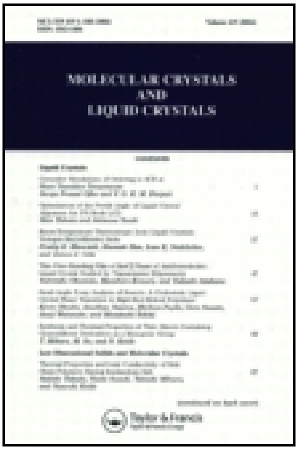

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Efficiency Variations in Organic Light-Emitting Devices Utilizing the 4,4′,4″-tris(N-(2-naphthyl)-Nphenylamino) triphenylamine Hole Transport Layer Doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane

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Efficiency Variations in Organic Light-Emitting Devices Utilizing the 4,4′,4″-tris(N-(2-naphthyl)-Nphenylamino) triphenylamine Hole Transport Layer Doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane

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The electrical and the optical properties of organic light emitting devices (OLEDs) with a 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4-TCNQ) doped 4,4′,4″-tris(N-(2-naphthyl)-Nphenylamino)triphenylamine (2-TNATA) hole transport layer (HTL) were investigated. In comparison with that of the OLEDs containing an undoped 2-TNATA layer, the hole transport efficiency of OLEDs with a F_4-TCNQ doped 2-TNATA HTL was significantly enhanced due to an increase in the doping concentration and resulted in enhancement of the luminance. The electroluminescence spectra for the OLEDs with a doped HTL showed a dominant emission peak corresponding to the Alq_3 layer. This peak was not affected by the existence of the F_4-TCNQ doped HTL.

Keywords: doped hole transport layer; doping concentration; efficiency; electrical properties; optical properties; organic light-emitting device

I. INTRODUCTION

Organic light-emitting devices (OLEDs) offer advantages of low operating voltage, low power consumption, wide viewing angle, low cost, large flexibility, and fast response [1–5]. As a result, there

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has been considerable research interest due to their promising applications in next-generation flat-panel displays [6,7], and potential for large-area flexible displays [8]. Moderate controls of the efficiencies of the carrier injection and transport for achieving carrier recombination and balance of the electrons and the holes are necessary for fabricating highly-efficient OLEDs. Potential applications of highly-efficient OLEDs have driven extensive efforts to enhance OLED efficiency. Among the various methods for improving the efficiency of OLEDs, the surface treatment of the indium tin oxide (ITO) layer and the insertion of the buffer layer between the ITO and the hole transport layer (HTL) are very important for enhancing hole injection efficiency [9–11]. The efficiencies of the carrier injection and transport in OLEDs have been enhanced by using the doped HTL [12–13]. Zinc phthalocyanine (ZnPc), 4,4,4-tris(N,N-diphenyl-amino)triphenylamine (TDATA) or N,N′-di(1-naphthyl)-N,N′-diphenylbenzidine (NPB) doped with a 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4-TCNQ), increase the conductivity of the carriers due to the strong electron acceptable property of F_4-TCNQ [14–16]. Even though some studies concerning the efficiency variation in OLEDs with an impurity doped HTL have been performed, systematic studies concerning the variation of luminance efficiency due to the existence of the doped HTL in OLEDs are necessary for improving the efficiency roll-off of the OLEDs.

This paper reports data for the electrical and the optical properties of OLEDs with a F_4-TCNQ doped 4,4′,4″-tris(N-(2-naphthyl)-Nphenylamino)-triphenylamine (2-TNATA) HTLs at various doping concentrations fabricated by using organic molecular-beam deposition (OMBD). Current density-voltage, luminance-voltage, luminous efficiency-current density, and electroluminescence (EL) spectra measurements were carried out to investigate the electrical and the optical properties of OLEDs with 2-TNATA HTLs containing various F_4-TCNQ doping concentrations.

II. EXPERIMENT DETAILS

The sheet resistivity of the ITO thin films coated on glass substrates used in this study was 15 Ω/square. The ITO substrates were cleaned using acetone and methanol at 60°C for 5 min, and then rinsed in de-ionized water thoroughly. After the chemically cleaned ITO substrates had been dried by using N_2 gas with a purity of 99.9999%, the substrates were treated with oxygen plasma for 10 min. The four types of samples used in this study were deposited on ITO thin films coated on glass substrates by using OMBD with effusion cells and

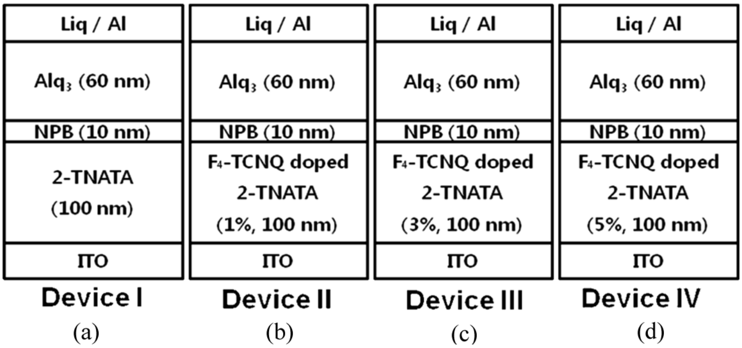


FIGURE 1 Schematic diagrams of the OLEDs of devices (a) I, (b) II, (c) III, and (d) IV.

shutters. The OLEDs of devices I, II, III, and IV consist of an aluminum (Al) cathode layer/a lithium quinolate (Liq) electron injection layer (EIL)/an 8-tris-hydroxyquinoline aluminum (Alq_3) electron transport and emitting layer (EML)/a NPB layer and a F_4-TCNQ doped 2-TNATA layer as a double HTL/an ITO anode layer/a glass substrate. The doping concentration of a F_4-TCNQ in devices I, II, III, and IV are

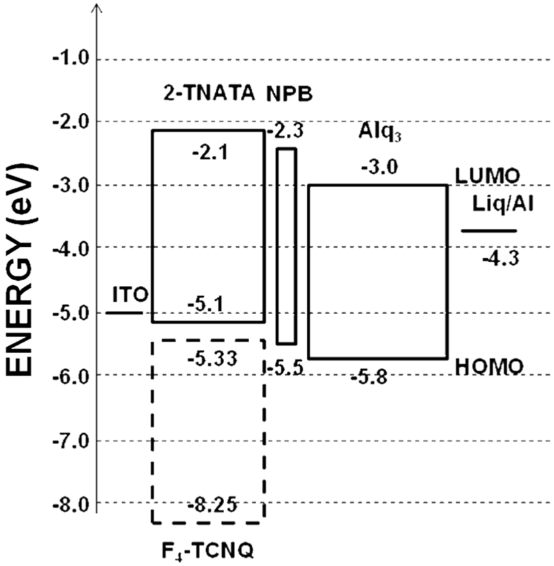
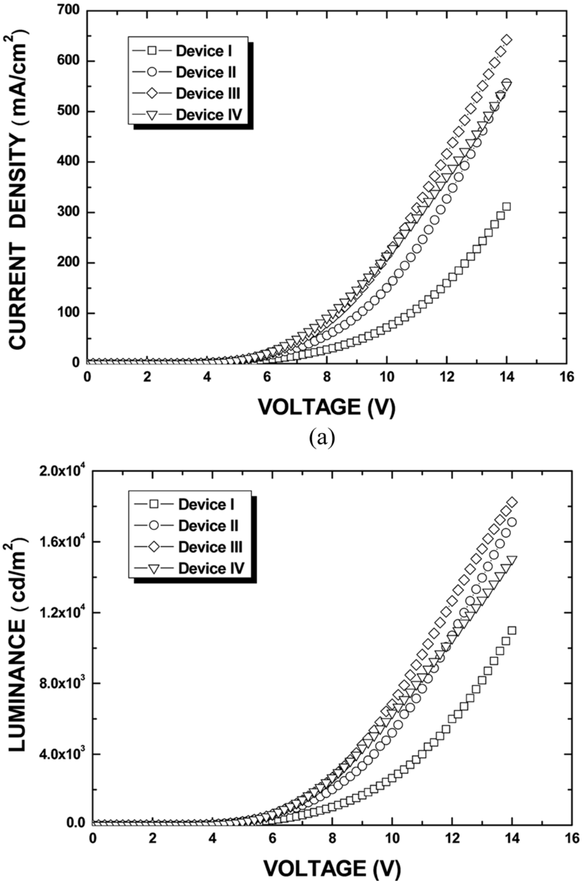


FIGURE 2 Schematic energy band diagrams of the OLEDs with a F_4-TCNQ doped 2-TNATA hole transport layer.

0, 1, 3, and 5 vol.%, respectively. The schematic diagrams of the devices (a) I, (b) II, (c) III, and (d) IV and the schematic energy band diagram of the OLEDs with a F_4-TCNQ doped 2-TNATA HTL are shown in Figures 1 and 2, respectively. The evaporation rates of the host and the dopant materials can be controlled independently by using two separate quartz thickness monitors, allowing the doping concentrations of the two materials to be adjusted. The depositions of the OLED layers were done at a substrate temperature of 27°C and a system pressure of 5×10^{-6} Torr. The growth rates of the organic layers, the dopant, and the metal layers were approximately 1, 0.01, and 0.5 Å/s, respectively. The emitting area was $5 \times 5\,\mathrm{mm}^2$. The current-voltage measurements of the OLEDs were performed on a programmable electrometer with built-in current and voltage measurement units (model 236, Keithely). The brightness was measured by using a brightness meter, chromameter CS-100A (Minolta). The EL spectrum was measured by using a luminescence spectrometer LS50B (Perkin-Elmer).

III. RESULTS AND DISCUSSION

Figure 3 shows (a) current densities as functions of the applied voltage and (b) luminances as functions of the applied voltage for OLEDs containing 2-TNATA HTLs with and without F_4-TCNQ dopants. The current densities of OLEDs with doped HTLs were larger than that of OLED with an undoped HTL. The efficiencies of the hole injection and the transport in the OLEDs were enhanced by utilizing the F_4-TCNQ doped HTL. Because the highest occupied molecular orbital (HOMO) level of a 2-TNATA layer was slightly larger than the lowest unoccupied molecular orbital (LUMO) level of a F_4-TCNQ dopant, as shown in Figure 2, the electrons existing in the HOMO level of 2-TNATA host molecules partially transferred to the LUMO level of F_4-TCNQ dopant molecules, resulting in the enhancement of the hole conductivity of the F_4-TCNQ doped 2-TNATA HTL [16]. The luminances of OLEDs with a F_4-TCNQ doped HTL increased in comparison with OLED with an undoped HTL, as shown in Figure 2(b). The current density and the luminance of device IV were lower than those of device III. The current density and the luminance for the OLEDs of device IV containing the F_4-TCNQ dopant with a 3 vol.% doping concentration had the highest value. Therefore, the optimized concentration of the F_4-TCNQ dopant among the fabricated OLEDs was 3 vol.%. When the concentration of the F_4-TCNQ dopant was larger than the optimized concentration of 3 vol.%, the dopants might be diffused through the HTL into the EML, resulting in the occurrence of an exciton quenching effect [16].



(a)

(b)

FIGURE 3 (a) Current densities as functions of applied voltages and (b) luminances as functions of applied voltages for OLEDs with various doping concentrations of devices I, II, III, and IV. Open squares, circles, diamond, down-triangles represent the OLEDs of devices I, II, III, and IV, respectively.

Figure 4 shows the luminous efficiencies as functions of the current density for devices I, II, III, and IV, respectively. The maximum luminous efficiencies of devices I, II, III, and IV at 50 mA/cm^2 were 3.7, 3.6, 3.3, and 2.9 cd/A, respectively. The efficiencies of the OLEDs with F_4-TCNQ doped HTLs were lower than that of OLEDs with an undoped HTL because the number of electrons and holes in the EML was not balanced due to an increase in the injection number of the hole. The maximum luminance efficiency of OLEDs with F_4-TCNQ doped HTLs decreases with increasing F_4-TCNQ dopant concentration due to an

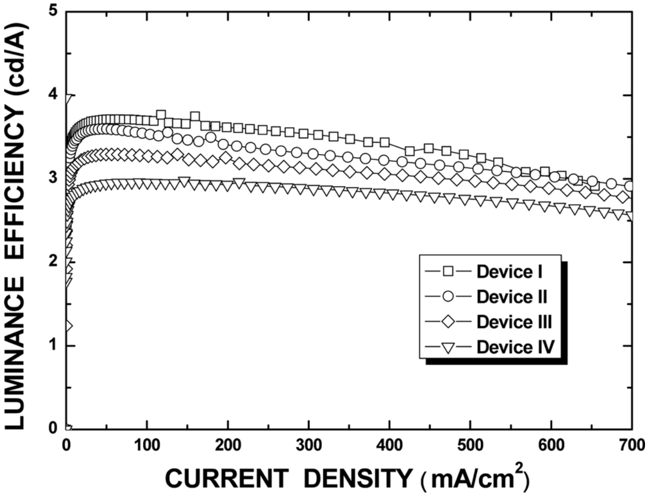


FIGURE 4 Luminous efficiencies as functions of current density for OLEDs with various doping concentrations of devices I, II, III, and IV. Open squares, circles, diamond, down-triangles represent the OLEDs of devices I, II, III, and IV, respectively.

increase in the holes existing in the EML. However, the luminance efficiencies of OLEDs containing a F_4-TCNQ dopant with higher concentrations become stable, regardless of the variation of the current density. Because the unbalance of the carriers in the fluorescent OLEDs with an undoped EML dominantly affects the roll-off of the luminance efficiency [17], the variation of the luminance efficiency of device I originates from the variation of the carrier balance in the EML. The holes at low voltage dominantly exists in the EML of device I due to the larger hole mobility of the organic layer in comparison with the electron mobility, resulting in the more formation of the excitons with the electrons in the EML. However, because the width of the electron blocking barrier of the HTL at high voltages decreases, the electrons tunneling into the anode increase, resulting in a decrease in the luminance efficiency of OLEDs with an undoped HTL. More holes existing in the F_4-TCNQ doped HTLs at high voltage inject into the EML, and the larger internal electric field originating from more holes in the EML prevent an increase in the leakage electrons. These processes result in an improvement of the efficiency stability for OLEDs with a F_4-TCNQ doped HTL.

Figure 5 shows the normalized EL spectra at 12 V of devices I, II, III, and IV. All of the EL spectra of devices I, II, III, and IV showed

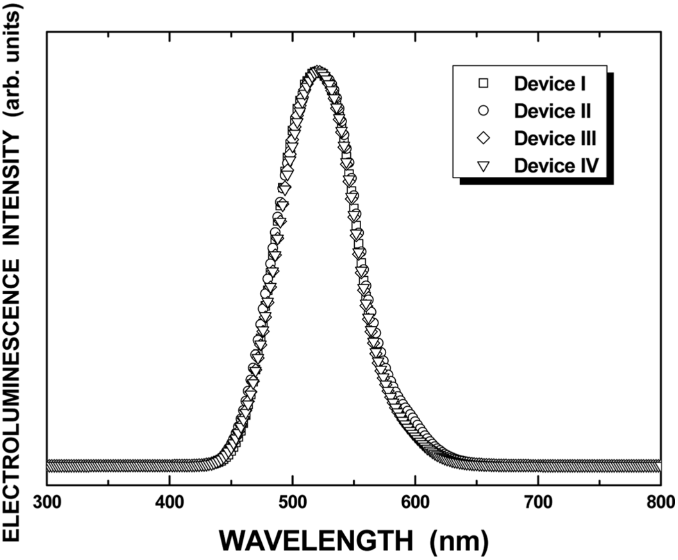


FIGURE 5 Electroluminescence spectra at 12 V for OLEDs with various doping concentrations of devices I, II, III, and IV. Open squares, circles, diamond, down-triangles represent the OLEDs of devices I, II, III, and IV, respectively.

a dominant peak corresponding to the Alq_3 layer, indicative of the green color of all of the devices. Because the F_4-TCNQ dopant in the HTL affects the conductivity and the mobility of the holes in the HTL, the position of the recombination zone in the EML shifted toward the EIL. The emission behaviors of the EL spectra for the OLED with the F_4-TCNQ dopant were in reasonable agreement with those of all OLEDs without a F_4-TCNQ doped HTL. While the current density, luminance, and the luminance efficiency were significantly affected by the existence and the concentration of the F_4-TCNQ dopant, the emission peaks of the EL spectra were invariant, regardless of the variation of the doping concentration.

IV. SUMMARY AND CONCLUSIONS

The electrical and the optical properties of OLEDs fabricated utilizing an undoped or a F_4-TCNQ doped 2-TNATA HTL were investigated. Because the LUMO level of the F_4-TCNQ molecules, acting as a p-type dopant, was lower than the HOMO level of the 2-TNATA molecules, the F_4-TCNQ molecules attracted the electrons in the HOMO level of the 2-TNATA molecules, resulting in an increase in the excess holes of the 2-TNATA layer. The hole transport efficiency of OLEDs with a F_4-TCNQ doped 2-TNATA HTL was significantly enhanced due to an increase of the excess holes in the 2-TNATA layer, resulting in the enhancement of the luminance. The EL spectra for the OLEDs with a doped HTL showed a dominant green color emission corresponding to the Alq_3 layer, regardless of the existence and the concentration in the dopants of the HTLs in OLEDs with an undoped HTL. These results can help improve understanding of the enhancement of the carrier injection and carrier transport in OLEDs utilizing a F_4-TCNQ-doped HTL.

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