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Performance of Three-Layered Organic Light-Emitting Diodes Using the Hole-Transport and Injection Layer of TPD and Teflon-AF, and the Electron-Injection Layer of Li_2CO_3 and LiF

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The performance of three-layered organic light-emitting diodes (OLEDs) was investigated using TPD hole-transport and injection layers, Teflon-AF, and the electron-injection layer of Li_2CO_3 and LiF. The OLEDs were manufactured in a structure of TPD/Alq_3/LiF, TPD/Alq_3/Li_2CO_3, and AF/Alq_3/LiF using low-molecular organic materials. In three different three-layered OLEDs, it was found that the device with the TPD/Alq_3/LiF structure shows higher performance in maximum luminance, and maximum external quantum efficiency compared to those of the device with TPD/Alq_3/Li_2CO_3 and TPD/Alq_3/LiF by 35% and 17%, and 193% and 133%, respectively. It is thought that the combined LiF/Al cathode contributes to a reduced work function and improves an electrical conduction mechanism due to the electron injection rather than the hole transport, which then increases a recombination rate of charge carriers.

Keywords: LiF/Al cathode, Hole transport layer, Organic light-emitting diodes, Electron-injection layer

1. INTRODUCTION

Recently, the importance of information display is increasing because information is easily communicated anytime and anywhere as society becomes more informed with development of advanced technology [1].

Even though the cathode ray tube has been the mainstay in display technology, it is being replaced by flat panel displays. These comply with the demands for ergonomic design, environmental friendliness, and high compatibility [2]. Liquid crystal displays are widely used as one type of flat panel display due to their light weight and thin film screen. It is expected that the display market and technology propagation effect will continuously increase since the application areas for flat panel displays are expanding [3].

Organic light-emitting diodes(OLEDs) emit light by exciting fluorescent organic materials electrically. Their merits include low power operation, self emission, wide view angle, excellent high resolution, full color, high repeatability, fast response time, and easy manufacturing process. The OLEDs using low-molecular weight materials are commercialized and attractive as the potential next generation display replacing liquid crystal displays which is a current representative one [4,5]. The injection of charge carriers and their movements in a structure of multi-layered OLEDs are

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significantly affected by the electrodes, charge-carrier transport materials, and interfacial properties [6,7]. Appropriate selection of materials and proper layer thickness are important in developing high performance OLEDs because the combination of organic materials and manufacturing process affects recombination rate of charge carriers in the emissive layer. Thus, a study optimizing electrical properties of the device is also important for improving surface status and adhesion between the layers [8,9].

In this paper, to improve OLEDs efficiency, three-layered OLEDs were fabricated with an insertion of hole-transport and injection layer N, N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1'-biphenyl-4, 4'-diamine (TPD) and amorphous fluoropolymer (Teflon-AF), and electron-injection layer lithium carbonate (Li_2CO_3) and lithium fluoride (LiF) at the same condition. Electrical and optical properties of the three-layered OLEDs, such as the luminance and efficiency were investigated.

2. EXPERIMENTAL

2.1 Specimens

Figures 1(a)~(c) show the three-layered device structures used in our experiment with the low-weight molecular organic materials. Figure 1(a) is the device inserted with the hole-transport layer of TPD and the electron-injection layer of Li_2O_3. Figure 1(b) is the device inserted with the hole-transport layer of TPD and the electron-injection layer of LiF. Figure 1(c) is the device inserted with the hole-injection layer of Teflon-AF and the electron-injection layer of LiF.

Since the physical adhesion between the electrode and organic layer is generally weak, it can be reinforced by inserting appropriate interfacial layers [10]. Thus, in our study, electrical properties of the device were investigated by inserting a 0.5 nm thick LiF layer, which was purchased from the Aldrich Co. A thin electron-injection layer of LiF was evaporated from the top of the Alq_3 emission layer, which has a work function of 3.2 eV. When the aluminum (Al) was evaporated, the device electrical and optical properties improved. This was due to a lowering of the work function of the modified LiF/

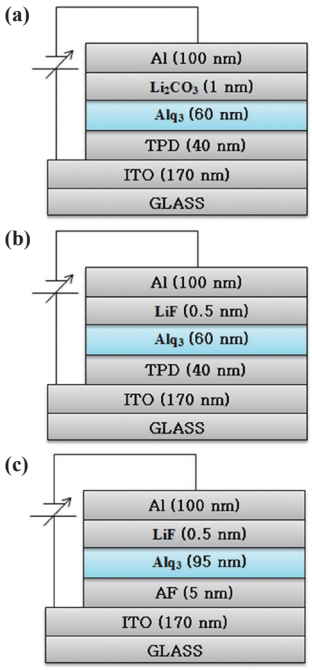

Fig. 1. Three-layered device structures used in our experiment.

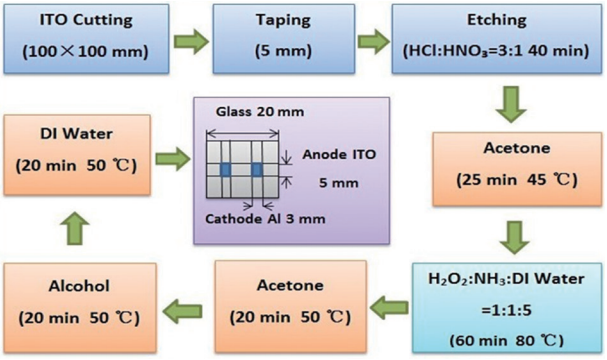

Fig. 2. Patterning and etching process of the ITO substrate.

Table 1. Chemical names and manufacturers of the used materials.

No	Materials	Manufacturer
1	Teflon-AF (amorphous fluoropolymer)	Dupont
2	TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl) -1,1'-biphenyl-4,4'-diamine)	TCI
3	Alq_3 (tris(8-hydroxyquinolinato)aluminum)	TCI
4	Li_2CO_3 (lithium carbonate)	Aldrich
5	LiF (lithium fluoride)	Aldrich

Al cathode from 4.3 eV to 4.1 eV. The LiF/Al cathode reduction of work function was confirmed by x-ray photoemission spectroscopy and ultraviolet photoemission spectroscopy [11,12].

The indium tin oxide (ITO) substrate, used as an anode, has a surface resistance of about 8 Ω/sq. Patterning and etching of the ITO substrate were carried out in our laboratory using the electrical insulation tape as shown in Fig. 2. The large sized ITO/glass plate was cut using a specialty glass cutter, and electrical insulating tape cut to 5 mm width was attached to the ITO/glass plate. The attached part was used later as the ITO anode. This taped ITO/glass plate was attached to the glass cap of a petri dish. Then the ITO/glass plate was etched using a vapor of solution made by mixing HCl and HNO_3 with a volume ratio of 3 : 1 in the petri dish for 30 minutes. At this time, the distance between the ITO substrate and the solution was set to be about 2 cm. After checking the etching status of the ITO/glass substrate, it was washed under flowing water. After the water moisture was completely dried with blowing nitrogen gas, it was cut to a size of 20 mm × 20 mm. It was then put in the photo carrier and placed inside a square shaped glass vessel for cleaning. Residual HCl and HNO_3 on the ITO substrate were rinsed with distilled water, and the ITO substrate was kept in isopropyl alcohol. The above process is summarized and presented in Fig. 2.

In our study, TPD and Teflon-AF were used as the hole-transport and hole-injection material, respectively. And tris (8-hydroxyquinolinato) aluminum (Alq_3), and Li_2CO_3 and LiF were used as the emissive and electron-injection materials, respectively. Thicknesses of the thermally evaporated organic layers were 5 nm of Teflon-AF, 40 nm of TPD, 60 nm and 95 nm of Alq_3, 1 nm of Li_2CO_3, and 0.5 nm of LiF, respectively. They were evaporated successively by varying the evaporation rates at a pressure of about 5×10^{-7} Torr. Table 1 shows a summary of the organics, and their manufacturers, used for the low-molecular weight materials.

2.2 Measurements

Devices were manufactured using the thermal evaporation method by heating the organics and the electrode materials by controlling the current under a high vacuum pressure of about 5×10^{-7} Torr. In general, it is important to prevent the low-molecular weight organic materials from oxidation during thermal

evaporation. Therefore, we tried to minimize the influence of oxidation effect on the materials by sufficiently removing the oxygen from the chamber at low vacuum pressure.

In our experiment, OLEDs performance was measured through the current density-voltage-luminance characteristics. This was done using a Keithley 6517 electrometer, a Keithley 2000 multimeter, and a programmable power supply from the Vupower Company. A Lab-view based measuring system was used to measure the voltage and current . Device Luminance was measured using a silicon photodetector placed in front of the device. The photodetector was connected to the Keithley 2000 multimeter, which gives a photocurrent depending on the amount of luminance. While the photocurrent is proportional to the number of photons coming out of the device, the direct current flowing through the device is proportional to the number of charge carriers. An external quantum efficiency of the device was obtained from the measured photocurrent and the direct current. The applied voltage to the device increased by a step of 0.25 V/s with a delay time of 100 ms. All the experiments were carried out at room temperature under ambient conditions.

3. RESULTS AND DISCUSSION

Figure 3 shows the current density-voltage characteristics for the three different three-layered OLEDs. Device ① has the hole-transport layer of TPD and electron-injection layer of Li_2CO_3. Device ② has the hole-transport layer of TPD and electron-injection layer of LiF. Device ③ has the hole-injection layer of Teflon AF and electron-injection layer of LiF. It shows that the current density increases in proportion to the fourth power of the applied voltage in a low voltage region of less than about 3 V. The current density in device ① increases with almost a constant slope as the applied voltage increases, and saturates near 9 V. However, the current density in devices ② and ③ show a negative resistance near 3.5 V and luminance starts to occur in this region. The current density significantly increases in the voltage region above 5 V. Especially, the current density-voltage characteristic of device ② is superior to the others.

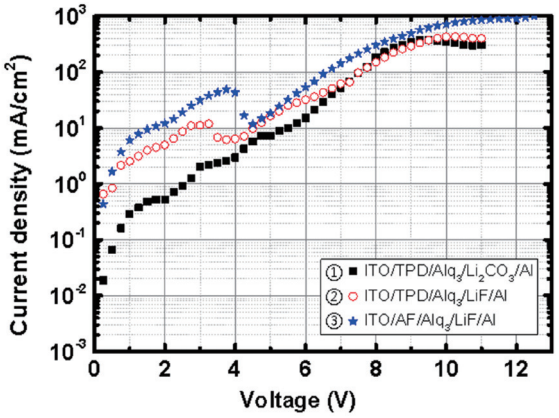

Fig. 3. Current density-voltage characteristics for three different three-layered OLEDs.

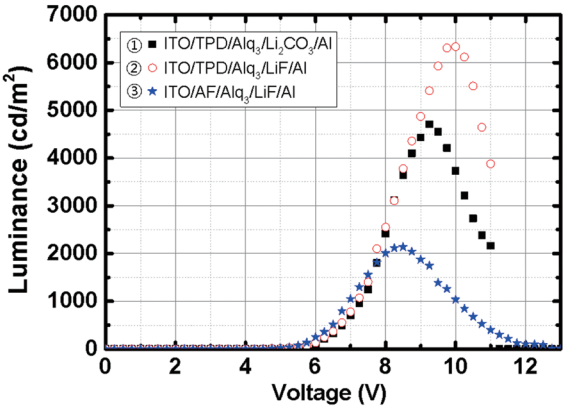

Fig. 4. Luminance-voltage characteristics for three different three-layered OLEDs corresponding to Fig. 3.

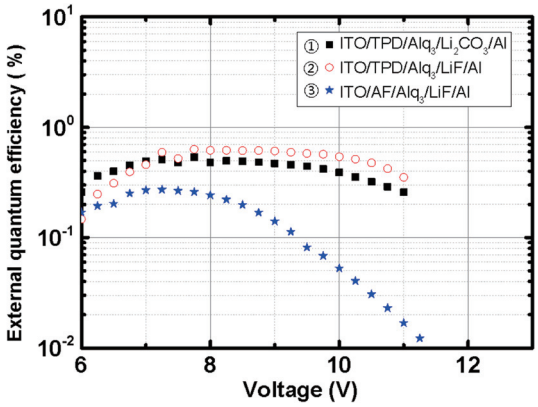

Fig. 5. External quantum efficiency (η_{ext}) as a function of applied voltage in the three-layered OLEDs.

Table 2. Maximum luminance and maximum external quantum efficiency of the device ①, ②, and ③ for the three-layered OLEDs.

Classification	L_{max}		η_{ext}	
	[cd/m^2]	[V]	[%]	[V]
TPD/Alq_3/Li_2CO_3	4,707	9.25	0.54	7.75
TPD/Alq_3/LiF	6,334	10	0.63	7.75
AF/Alq_3/LiF	2,163	8.5	0.27	7.25

Figure 4 shows the corresponding voltage dependent luminance of devices ①, ②, and ③. It shows that the luminance starts to occur in the voltage above the negative-resistance region and reaches a maximum. The performance of device ② is superior to the others, where device ② is the one which uses TPD and LiF as the hole-transport layer and the electron-injection layer, respectively. It is thought that a using a 0.5 nm thick LiF electron-injection layer contributes physical interface adhesion and a reduction of work function for the cathode. The maximum luminance of devices ①, ②, and ③ was 4,707 cd/m^2 at 9.25 V, 6,334 cd/ m^2 at 10 V, and 2,163 cd/m^2 at 8.5 V, respectively. From these results, it was found that electron transport has a greater affect than electron injection on the performance of three-layered OLEDs. It is thought that electron transport contributes more to the charge-carrier recombination in the emission layer than electron injection. Device ② showed improved luminance of approximately 35% and 193% compared to that of devices ① and ③, respectively. In particular, the operating voltage for the maximum luminance increased from 8.5 V to 10 V in the voltage-dependent luminance characteristics.

Figure 5 shows the characteristics of external quantum efficiency (ext) of the OLEDs depending on the applied voltage. It shows that the external quantum efficiency of devices ① and ② slowly increase as the applied voltage increases up to 8 V and then slowly decreases as the voltage increases further. However, the efficiency of device ③ decreases rather rapidly above 7 V. It was observed that device ②, with the hole-transport layer of TPD and the electron-injection layer of LiF, showed higher external quantum efficiency of 0.63% at 7.75

V, while that of devices ① and ③ were 0.54% and 0.27% at 7.75 V and 7.25 V, respectively. Therefore, the external quantum efficiency of device ② is higher than that of the devices ① and ③ by 17% and 133%, respectively. It is thought that the higher quantum efficiency of device ② is due to the contribution of the hole transport rather than the electron injection in three-layered OLEDs. Maximum luminance and maximum external quantum efficiency of devices ①, ②, and ③ are summarized in Table 2.

4. CONCLUSIONS

Three-layered OLED performance was investigated using a hole-transport and injection layer of TPD and Teflon-AF, and a electron-injection layer of Li_2CO_3 and LiF. It is thought that OLED performance improved using a LiF/Al cathode due to a modification of physical properties and a reduction of work function of the cathode from 4.3 eV to 4.1 eV. Among the three different types of three-layered OLEDs, it was found that the device with TPD/Alq_3/LiF structure showed a higher performance in maximum luminance and maximum external quantum efficiency compared to those of the devices with TPD/Alq_3/Li_2CO_3 by 35 and 17%, respectively. Furthermore, the device with TPD/Alq_3/LiF showed a higher performance in maximum luminance and maximum external quantum efficiency compared to those of the device with AF/Alq_3/LiF by 193% and 133%, respectively. Therefore, it was found that using a combined LiF/Al cathode contributes to a reduction of work function and improves an electrical conduction mechanism due to the electron injection rather than the hole transport. Also, a recombination rate of charge carriers is thought to be increased in the three-layered device with TPD/Alq_3/LiF structure.

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