Fabrication of Red, Green, and Blue Organic Light-Emitting Diodes Using m-MTDATA as a Common Hole-Injection Layer

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Abstract–Organic light-emitting diodes (OLEDs) of metal-semiconductor-metal (MSM) structure have been fabricated by using m-MTDATA [4,4',4''-tris (3-methylphenylphenylamino) triphenylamine] as a hole-injection layer (HIL). The m-MTDATA is shown to be an effective hole-injecting material for the OLED, in that the insertion of m-MTDATA greatly reduces the roughness of anode surface, lowers the turn-on voltage, and increases the luminous efficiency. Red, green and blue OLEDs were fabricated, and their color coordinates in CIE chromaticity were found to be (0.600, 0.389), (0.240, 0.525) and (0.171, 0.171), respectively. The luminous efficiencies of the fabricated OLEDs were 1.4 lm/W at 106 cd/m^2 for red, 1.4 lm/W at 100 cd/m^2 for green, and 2.0 lm/W at 104 cd/m^2 for blue.

Key words: Organic Light-emitting Diode (OLED), Hole-injection Layer (HIL), Metal-semiconductor-metal (MSM) Structure, Luminous Efficiency

INTRODUCTION

Organic light-emitting diodes (OLEDs) have recently drawn much attention in the flat panel display (FPD) industry due to their fast response speed, no viewing-angle dependence, and full-color capability. OLEDs can be made thin and flexible with relatively low driving voltage (<5 V), which makes them attractive for flexible display applications [Kwon et al., 2002; Parker 1994]. Since the bilayer OLED consisted of hole-transport and emitting layer was first reported in 1987 [Tang and VanSlyke, 1987], a great deal of research has been needed to realize devices with higher brightness and luminous efficiency [Chen and Shi, 1998; Kalinowski, 1999].

Brightness of OLED at a fixed operating voltage can be improved if luminous efficiency is enhanced, and for this, it is desirable to have lower driving voltage possible with high enough luminous efficiency. There is an optimum thickness for the emitting layer to achieve the best performance of an OLED, and the optimum thickness is related to many factors such as the formation of excitons, charge trapping probability, driving voltage, etc. An emitting layer that is too thick will increase the electric resistance, which will in turn demand higher driving voltage. Absorption of emitted light can degrade the luminous efficiency in a small amount for this case. An emitting layer that is too thin is also not desirable, since the decreased thickness will lower the number of excitons produced in the layer. Leakage current may develop in the device by defects or pinholes, if the film formation process is not properly managed. Therefore, it is necessary to carefully control the thickness and integrity of the emitting layer to obtain the best device performance. The difference in energy band structures of electrodes and emitting material can also cause the increase in electric resistance at the interface due to the inherent energy barrier for charge transport [Winkler et al, 1999], and thus it is important to match the energy band structures as closely as possible between electrodes and emitting material [Kalinowski, 1999].

The technique of inserting a charge-injection layer between the electrode and emitting layer is widely adopted to address the issues described above [Giebeler et al., 1999; Lee and Cho, 2002; Shirota et al., 1994; Yamamori et al., 1994], and most commercial OLEDs include some type of charge-injection and/or transport layer in their device structures. The materials used for these layers should be transparent to the light generated in the emitting layer and have proper energy band structures to lower the energy barrier between electrode and emitting layer. Formation of dense and amorphous film without pinholes is crucial for the charge-injection layers in order to minimize non-uniform charge transport or leakage current related to the surface morphology of the electrodes. It is also desirable that the OLEDs fabricated with charge-injection layers be less sensitive to the variation of the injection layer thickness for the process controllability.

The m-MTDATA [4,4',4''-tris (3-methylphenylphenylamino) triphenyl amine] has been recently investigated as a candidate for hole injecting and transport material, and it was shown that m-MTDATA can form an excellent amorphous film with suitable material characteristics as hole-injection layer (HIL) [Moriwaki et al., 1998; Nakano et al., 1996]. Multi-layer OLEDs using m-MTDATA have been demonstrated, and the results showed that the device performance obtained was superior to that without m-MTDATA [Fujii et al., 1998; Giebeler et al., 1998, 1999; Shirota et al., 1994; Staudigel et al., 1999]. In those studies, however, the function of m-MTDATA was usually two-fold, hole-injection and hole-transport, and thus the role of m-MTDATA as the HIL alone was not distinctively investigated. OLEDs emitting several different mono-colors were demonstrated by using m-MTDATA as HIL material, but the material combinations (and thus band structures) for different-color devices were also varied, which makes it hard to interpret the improved device performance by the sole effect of inserted HIL. The red, green, and blue OLEDs with m-MTDATA as the invariant HIL material have not yet been reported. The use of similar material combinations for different-color OLEDs has the benefit of enhancing the production throughput and process controllability in the manufacture of multi-

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color OLED displays.

In this study, the use of m-MTDATA as HIL for OLEDs was revisited to further elucidate the distinctive property of m-MTDATA as HIL and to seek the feasibility of using m-MTDATA as the invariant HIL for multi-color OLED displays. Comparison of m-MTDATA with other commonly used hole-injecting materials such as PEDOT (poly-3,4 ethylene dioxythiophenes) and CuPc (copper phthalocyanine) was made in the context of surface reconstruction and device performance. Three different-color (red, green, and blue) OLEDs were fabricated using m-MTDATA as the common HIL in these devices, and their device characteristics were analyzed.

EXPERIMENTAL

Substrates used in this study were ITO-coated glasses with the ITO film thickness of ~2000 Å and a sheet resistance of ~10 Ω/sq. After being cut to 2 cm×2 cm in size, the substrates went through typical photolithographic steps followed by wet chemical etching with HCl : HNO_3 : H_2O (4.5 : 0.5 : 5.0) solution for 40 min to form stripe-pattern anode structures. The patterned ITO substrates were
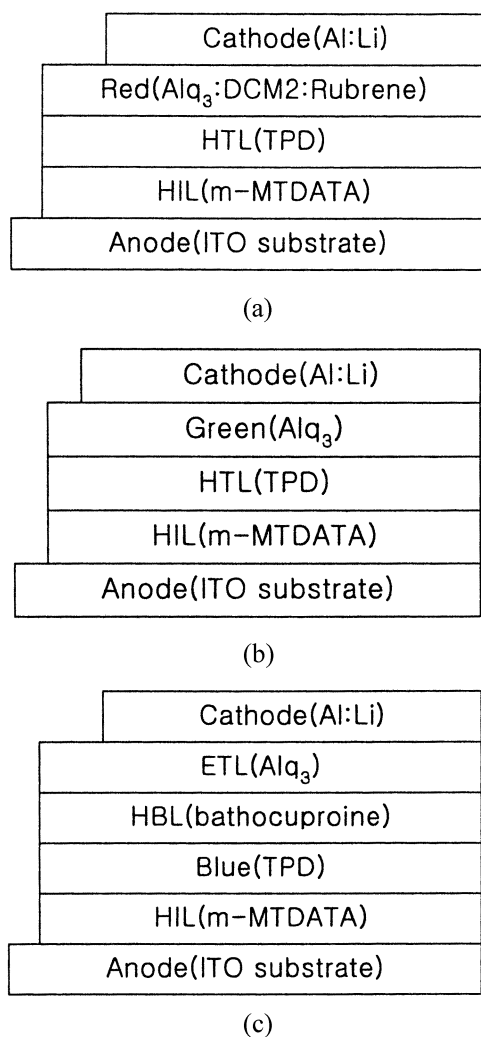

(a)

(b)

(c)

Fig. 1. Schematic cross-sections of the fabricated OLED structures: (a) red OLED, (b) green OLED, (c) blue OLED.

then rinsed by DI-water, and chemically cleaned by TCE (trichloro ethylene), acetone, and methanol in series with ultrasonification for 10 min each. After being blow-dried by nitrogen, the substrates were further treated by O_2 plasma. The cleaning process removes most of the surface organic contaminants and improves the interfacial integrity between the anode surface and organic layer [Kim et al., 2002].

The organic light-emitting materials used in this research were Alq_3 [aluminum tris (8-hydroxyquinolines)] for green-light emission, Alq_3 doped with DCM2 [[2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzoquinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene] propane-dinitrile] and Rubrene [5,6,11,12-tetraphenyl naphthacene] for red-light emission, and TPD [N,N'-diphenyl-N,N'-bis (3-methyl phenyl)-1,1'-diphenyl-4,4'-diamine] for blue-light emission. Fig. 1 shows the configurations of the structure of OLEDs fabricated in this study. The structures were designed on the premise of reducing unnecessary change of materials, keeping the production of full-color display panels in mind. Use of similar material combination for different-color diodes can increase the production throughput and reduce the equipment cost tremendously.

Three different materials (m-MTDATA, PEDOT and CuPc) were compared as the candidate HILs, and TPD was primarily incorporated as the hole-transport layer. In the blue OLED structure, however, bathocuproine [2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline] was inserted as a hole-blocking layer between the electron-transport layer (Alq_3) and emission layer (TPD) to adjust the electron-hole recombination zone by limiting the movement of holes [Park et al., 2000].

All the organic materials except PEDOT were thermally evaporated under vacuum (base pressure of 4×10⁻⁶ Torr), and the deposition rate was controlled to 1-2 Å/s. PEDOT was dissolved into water and spin-coated at 4,000 rpm. Thickness of hole-injection layer was controlled to ~10 nm, thickness of hole and electron transport layer was controlled to ~30 nm, and thickness of emitting layer was controlled to ~15 nm. Finally, Al : Li alloy with 0.26 at% Li was thermally evaporated via shadow mask to form the stripe-patterned cathodes with ~200 nm thickness aligned perpendicular to the anodes, which completes the diode structure. Deposition of organic and cathode materials was made continuously in a single chamber without breaking vacuum to prevent any material deterioration due to the exposure of substrates to the ambient.

Deposited film thickness was measured by Dektak 3030 stage profiler, and surface morphology was analyzed by atomic force microscopy (AFM). The electrical characteristics of fabricated diodes were analyzed by semiconductor parameter analyzer (HP 4145B), and luminance was measured by photometer (CS-100, Minolta) with close-up lens (No. 110, Φ=40.5 mm) attached.

RESULTS AND DISCUSSION

The surface morphology of ITO-glass before and after coating the three HIL materials (PEDOT, m-MTDATA and CuPc) were analyzed and compared by AFM, and the results are shown in Fig. 2. The RMS (root-mean-square) roughness decreased upon coating of hole-injection layer, and substrates coated with m-MTDATA showed the lowest surface roughness (1.096 nm) among the three hole-injecting materials tested in this study. In the CuPc case, surface
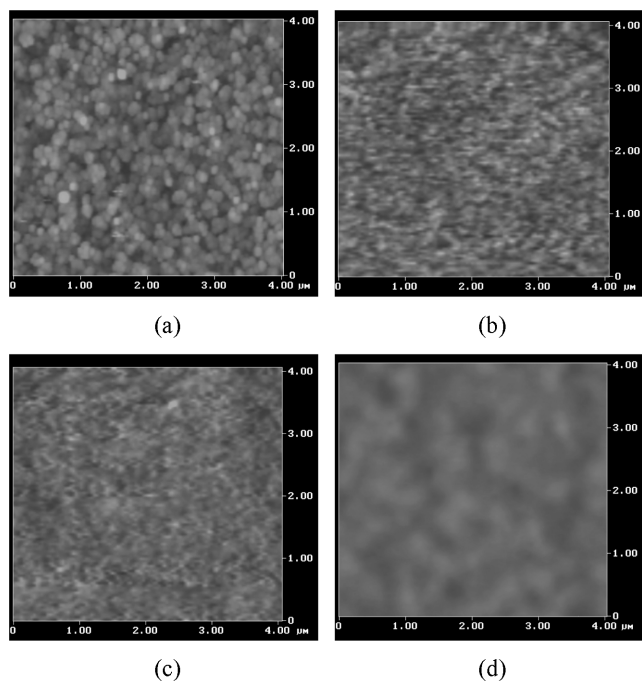
(a)   (b)

(c)   (d)

Fig. 2. AFM images of the surfaces of: (a) bare ITO (RMS roughness: 2.737 nm), (b) ITO/CuPc (RMS roughness: 2.519 nm), (c) ITO/PEDOT (RMS roughness: 1.118 nm), (d) ITO/m-MTDATA (RMS roughness: 1.096 nm).
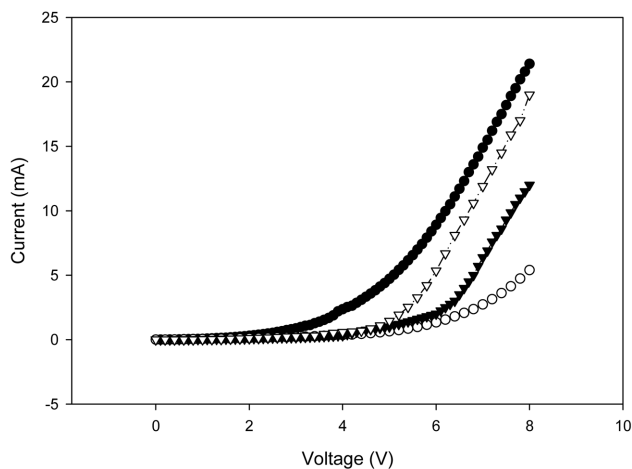

Fig. 3. I-V characteristic curves of green OLEDs: (○) ITO/TPD/Alq₃/Al : Li, turn-on voltage: 3.5 V, brightness at 6 V: 2,750 cd/m², (▲) ITO/CuPc/TPD/Alq₃/Al : Li, turn-on voltage: 3.0 V, brightness at 6 V: 4,510 cd/m², (△) ITO/PEDOT/TPD/Alq₃/Al : Li, turn-on voltage: 2.7 V, brightness at 6 V: 3,000 cd/m², (●) ITO/m-MTDATA/TPD/Alq₃/Al : Li, turn-on voltage: 2.3 V, brightness at 6 V: 3,910 cd/m².

roughness was only slightly improved (2.519 nm) from that of bare ITO (2.737 nm). Interestingly, thermally evaporated m-MTDATA film shows comparable or even better surface roughness compared with the roughness (1.118 nm) of spin-coated PEDOT surface. The improvement of surface roughness by m-MTDATA coating is attributed to its dense and amorphous film forming capability as observed by previous investigators [Moriwaki et al., 1998; Nakano et al., 1996],
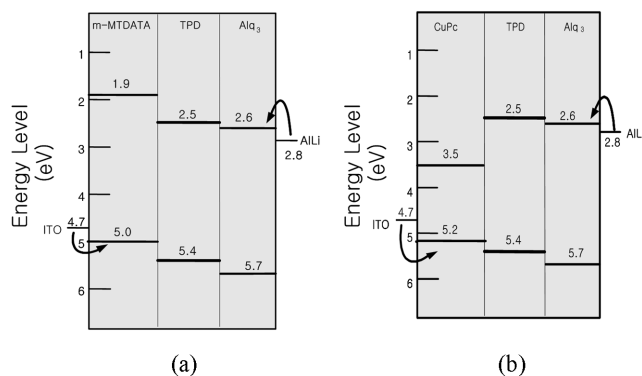

Fig. 4. Energy band diagrams of (a) green OLED with m-MTDATA, (b) green OLED with CuPc.

and such an improvement in surface morphology can help enhance the device performance by allowing more uniform charge transport from the anode to the hole-transport layer, resulting in the reduced short-term device degradations mostly caused by local joule-heating effects.

The electrical and optical characteristics of the green OLEDs fabricated with or without using HIL were investigated and compared. Fig. 3 shows I-V characteristic curves of green OLEDs made by using CuPc, PEDOT, or m-MTDATA as HIL, together with the I-V curve of green OLED without the HIL. As clearly shown in the figure, the turn-on voltage was lowered when HIL was inserted, indicating that the charge injection from the anode was facilitated by the presence of HIL. The lowest turn-on voltage (2.3 V) was obtained with m-MTDATA among three HIL materials tested in this study. Fig. 4 shows the energy band diagrams of the green OLEDs made with m-MTDATA (Fig. 4(a)) and with CuPc (Fig. 4(b)), respectively. As clearly shown in the figure, the energy barrier between the anode and HIL is lower in the m-MTDATA case, explaining the lower turn-on voltage observed in the m-MTDATA inserted OLED.

Improvement in the luminous efficiency was also observed with the insertion of HIL. Brightness measured at 6 V increased from 2,750 cd/m² (without HIL) to 4,510 cd/m² (with CuPc). In the m-MTDATA case, the brightness measured at 6 V was 3,910 cd/m², and the calculated luminous efficiency was 1.4 lm/W at 100 cd/m². The corresponding green emission spectra were centered at 530 nm, and its CIE coordinate was (0.240, 0.525). The turn-on voltage decrease by the insertion of HIL is considered to be due to the combined effect of improved surface morphology and lowering of the energy barrier between the anode and hole-transport layer. Among the three HIL materials tested, m-MTDATA showed the best characteristics in surface roughness and turn-on voltage. These results clearly indicate that the HIL enhances the OLED performance by smoothing the anode surface (allowing more uniform charge transport) and facilitating the injection of holes (by lowering the energy barrier between the anode and hole-transport layer). One apparently unexpected behavior was, however, observed in the case of OLED using CuPc. The turn-on voltage of OLED with CuPc was higher (3.0 V) than that of OLED with m-MTDATA (2.3 V), but the brightness measured at 6 V was also higher (4,510 cd/m²) in the CuPc case than that of m-MTDATA case (3,910 cd/m²), indicating that the luminous efficiency is better in the CuPc case. This apparent

contradiction can be explained by considering the possible shift of electron-hole recombination zone toward the anode by retarding the injection of holes from the anode, which improves the charge balance in the device operation. This is due to the fact that the mobility of holes is much higher than that of electrons in OLEDs, and the optimum recombination zone setting could be obtained by controlling the hole-injection and hole-transport. Since TPD of same thickness was used as the hole-transport layer for all the green OLEDs fabricated in this study, the higher luminous efficiency of OLEDs with CuPc is thought to be mostly caused by the recombination zone shift and its positive effect on charge balance. Some drawbacks, however, were noticed in the OLEDs made with CuPc, if the mass production is considered. The OLEDs with CuPc were in general more vulnerable to the process fluctuations (thickness variation, base pressure variation of thermal evaporator, etc) and had higher tendency to be recrystallized, giving out poorer reproducibility when compared with OLEDs by using m-MTDATA. Therefore, m-MTDATA is considered to be the best HIL material tested in this study.

Red, green, and blue OLEDs were fabricated by using m-MTDATA as HIL, and their structures and device characteristics are summarized in Table 1. As stated earlier, m-MTDATA was used as the invariant HIL material for all these OLEDs, and the material combinations (Fig. 1) were designed in such a way that unnecessary change of materials is minimized. The fabricated OLEDs showed fairly good and comparable device characteristics among different color devices in the turn-on voltage (<5 V) and luminous efficiency (>1 lm/W), even though the material combination is not individually optimized for the best performance. The band diagrams for the OLEDs are drawn in Fig. 5, and they show that the observed device characteristics match very well with those expected from the diagrams. First, the role of m-MTDATA in lowering the energy barrier (0.7 eV) between the ITO and TPD is expected, and this agrees very well with the reduced turn-on voltages. In the blue OLED case, the hole-blocking nature of bathocuproine is also clearly indicated, shifting the electron-hole recombination zone from Alq_3 to TPD. In the

case of red OLED, Alq_3 acts as electron-transport material and the emission is mostly dominated by the transitions between energy levels provided by DCM2. Rubrene acts as a red-emitting assist dopant, which assists energy transfer from Alq_3 to DCM2. Central emission wavelengths and corresponding CIE coordinates were measured to be 597 nm and (0.600, 0.389) for red emission, 530 nm and (0.240, 0.525) for green emission, and 480 nm and (0.171, 0.171) for blue emission, respectively. The OLEDs made with m-MTDATA also showed suitable characteristics as commercial devices, in that the devices were less sensitive to the variation of HIL thickness (10 nm to 50 nm), interfacial integrity, and process reproducibility.

CONCLUSION

In this research, red, green, and blue OLEDs using m-MTDATA as a common hole-injection layer were fabricated, and their device characteristics were measured and compared. It was found that the m-MTDATA could be successfully incorporated as a common hole-injection layer for multi-color OLED display devices in the commercial applications. The improved device performance by the m-MTDATA could be explained by the improved anode surface morphology and lowered hole-injection barrier height. The m-MTDATA also provided suitable characteristics for mass production such as process reproducibility and controllability.

ACKNOWLEDGMENTS

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Table 1. Device characteristics of the fabricated OLEDs

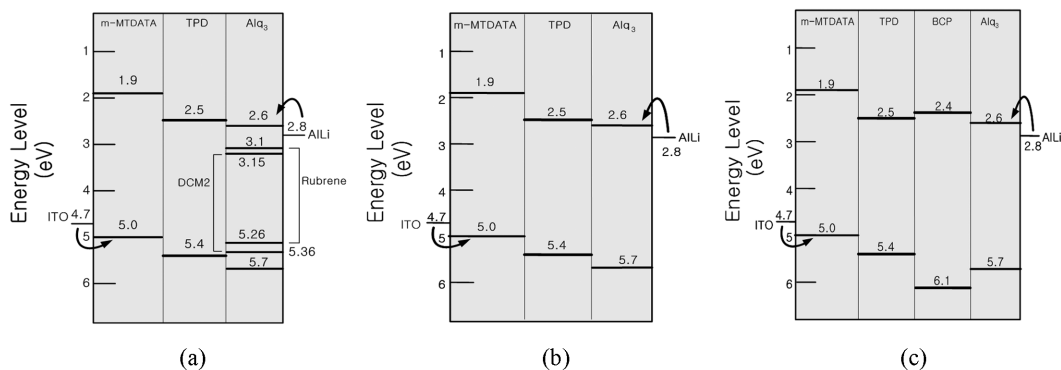| Structure	Turn-on (V)	Maximum luminescence (cd/m^2)	Luminous efficiency (lm/W)
Red (ITO/m-MTDATA/TPD/Alq$_3$: DCM2 : Rubrene/Al : Li)	4.6	1,900 at 16 V	1.4 at 106 cd/m^2
Green (ITO/m-MTDATA/TPD/Alq$_3$/Al : Li)	2.3	3,910 at 6 V	1.4 at 100 cd/m^2
Blue (ITO/m-MTDATA/TPD/bathocuproine/Alq$_3$/Al : Li)	3.4	125 at 10 V	2.0 at 104 cd/m^2

Fig. 5. Energy band diagrams of (a) red OLED, (b) green OLED, (c) blue OLED.

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