Organic EL Devices Having Lewis-Acid-Doped Polymer As a Hole-Injecting Layer

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We have fabricated organic EL devices having Lewis-acid-doped polymer as a hole-injecting layer. The polymer used is polyarylamine and Lewis acids used are tris(pentafluorophenyl)borane and tris(b-perfluoronaphthyl)borane. The EL device with a structure of glass substrate/indium-tin oxide/Lewis-acid-doped polyarylamine/naphthyl phenyl diamine (α -NPD)/tris(8-quinolinolato)aluminum(III) (Alq)/LiF/Al showed higher luminance and luminous efficiencies compared with the device without a hole-injecting layer.

Keywords: Organic electroluminescent device, Lewis acid, polyarylamine, hole-injecting layer1.

1. Introduction

Organic electroluminescent (EL) devices (OLEDs) are a class of light-emitting devices having organic thin layers sandwiched between two electrodes. Since a bilayer device structure composed of anode/ hole transport layer/ electron-transporting emitter layer/ cathode was proposed by Tang and VanSlyke [1], various structures have been proposed to improve the efficiency of devices.

As the barrier height of the electrode/organic interfaces is one of the factors that influence the drive voltages and performance of the device, carrier-injecting layers, or buffer layers, are inserted into these interfaces to lower the barrier height for carrier injection. Typical hole-injecting materials for small molecule-based devices are copper phthalocyanine (CuPc), high molecular weight arylamines, such as starburst amine derivatives, which possess low ionization potentials (Ip). In our previous report, we demonstrated that, by using α -NPD codeposited with a Lewis acid FeCl_3 as a hole-injecting layer, the performance of device was improved in terms of the drive voltage [2]. Recently, Yamamori et al. reported tris (4-bromophenyl) aminium hexachloroantimonate (TBAHA)-doped tetraphenyl benzidine -containing polymer as a thick hole injection layer [3]. Very recently, we demonstrated that devices with a TBAHA-doped thermally stable polymer buffer layer

exhibit longer lifetime and higher thermal stability than devices with CuPc as a buffer layer [4].

In this study, we used tris(pentafluorophenyl)borane (PPB) and tris(b-perfluoronaphthyl)borane (PNB) as Lewis acid doped to polyarylamine, which are reported to be strong Lewis acids and were used as cocatalyst for olefin polymerization[5]. The polyarylamine is poly(N-phenyl)biphenyl amine (PPBA) which was used as a host polymer for TBAHA doped-polymer system [6][7].

2. Method

2-1. Hole-injecting materials

PPBA was synthesized by the reaction of 4,4'-dibromobiphenyl with aniline under palladium catalyst [6]. PPB was purchased from Aldrich Co. Ltd. and used without further purification. PNB was prepared according to the literature [4].

2-2. Hole transporting material and emitter material

α -NPD and Alq were prepared via published methods and used as hole transporting and emitter material, respectively. These materials were purified by train sublimation.

2-3. Fabrication of OEL devices

Indium-tin oxide (ITO)-coated glass

substrates were cleaned in a ultrasonic bath using several solvents and were treated in a UV-ozone chamber just before device fabrication. A 200 Å-thick hole-injecting polymer layer was formed on the ITO by spin-coating using 5g/L chloroform solutions of the polymer and the Lewis acid, with concentrations of 10, 20, 30, 40, or 50 wt% against polymer. On top of the polymer layer, α -NPD (200 Å) and Alq (700 Å) were vacuum-deposited at 5×10^{-6} Torr. Finally, 5 Å-thick LiF and 1000 Å-thick Al cathode were deposited on the Alq layer surface at 10^{-5} Torr. Device structure and molecular structure are shown in Figure 1.

Luminance was measured using a Topcon BM-8 luminance meter and electroluminescence spectra were taken on a Hamamatsu photonics PMA-10 optical multichannel analyzer. UV-Vis absorption spectra were measured with a Shimadzu UV-2200A spectrophotometer.

Fig.1 Configuration of EL cell and molecular structures.

3. Results and Discussion

3-1. Absorption spectra of doped polymer

Figure 2 shows the UV-Vis spectra of undoped and doped polymer films. An additional absorption peak at around 500 nm is observed from both PPB and PNB-doped polymer spectra. These peaks can be attributed to the charge transfer (CT) complexes between the polymer and the Lewis acid. In order to evaluate the conductivity of the polymer films, we prepared hole-only devices with following structure: ITO/ undoped or doped polymer (1000 Å) / Al (2000 Å). The current density-voltage characteristics of these devices are shown in Figure 3. Higher current densities are observed for doped-polymer systems compared with that observed

for undoped systems, which indicates higher conductivity of the doped polymer films than that of undoped system. The increase in current density can be attributed to the formation of radical cations in the polymer layer by doping, which results in increasing carrier density.

Fig.2 UV-Vis spectra of Lewis acid doped polymer films.

- (a) Undoped polymer
- (b) PNB 50 wt % doped polymer
- (c) PPB 50 wt % doped polymer

Fig.3 Current density-voltage characteristics of ITO/undoped or doped polymer/Al devices.

3-2. EL characteristics of PPB-doped system

To optimize the doping concentration of PPB, the doping concentration was varied from 10 to 50 wt%. The luminance-voltage (L-V) and current

density-voltage (J-V) characteristics are displayed in Figures 4 and 5, and summarized in Table 1.

Table 1. EL characteristics of ITO/PPBA:PPB/ α -NPD/Alq/LiF/Al devices.

Hole-injecting layer	Max. luminance (cd/m ²)	Max. efficiency (lm/W)	Max. η_{ex} (p/e%)
None	23000 (at 10 V)	3.3 (at 4 V)	1.7 (at 9 V)
PPB10wt%	27600 (at 10 V)	3.6 (at 3 V)	1.7 (at 9 V)
PPB 20wt%	25500 (at 9 V)	3.2 (at 4 V)	1.9 (at 9 V)
PPB 30wt%	36000 (at 9 V)	3.8 (at 3 V)	2.0 (at 9 V)
PPB 40wt%	26600 (at 9 V)	3.8 (at 3 V)	1.6 (at 8 V)
PPB 50wt%	22900 (at 10 V)	3.5 (at 5 V)	1.5 (at 9 V)

Fig.4 Luminance-voltage characteristics of ITO/PPBA:PPB/ α -NPD/Alq/LiF/Al devices.

(○) Without hole-injecting layer, (□) PPB 10 wt%, (△) PPB 20 wt%, (◇) PPB 30 wt%, (⊕) PPB 40 wt%, (⊞) PPB 50 wt%.

By inserting PPB doped-polymer layer as a hole-injecting layer, higher luminance, higher current density, higher luminous efficiency were obtained compared with the device without the polymer layer. Among the devices, a device having a polymer layer with 30 wt% of PPB shows the highest performance and this value is the optimum PPB concentration. In Table 1, the maximum external quantum efficiency was increased when the doping concentration is increased from 20 to 30 wt% and then decreased gradually when the concentration exceeded 40 wt%. This indicates that hole and electron-injecting was balanced at the concentration of 30 wt%.

Fig.5 Current density-voltage characteristics of ITO/PPBA:PPB/ α -NPD/Alq/LiF/Al devices.

(○) Without hole-injecting layer, (□) PPB 10 wt%, (△) PPB 20 wt%, (◇) PPB 30 wt%, (⊕) PPB 40 wt%, (⊞) PPB 50 wt%.

Fig.6 Luminance-voltage characteristics of ITO/PPBA:PNB/ α -NPD/Alq/LiF/Al devices.

(○) Without hole-injecting layer, (□) PNB 10 wt%, (△) PNB 20 wt%, (◇) PNB 30 wt%, (⊕) PNB 40 wt%, (⊞) PNB 50 wt%.

3-3. EL characteristics of PNB-doped systems

We also carried out optimizing doping concentration of PNB. L-V, J-V characteristics of the devices were shown in Figures 6 and 7. Maximum luminance, luminous efficiency and external quantum efficiency are summarized in Table 2. Performance of the EL devices was also improved by using the PNB-doped PPBA hole-injecting layer similar to the devices having the PPB-doped polymer.

Fig.7 Current density-voltage characteristics of ITO/PPBA:PNB/ α -NPD/Alq/LiF/Al devices.

(○) Without hole-injecting layer, (□) PNB 10 wt%,
(△) PNB 20 wt%, (◇) PNB 30 wt%,
(⊕) PNB 40 wt%, (⊞) PNB 50 wt%.

Table 2. EL characteristics of ITO/PPBA:PNB/
 α -NPD/Alq/LiF/Al devices.

Hole-injecting layer	Max. luminance (cd/m ²)	Max. efficiency (lm/W)	Max. η_{ex} (p/e%)
None	23000 (at 10 V)	3.3 (at 4 V)	1.7 (at 9 V)
PNB10wt%	19700 (at 9 V)	3.5 (at 3 V)	1.6 (at 8 V)
PNB 20wt%	33000 (at 9 V)	3.6 (at 3 V)	1.7 (at 8 V)
PNB 30wt%	28100 (at 9 V)	3.0 (at 3 V)	1.9 (at 9 V)
PNB 40wt%	23500 (at 9 V)	3.0 (at 4 V)	1.7 (at 9 V)
PNB 50wt%	27400 (at 9 V)	2.5 (at 4 V)	1.9 (at 9 V)

hole-injecting layer similar to the devices having the PPB-doped polymer.

3-4. Difference between PPB and PNB doped device

Comparing the PPB system and PNB system, the PPB doped device showed slightly higher performance than the PNB doped one although the Lewis acidity of PNB is higher than that of PPB as

reported in literature. Therefore, the difference may be due to the purity of these dopants. The purity of the purchased PPB is 95%, reported value, and that of the synthesized PNB is 90%, determined by high performance liquid chromatography. So, the kinds of impurities and concentrations are assumed to lead to the difference in performance of devices, which may act as carrier traps that lead to the decrease in the carrier mobility.

4. Conclusion

In conclusion, we successfully improved the performance of OEL devices by inserting a hole-injecting layer having Lewis acid, PPB or PNB, as dopant. The lifetime and thermal stability of the devices will be measured and reported elsewhere.

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