Organic Electroluminescent Devices Using a Mixed Single Layer

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Electroluminescent devices with mixed single-layer organic materials that consist of hole transport material, electron transport material and dopant material are studied. High luminance could be obtained by optimizing the weight ratios of hole and electron transport materials.

KEYWORDS: electroluminescence, mixed layer, single source deposition, single-layer device, injected carrier balance

Organic electroluminescent (EL) devices are promising for low driving voltage,[1-8] bright emission[1, 4-7] and multicolor display.[2, 4] These devices are carrier injection types such as light emitting diodes (LED), and consist of many device configurations such as two or three organic-layer devices.[1-7] In these multilayer structures, a hetero interface is necessary to achieve effective carrier blocking and recombination. Doping in the emission layer is also effective for improving the EL efficiency.[4, 8] In multilayer devices and doped devices, however, many evaporation sources are needed for fabrication, and the process control is difficult.

In this paper, the characteristics of efficient EL devices with mixed single-layer organic materials are described and compared with multilayer organic EL devices. In these devices, the ratio of injected carriers from anode and cathode can be optimized by the weight ratios of hole and electron transport materials. Also the fabrication process of EL devices can be simplified.

Three organic materials were prepared, as shown in Fig .1, to fabricate the mixed single layer. The weight ratios of N, N'-diphenyl-N, N'-*bis*(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) as the hole transport material and 8-hydroxyquinoline aluminum (Alq$_3$) as the emission material with electron transport characteristics were x:100–x, where the x value was changed from 0 to 80. The 1 wt% of 4-(dicyanomethylene)-2-methyl-6-(p-dimethyl aminostyryl)-4H-pyran(DCM) as the dopant material was added to the mixture of TPD and Alq$_3$.

The EL devices were fabricated by the vacuum vapor deposition technique. The mixed organic layer was deposited on ITO-coated glass substrate from a single evaporation source at 1×10^{-5} Torr. The evaporation source temperature was raised to 400°C within 10 s. The deposition rate of the organic layer was about 200 Å/s. The thickness of the organic layer was varied between 500–1500 Å and the error of thickness was within 100 Å. The deposition rate and the thickness of evaporated films were monitored by oscillator. The glass substrate was kept at room temperature. The top Mg cathode was prepared at the rate of about 500 Å/s by electron beam deposition at 5×10^{-5} Torr. The thickness of the Mg was about 2000 Å.

The area of EL devices was 2×2 mm^2. All measurements were carried out at room temperature in air. The power supply (Metronix model CMS 100-05) that increased the applied voltage at a rate of 1 V/s was controlled using a personal computer (NEC PC-9801 BX)

and GP-IB. The EL intensity was measured by a luminance meter (Topcom BM-3). Current and luminance values were obtained using a digital multimeter (Advantest TR-6846 and TR-6848).

The weight ratio dependence of EL efficiency at luminance of 10 cd/m^2 is shown in Fig. 2. The EL efficiency (η) is estimated as ,
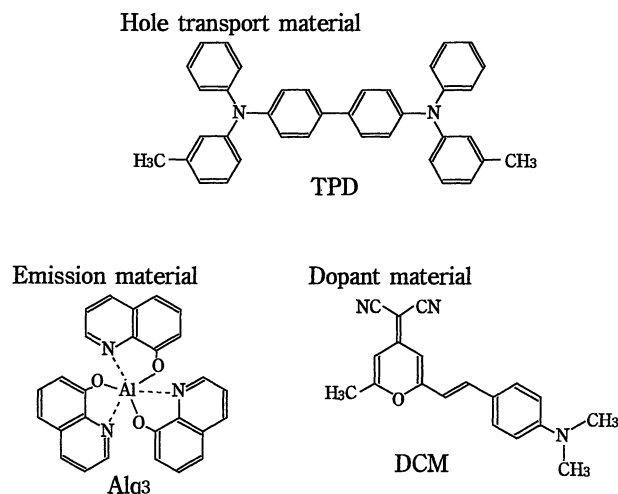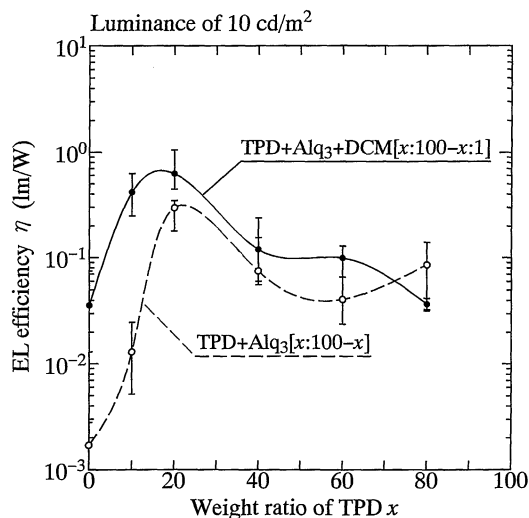

Fig. 1.   Molecular structures of TPD, Alq$_3$ and DCM.

Fig. 2.   EL efficiency (η) vs weight ratio of TPD (x) at luminance of 10 cd/m^2 for the following devices:
(o) ITO/TPD+Alq$_3$[x:100–x](1000 Å)/Mg,
(•) ITO/TPD+Alq$_3$+DCM[x:100–x:1](1000 Å)/Mg.

$$\eta = \pi \frac{L}{V \cdot J}, \tag{1}$$

where L, V and J are the luminance, the applied voltage and the current density, respectively.[9] The thickness of the mixed single layer is fixed at 1000 Å. The EL efficiency is rapidly increased with increase of the x value from 0 to 20. In this range, the applied voltage exhibiting the luminance of 10 cd/m^2 is decreased. In the film without TPD (x=0), hole injection from the ITO anode is very small because Alq$_3$ has poor hole injection characteristics. The efficiency of hole injection is improved with increase of the weight ratio of TPD. The EL efficiency is gradually decreased with increase in the x value from x=20 to 80. Optimum weight ratio of TPD is obtained as x=20. In mixed single-layer devices, the recombination area is probably distributed around a specified area and is controlled by the mixed ratio. The recombination in the organic layer without TPD (x=0) takes place near the anode because the electron transport property is superior to that of the hole. The radiation is decreased because of the quenching at the anode.[8] With increase of the weight ratio of TPD, the recombination area shifts from anode to cathode. With further increase of the TPD, the recombination will occur near the cathode and quenching will also occur. Under the optimum condition, electron and hole transport properties are balanced and the recombination will occur at the center of the mixed layer. As a result of carrier transport properties, the quenching at the electrode is minimized. In the doped DCM devices, EL efficiency is larger than that without DCM devices.

Figure 3 shows the film thickness dependence of luminance at current density of 100 mA/cm^2 and of EL efficiency at luminance of 10 cd/m^2 for doped DCM devices. The weight ratio of TPD and Alq$_3$ is 20:80 and the thickness of the mixed single layer is varied from 500 to 1500 Å. The luminance is slightly increased at thickness below 1000 Å and is saturated at thickness over 1000 Å. At the thickness over 1000 Å, however, EL efficiency is slightly decreased because of the increase of applied voltage with the same luminance from eq. (1). In thin ($<$1000 Å) devices, large leakage-current is caused and electron-hole recombination is decreased. In the 1000 Å-thick device, excitons created by electron-hole recombination migrate across the organic layer and are quenched at the electrode.

The emission spectrum of TPD+Alq$_3$ and TPD + Alq$_3$ + DCM devices is similar to the photoluminescence spectrum of the Alq$_3$ and the DCM, respectively. This result indicates that the radiation takes place at the Alq$_3$ and the DCM.

The luminance versus current density characteristics of mixed single-layer and multilayer devices are shown in Fig. 4. The structures of the four types of devices are
(A) ITO/TPD+Alq$_3$[20:80](1000 Å)/Mg,
(B) ITO/TPD+Alq$_3$+DCM[20:80:1](1000 Å)/Mg,
(C) ITO/TPD(500 Å)/Alq$_3$(500 Å)/Mg,
(D) ITO/TPD(500 Å)/Alq$_3$+DCM[100:1](500 Å)/Mg.
The luminance values of all devices are proportional to the current density in the overall range. The characteristics are about the same between B- and D-type devices,
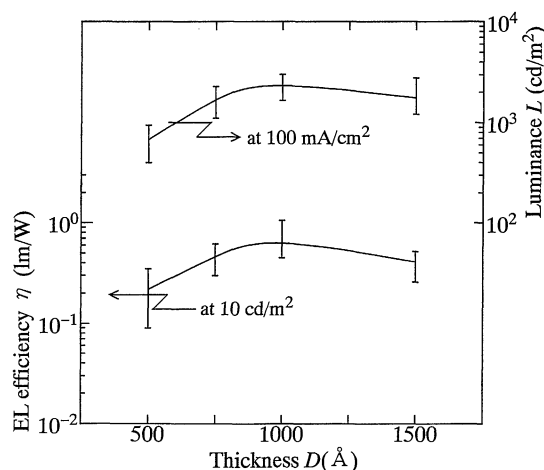

Fig. 3. EL efficiency (η) (luminance of 10 cd/m^2) and luminance (L) (current density of 100 mA/cm^2) vs thickness of organic layer (D) for ITO/TPD+Alq$_3$+DCM[20:80:1](D Å)/Mg devices.
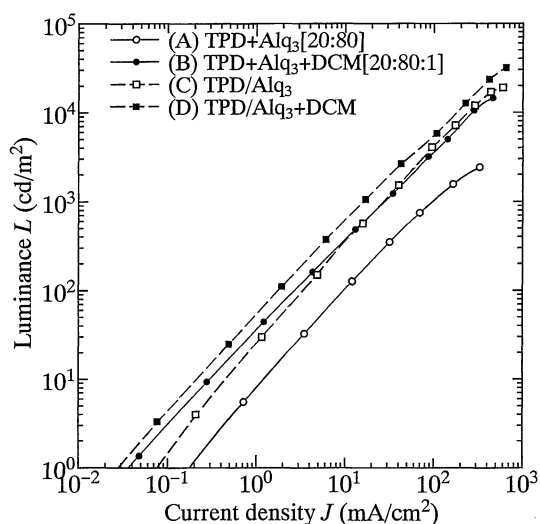

Fig. 4. The luminance (L) vs current density (J) characteristics of mixed single-layer and multilayer devices.

and high luminance exceeding 10,000 cd/m^2 is obtained from both devices. The EL efficiency of the A-type device is inferior to that of the C-type device. It is supposed that the majority of injected carriers will pass through the A-type device without recombination and/or without radiative recombination. At current density of 100 mA/cm^2, the gain of the luminance of DCM-doped devices (Type B, Type D) is about 3 times larger than that of the undoped single-layer device (Type A) and is also about 1.5 times larger than that of the undoped multilayer device (Type C). One of the most likely reasons for the large gain in the B-type device is the carrier trapping effect in the DCM molecule.

The luminance versus current density characteristic is the same whether measured initially on after a few days in mixed single-layer devices, but it is not the same in multilayer devices. This result indicates that a mixed single layer resists condensation and maintains the initial film condition.

Organic electroluminescent devices with mixed single-

layer organic materials that consist of hole transport material, electron transport material and dopant material were studied. The fabrication of these EL devices is a simple process, and high luminance of over 10,000 cd/m^2 is obtained by optimizing the weight ratio of hole and electron transport materials.

1) C. W. Tang and S. A. Vanslyke: Appl. Phys. Lett. **51** (1987) 913.
2) C. Adachi, S. Tokito, T. Tsutsui and S. Saito: Jpn. J. Appl. Phys. **27** (1988) L269.
3) C. Adachi, S. Tokito, T. Tsutsui and S. Saito: Jpn. J. Appl. Phys. **27** (1988) L713.
4) C. W. Tang, S. A. Vanslyke and C. H. Chen: J. Appl. Phys. **65** (1989) 3610.
5) C. Adachi, T. Tsutsui and S. Saito: Appl. Phys. Lett. **55** (1989) 1489.
6) C. Adachi, T. Tsutsui and S. Saito: Appl. Phys. Lett. **56** (1990) 799.
7) C. Adachi, T. Tsutsui and S. Saito: Appl. Phys. Lett. **57** (1990) 531.
8) J. Littman and P. Martic: J. Appl. Phys. **72** (1992) 1957.
9) S. Shionoya and S. Ibuki: Oyo Buturi **57** (1988) 935 [in Japanese].