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Red EL Properties of OLED Having Hole Blocking Layer

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SUMMARY In this study, we prepared red organic light-emitting-diode (OLED) with a fluorescent dye(Sq)-doped and inserted 1,3-bis (5-p-t-butylphenyl)-1,3,4-oxadiazol-2-yl) benzene (OXD7) or/and tris (8-hydroxyquinoline) aluminum (Alq3) layers between emission layer and cathode in order to increase electroluminescent (EL) efficiency. This inserting effect has been observed and EL mechanism characteristics have been examined. The hole transport layer was N,N′-diphenyl-N, N′bis-(3-methylphenyl)-1,1′diphenyl-4,4′-diamine (TPD); the host material of emission layer was Alq3; the guest material of emission layer was Sq. When Alq3 was inserted between the emission layer and the cathode, emission efficiency increased. Highly pure red emission, however, was not attaina ble with Alq3. On the other hand, the insertion of OXD7 between the two layers blocked and accumulated holes. Because of its increasing recombination probability of electron and hole, luminance characteristics and emission efficiency were improved with holding highly pure red color.

key words: *red organic light-emitting-diode(OLED), emission layer, hole transport layer, electroluminescent (EL)*

1. Introduction

Organic electroluminescence (EL) was first discovered in 1963 [1]. It has been researched actively, however, since 1987 when Tang et al. published the organic EL(LED) that had high luminance of above 1000 cd/m^2 under the voltage below D.C. 10 V, with the double layer of organic ultra-thin films [2]. Researches are carrying out to improve luminance and efficiency by inserting hole or electron transport layer into the basic double layer structure or emitting various colors by doping appropriate dye on the emitter layer. The study to develop materials of good efficiency with holding necessary light emission characteristics also has been processed.

Organic LED is the carrier injection type emission that has the same structure with inorganic light emitting diode (LED), and emits light by carrier injection through applied electric field. Therefore, after carrier injection and bulk transport, light is emitted through recombination of electrons and holes inside of the emitter layer. On the other hand, organic LED emits light through exciton. Thus, in order to make organic light emission device highly efficient, not only the elucidation of the light emission mechanism but also of the basic processes such as carrier transport of the organic material and injection are essential.

For high efficiency of organic LED and the choice of light emission color, there is a dye-doped device which is doped with guest fluorescent dye on the host emitter layer. Using Alq3 as host material of emitter layer, Tang realized more efficient device in the doped sample than the undoped one by doping with coumarin derivative and styrene dye, both of which are used for laser [3].

In organic LED that has Alq3 as host material of light emission layer and Sq as its guest material, because host emission changes with applied current and dope concentration, variable color device can be made from the device [4].

Sq does not show any photoluminescence(PL) because of its strong fluorescence quenching when it is solely made to thin film. But as it has red color of high purity, this material will be very useful if it emits light with high efficiency.

This study investigated the light emission characteristics of samples doped and undoped with Sq dye respectively, and examined the effects of OXD7 and Alq3 layer insertion in Sq 14 mol% doped samples and the mechanism characteristics.

2. Experiments and Measuring Methods

2.1 Preparation of Samples

The material of hole transport layer used was an aromatic diamine derivative, N,N′-diphenyl-N,N′-bis-(3-methylphenyl)-1, 1′-diphenyl-4, 4′-diamine (TPD). The material of emitter layer was an aluminum quinoline complex, tris(8-hydroxyquinoline) aluminum (Alq3). The material of guest that was doped on the emitter layer for red light emission was a squarylium dye, bis[1-methyl-3,3′-dimethyl-2-indorindiylmethyl] squaraine (Sq). The material of blocking layer was an oxadiazole derivative, 1,3-bis(5-p-t-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD7).

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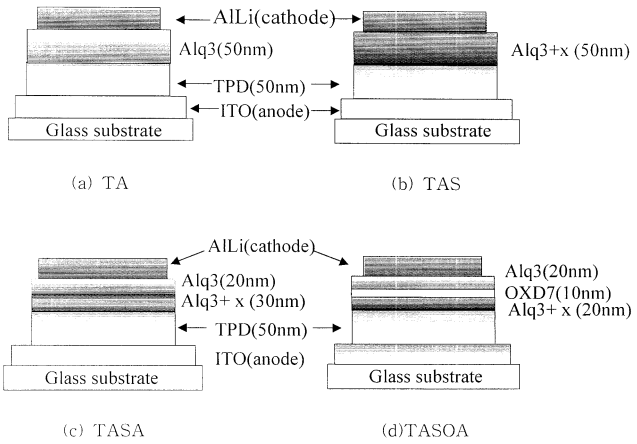

Fig. 1 The structures of OLED devices.

Devices were made by the multiple vapor deposition according to the vacuum vapor deposition method using the radiant heat of halogen lamp as its heat source. The substrate which formed indium tin oxide (ITO) that has the resistivity of 30 Ω/square on a glass board by the electron beam vapor deposition method was used as an anode, on which deposition rate of TPD and Alq3 were 0.2 nm/s with a temperature controller and a quartz oscillator film thickness measuring instrument. And Al-Li alloy was formed by the heat vapor deposition method as a cathode. The area of each electrode is $2 \times 2\,\mathrm{mm}^2$. Figure 1 shows the structure of the samples.

2.2 Measuring Methods

The current change and the characteristics of luminance according to the applied voltage change were measured by a source measurement unit (SMU; Keithley, model 238) and luminance meter (TOPCON, BM-8). Using a personal computer as a measuring system, SMU controlled the apply of voltage through GP-IB interface and measured the current. At the same time, a luminance meter measured luminance through RS-232C interface. The increase rate of the applied voltage was 0.5 V/0.5 s. The electroluminescence(EL) spectra were measured by a multi-channel analyzer (HAMAMATSU Photonics, PMA-10). The measurement system consisted of a controller (C4196) and a spectrometer head (M4197) in which a spectrophotometer and a multi channel detector are integrated. The system was controlled using a keyboard. SMU was manually controlled in order to apply current and voltage. All measurements were carried out under vacuum (2×10^{-3} Torr).

3. Results and Consideration

3.1 Dependence of the Dope Concentration of Sq

Figure 2 shows the characteristics of applied voltage to current density in the samples of ITO/ TPD[50 nm]/ Alq3+Sq(x)[50 nm]/AlLi, x=0, 8, 14, 25 mol%. In 8 mol%-doped sample it is more difficult than in the undoped sample (x=0 mol%) for current to flow. However, in 14 mol%-doped sample, it is easier for electric current to flow than in 8 mol%-doped sample.

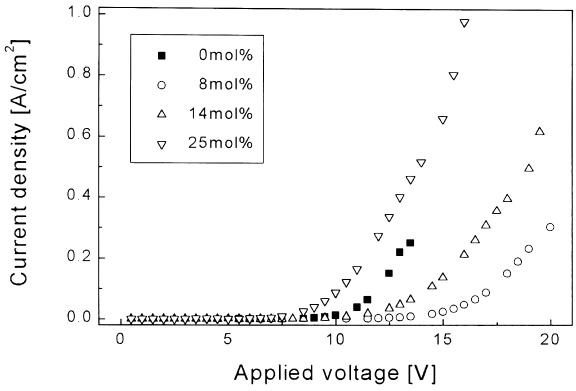

Fig. 2 The Sq-doping concentration dependence of the current density vs. applied voltage characteristics.

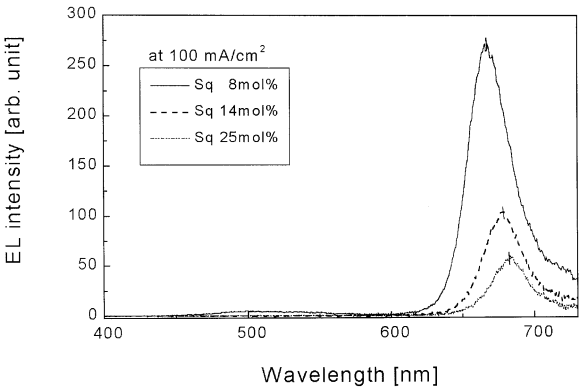

Fig. 3 The Sq-doping concentration dependence of EL spectra for Sq-doped Alq3 LEDs.

Furthermore, in 25 mol%-doped sample it is easier for current to flow than even in the undoped sample. This means Sq molecules act as a carrier trap in Alq3 when the dope amount of Sq molecules is small. As the dope amount increases, it becomes close to hybrid layer of Alq3 and Sq, and as the level of Sq increases, carriers are not injected into the energy level of Alq3 but transit at the level of Sq molecules that have low HOMO level [5]. Thus, it is thought that carriers can move from the anode to the cathode of the emitter layer through continuous bulk of the Sq molecules.

Figure 3 shows the EL spectrum of ITO/TPD [50 nm]/Alq3+ Sq(x) [50 nm]/AlLi doped with guest dye Sq among host dye Alq3 in light emitter layer when 100 mA/cm^2 was applied.

In organic EL device, emission peak of Alq3 can be observed around 520 nm, and that of Sq around 670 nm. But Sq(8 mol%)-doped sample has an additional peak of Alq3 around 520 nm in addition to 667 nm peak of

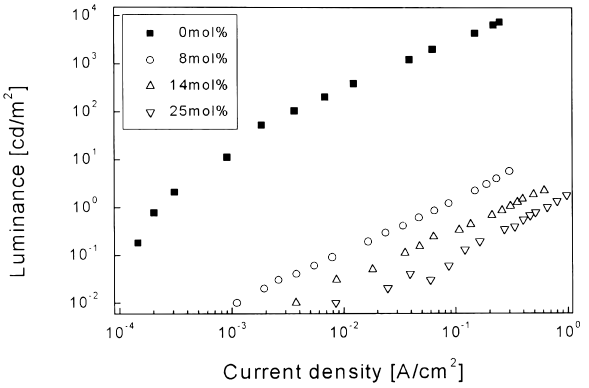

Fig. 4 The Sq-doping concentration dependence of the luminance vs. current density characteristics.

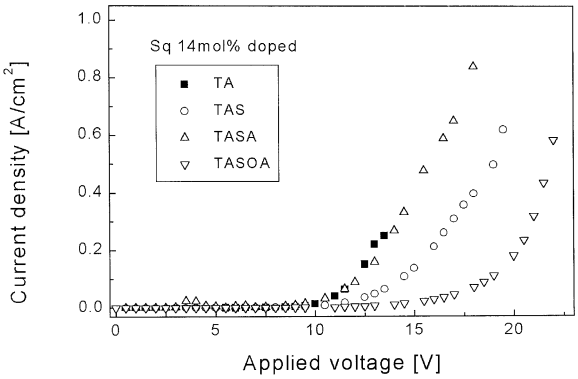

Fig. 5 The hole blocking barrier dependence of the current density vs. applied voltage characteristics.

Sq. Thus Sq(8 mol%)-doped sample does not emit pure red light, but red light mixed with orange light. On the other hand, Sq(14 mol%)-doped and Sq(25 mol%)-doped samples have 673 nm and 680 nm peak respectively, and do not have 520 nm peak. Emission peak wavelength shifts to long wavelength as dope amount increases, and the half width of Sq emission spectrum is 30 nm. When the area of EL spectra are converted to the number of photons, that of the undoped sample is 8.7×10^5; of 8 mol%-doped is 6.8×10^3; of 14 mol%-doped is 2.6×10^3, and of 25 mol%-doped is 1.2×10^3.

The difference between those of the undoped sample and 14 mol% doped sample is about 3×10^2. As Sq dope concentration increases, the amount of red light emission decreases and the emission peak shifts to long wavelength. Decreasing emission efficiency due to fluorescence quenching and the decreased EL of high energy level might cause this.

Figure 4 shows the characteristics of luminance—current density depending on dope concentration. The undoped sample shows luminance of 3200 cd/m^2 under the current density of 0.1 A/cm^2. Sq (8 mol%)-doped sample shows luminance of 2 cd/m^2 under current density of 0.1 A/cm^2. Sq(14 mol%)-doped and 25 mol%-doped sample shows respectively the luminance of 0.32 cd/m^2 and 0.12 cd/m^2 under current density of 0.1 A/cm^2. The difference of luminance between Sq undoped sample and Sq(14 mol%)-doped sample is about 3.2×10^4. As mentioned the above, numbers of photons are different by about 10^2, but luminances are different by about 10^4. Because main emission of the undoped sample is green light emission of Alq3, while that of the doped samples with Sq of high concentration is red, they can not be compared directly. That is, luminance is measured by the standard visual sensitivity decided by setting 555 nm as maximum value, 1, to the human visual sensitivity. As a result, just luminance cannot reflect the exact original intensity of EL.

3.2 The Effect of Hole Blocking Layer

As stated the above section, high concentration dope of Sq can achieve highly pure red color but cannot achieve satisfactory luminance. The probable reason of this is that the carriers transported through electron transport layer do not transfer energy to Alq3 but transit to the level of Sq molecules dispersed in Alq3, conducting through continuous Sq bulk and decreasing the probability of recombination. Therefore, in order to improve luminance, hole-blocking layer was inserted to prevent holes from reaching directly to the cathode through continuous Sq bulk,

Figure 5 shows the hole blocking layer dependence of current to voltage characteristics of ITO/TPD [50 nm]/Alq3 [50 nm]/AlLi (TA), ITO/TPD [50 nm]/Alq3+Sq [50 nm]/AlLi (TAS), ITO/TPD [50 nm]/Alq3+Sq [30 nm]/Alq3 [20 nm]/AlLi (TASA), and ITO/TPD [50 nm]/Alq3+Sq [20 nm]/OXD7 [10 nm]/Alq3 [20 nm]/AlLi (TASOA). These samples are doped with 14 mol% Sq. As shown in Fig. 2, in TAS doped with Sq, it is more difficult for current to flow than in the undoped one. TASA sample doped with Sq and set Alq3 as hole-blocking layer shows similar tendency with TA. In TASOA with OXD7 as hole blocking layer it is more difficult for current to flow than in TAS. Samples without hole-blocking layer show good conductivity of current owing to the dispersed Sq. When Alq3 was inserted between the emitter layer and the cathode, however, the samples show the same tendency with TA because Alq3 fails to act as effective hole blocking layer. When OXD7 is inserted between the emitter layer and the cathode, the probable reason of low conductivity is that OXD7 prevents the direct transport of holes to the cathode.

Figure 6 shows the effect of hole blocking layer on EL spectra of Sq doped TAS without the blocking layer, and Sq doped TASA and TASOA with the blocking layer. When Alq3 was used as blocking layer (TASA), 680 nm emission peak of Sq was smaller than

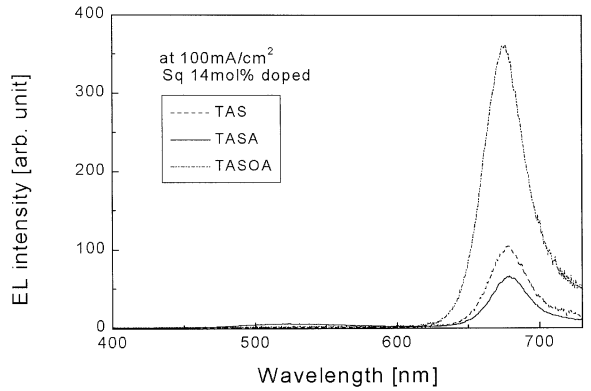

Fig. 6 The hole blocking barrier dependence of the EL spectra for organic Sq-doped LEDs.

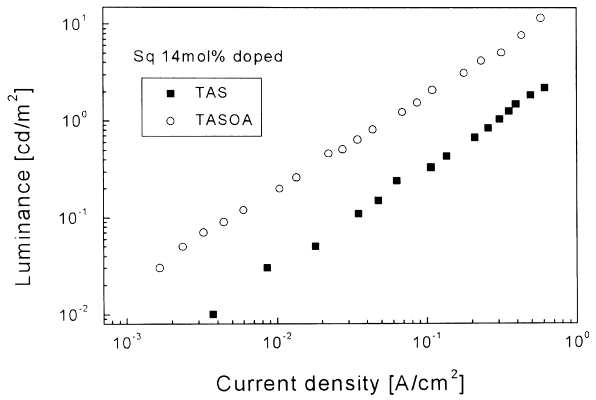

Fig. 7 The luminance vs. current density characteristics of the Sq doped Alq3 LEDs unusing and using OXD7 as blocking layer.

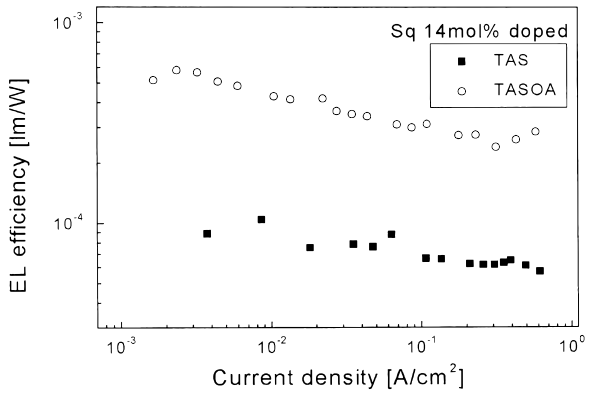

Fig. 8 The EL efficiency vs. current density characteristics of the Sq doped Alq3 LEDs without and with OXD7 as blocking layer.

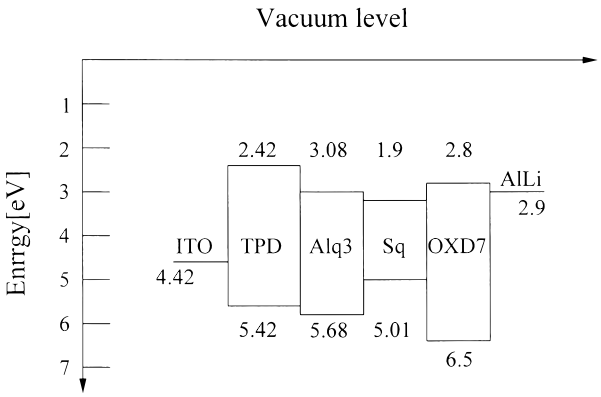

Fig. 9 The energy diagram of ITO, TPD, Alq3, Sq, OXD7, AlLi.

when there was no blocking layer(TAS), and emission of Alq3 around 520 nm was observed. This means that the holes that passed through Sq without recombination recombine with electrons in Alq3. In addition, when OXD7 was used as blocking layer, the emission intensity of Sq was three times stronger than when there was no blocking layer. It seemed that because the OXD7 blocked holes from transport directly to the cathode, the recombination probability between electrons and holes in the emitter layer increased.

Figure 7 shows the luminance characteristics according to current density of the samples with the blocking layer (TASOA) doped with Sq 14 mol% in the emitter layers and without the blocking layer (TAS). The sample without the hole blocking layer and doped with Sq 14 mol% shows the luminance of 0.3 cd/m^2 under the current density of 0.1 A/cm^2; the sample with OXD7 as hole blocking layer shows the luminance of 2 cd/m^2 under the current density of 0.1 A/cm^2. The luminance of the sample with OXD7 is 7 times higher than that of the sample without OXD7. This is thought to be caused by the increased recombination probability because of the hole blocking.

Figure 8 shows the EL characteristics according to current density of the sample with blocking layer doped with Sq 14 mol% (TASOA) and without blocking layer (TAS). The efficiency of the sample without blocking is 10^{-4}–6×10^{-5} lm/W under the current density of 10^{-3}–10^{-1} A/cm^2, and that of the sample with OXD7 is 6×10^{-4}–2.4×10^{-4} lm/W under the current density of 10^{-3}–10^{-1} A/cm^2. The EL efficiency has 4 times difference between the samples with and without blocking layer.

3.3 Consideration Using Energy Diagrams

Figure 9 shows work functions of ITO and Al-Li electrodes, HOMO and LUMO levels of TPD, Alq3, Sq, and OXD7. Alq3 and OXD7 were inserted between the emitter layer and the cathode in order to block the transfer of holes to the cathode through Sq, and to increase the recombination probability. The HOMO level difference between OXD7 and Alq3 is 0.82 eV; the difference between OXD7 and Sq is 1.49 eV.

Because holes are suspected to flow at the energy level of Sq in the samples doped with Sq. The height of injection barrier from Alq3+Sq to OXD7 can be estimated at 1.49 eV, while the height of injection barrier of holes in the samples using Alq3 as blocking barrier

can be estimated at 0.67 eV, the difference between the HOMO energy levels of Sq and Alq3. When Alq3 is used as blocking barrier, it can be thought that the holes injected through Sq and Alq3 from Alq3+Sq emit light even in the Alq3 of blocking layer. Therefore, in order to set barrier for hole blocking, OXD7 layer is more effective than Alq3 of hole blocking.

As for current, if a majority of carriers are holes, the current in the sample with blocking layer is suppressed compared with that of hole blocking layer. About the definition of the efficiency, when current decreases, first the EL efficiency increases. Therefore, the EL efficiency is suspected to have been increased by the hole blocking. As holes being accumulated around Alq3+Sq in the interface of Alq3+Sq/OXD, the hole density increases around the interface. That is, the accumulation of holes occurs in the anode side of OXD7. If the electron injection to Alq3+Sq is not affected by OXD7, the recombination between electrons and holes will increase as concentrations of electrons and holes increase; as the recombination probability increases, the EL amount increases, and consequently luminance and EL probability increase. Therefore, with proper blocking, we can get high efficient devices.

4. Conclusion

In this study, we examined the EL characteristics of the samples doped and undoped with Sq dye, the effects of OXD7 and Alq3 layer insertions in the samples doped with Sq(14 mol%), and the mechanism characteristics of light emission device. The conclusions are as follows:

1) Organic EL doped with more than Sq(14 mol%)-doped as host material using Alq3 emitted highly pure red light with narrow half power width. But the emission was not suitable to practical usage because of its low luminance and efficiency. Therefore, the simple double layer structure with TPD is not suitable to practical purposes;

2) The insertion of Alq3 could increase the efficiency but could not increase red emission of high purity because of the emission from inserted Alq3 layer;

3) With blocking holes flowing to the cathode by the insertion of OXD7 and accumulating the holes, the recombination probability between electrons and holes were increased, and high purity could be maintained, and luminance characteristics and efficiency of light emission could be improved.

Consequently, with proper blocking barriers, we can get devices of high efficiency.

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