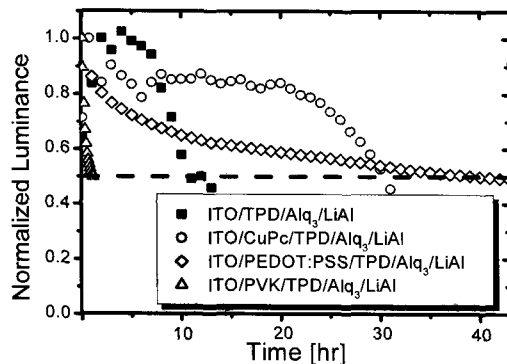


Fig 8. Lifetime of ITO/Buffer layer/TPD/Alq₃/LiAl device structure.

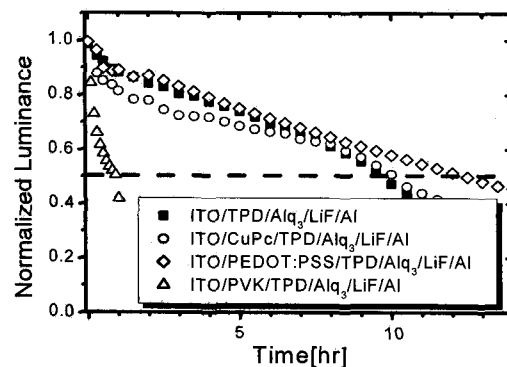


Fig 9. Lifetime of ITO/Buffer layer/TPD/Alq₃/LiF/Al device structure.

3.2 Lifetime

The glass transition temperature T_g is also an important issue when choosing materials for the device[11]. Each organic material has a T_g where the

material changes its state. When a material is used below this temperature, the material tends to be more hard and fragile like glass.

If the material is used over the T_g , it poses more soft and flexible rubber like structure. When it is used in temperature over T_g , the display does not obtain a proper functionality and the lifetime is reduced[11].

In Figs. 7, 8 and 9, half-decay lifetime was defined to be the time taken for the luminance drop to 50 % of the initial luminance[12]. The lifetime of organic light-emitting diodes was measured at the initial luminance of 300 cd/m², which is a reference luminance for application.

We considered the case of cathode metal. The electron injection energy barrier into organic material is different depending on the work function of cathodes. Theoretically, the energy barriers for the electron injection are 1.2 eV, -0.1 eV, and 0.0 eV for Al, LiAl, and LiF/Al at 300 K, respectively. Energy barriers in the device of LiAl and LiF/Al are lower. Thus, a current stress on the device is less in LiAl and LiF/Al cathode because of low energy barriers[13].

As the stress on the device is smaller, a lifetime of device could be longer. The device with Al cathode has more stress because of high barrier of 1.2 eV. So, the lifetime of this device becomes shorter. However, since the carrier energy barrier is -0.1 eV in case of LiAl, the stress on the device is low for the same amount of carrier injection. Thus, the lifetime of this device is relatively longer. The lifetime of device with LiAl cathode is relatively longer, and that of Al cathode is relatively shorter.

We considered that the electron injection energy barrier is constant and the hole injection energy barrier is different. By inserting the buffer layer, the hole injection energy barrier is different because of different ionization potential of buffer layer materials. Reported values of the hole injection energy barriers are 0.5 eV, 0.4 eV, 0.7 eV and 1.0 eV for CuPc, PEDOT:PSS, non buffer layer, and PVK. The low hole injection energy barriers at the CuPc/TPD or PEDOT:PSS/TPD interface are the probable reasons for the low accumulation of the holes. In case of non buffer layer and PVK, the accumulation of holes is high because the hole injection energy barrier is higher than the others.

The expectation agrees with the results that the lifetime of devices becomes longer as the hole injection energy barrier decreases. Therefore, the device structure of optimal lifetime condition is ITO/PEDOT:PSS/TPD/Alq₃/LiAl at an initial luminance of 300 cd/m².

4. CONCLUSION

The stability was studied in the device structure for ITO/Buffer layer/TPD/Alq₃/Cathode. Current stress on

the device is less in LiAl and LiF/Al cathode because of low energy barriers. And low hole injection energy barriers at the CuPc/TPD or PEDOT:PSS/TDP interface are the probable reasons for the low accumulation of the holes. The device structure with optimal lifetime condition was identified to be ITO/PEDOT:PSS/TPD/Alq₃/LiAl in our study at an initial luminance of 300 cd/m².

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