Electroluminescent Properties of Organic Light-Emitting Diodes with Blue-Emitting Alq

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Aluminum(III) bis(2-methyl-8-quinolate)4-phenylphenolate (BALq) is well-known to be a hole blocking material against phosphorescent light-emitting diodes. The authors investigated the EL mechanism of BALq. The PL intensity of BALq was stronger than that of Alq₃, but the EL performance of BALq LED was poorer than that of Alq₃ LED because of lower electron injection. The introduction of Alq₃ electron injection layer improved EL performance, but EL decreased with decreasing BALq thickness beyond the optimal Alq₃ thickness. The authors clarified by doping method that the recombination zone of BALq/Alq₃ LED is located near the interface between BALq and Alq₃ and Alq₃ may act as quencher to BALq.

Keywords : blue-emitting Alq (BALq), EL spectrum, recombination zone, dye-doping, electron injection

1. Introduction

The organic light-emitting diodes (OLEDs) which are reported by Tang & VanSlyke [1,2] are noted as one of components for a flat panel display. Kodak group used aluminum quinine (Alq₃). This metal complex is very popular and excellent as an emitting material, a host emitting material and an electron transport material. However, the emission of Alq₃ OLED is greenish yellow and its EL efficiency is much lower than those of the other practical dyes. Kodak group reported blue-emitting Alq complex (BALq) at 1996[3]. BALq is aluminum(III) bis(2-methyl-8-quinolate)4-phenylphenolate. BALq is introduced as a blue-emitting material and a host material to the other blue-emitting dye (i.e. perylene). However, BALq is well-known and widely used as a hole-blocking material[4-8], but its EL properties have little been reported since 1996.

In this paper, the authors reported the basic EL properties of BALq LED as compared with conventional Alq₃ LED.

2. Experimental

The authors have used Phthalocyanine Copper (CuPc) as a hole injection layer, N,N'-di(1-naphthyl)-N,N'-diphenyl-1,1'-diphenyl-1,4'-diamine (NPD) as a hole transport layer, and 8-

Fig. 1 Molecular structures of dyes.

Fig. 2 Devices structure

hydroxyquinoline aluminum (Alq3) and BALq as an emitting material. Sublimated organic materials are obtained from Nippon Steel Chemical Co., Ltd. A NPD thin film was prepared on a glass substrate with an indium-tin-oxide (ITO) transparent electrode (anode). The organic thin films were prepared using the vacuum deposition at a pressure of $0.8 \sim 1 \times 10^{-3}$ Pa at room temperature. Typical deposition rates of organic materials were about 0.2 ~ 0.3 nm/s. Then for the upper metal electrode (cathode), The effective electrode area of the specimens was $2 \times 2 \text{ mm}^2$.

Absorption spectra were measured by spectrophotometer (U-3000; Hitachi Co., Ltd.). Photoluminescence (PL) spectra were measured using a spectrophotometer (FP-777; JASCO Corp.). The ionization potentials of organic films and the work functions of ITO and metal were estimated by means of an atmosphere ultraviolet photoelectron analysis device, AC-2 (Riken Keiki Co.Ltd).

Efficiency-current-voltage characteristics were measured by a source measure unit (238 High Current Source Measure unit, Keithley Instrs., Inc.) and a luminance meter (BM-8; TOPCON Corp.). Measurements of luminance-current-voltage characteristics were carried out under vacuum of ~ 0.1 Pa. Electroluminescence spectra were obtained using a photonic multi-channel analyzer-10 (PMA-10; Hamamatsu Photnics.). Operating time dependences of EL spectra were obtained using a high-sensitivity spectro-multi-channel photo detector (MCPD-4500; Otsuka Electronics Co., Ltd.). The external quantum efficiency of OLED, η_{ext} was calculated by a front luminance and EL spectra under the assumption of surface of uniform diffuser, that is,

$$\eta_{\text{ext}} = \frac{\pi e L_0}{K_m h c J} \frac{\int i_{\text{el}}(\lambda) \lambda d\lambda}{\int i_{\text{el}}(\lambda) \cdot V(\lambda) d\lambda},$$

where e is elementary charge, L_0 is a front luminance, K_m is a constant, $683 [\text{lm/W}]$, h is wavelength, c is light velocity, $i_{\text{el}}(\lambda)$ is a relative EL intensity at a wavelength, λ , and $V(\lambda)$ is spectral luminous efficiency at λ .

3. Results and discussion

Figures 3a and 3b show the absorption spectra and PL spectra of BALq and Alq3 thin films. The maximum of absorption spectra of BALq and Alq3 thin film are 362nm and 395nm, respectively. The emission peak of PL spectra of BALq and Alq3 thin film are 476nm and 517nm, respectively. The blue shift of absorption and PL spectra is caused by the reduction of π -conjugated electron system due to

Fig. 3 Absorption spectra (a) and corrected PL spectra (b) of BALq and Alq3 thin films.

steric hindrance of 2-methyl group substituted at quinoline ring. PL intensity is corrected by absorption coefficient in Fig. 3b. The PL intensity of BALq film is about three times higher than that of Alq3 film. Therefore, BALq is thought to have a potential as compared with Alq3.

Figures 4a-4d show the initial electrical and EL properties of BALq and Alq3 LEDs. Although Alq3 reference has a leakage current in the low voltage region of $< 5\text{V}$, the current of BALq is regarded to be more suppressed than that of Alq3. The threshold voltage of BALq LED at 1 cd/m^2 is $\sim 5.2\text{V}$ and it is higher than $\sim 3.5\text{V}$ of Alq3 LED. The luminance is also proportional to current density for BALq LED. The current efficiency of BALq, 1.7 cd/A is about half that of Alq3, 3.5 cd/A . The external quantum efficiencies of BALq and Alq3 is $\sim 0.7\%$ and $\sim 1.1\%$, respectively.

Figs. 4 (a) Current density-voltage characteristics, (b) Luminance-voltage characteristics, (c) Current efficiency-voltage characteristics, (d) External quantum efficiency-current density characteristics for BALq (solid circle) and Alq3 (square) LEDs.

In spite of stronger PL intensity, BALq has a poorer EL performance than Alq3 which is not always excellent EL material. The reasons are thought to be that it is not easy to inject electron into BALq from cathode since the LUMO level of BALq is higher than that of Alq3 and that the conductivity of BALq may be lower than that of Alq3.

Fig. 5 Applied current density dependence of EL spectra for BALq LED.

Figure 5 shows the applied current density dependence of EL spectra for BALq LED. In the EL spectra of BALq LED, the high energy EL component around 460 nm increases with current density. EL spectra are well-known to be changed as a recombination zone moves in the emission layer because of the interference effect due to cathode mirror[9,10]. However, the configuration of EL spectrum is not thought to be strongly deformed, and its emission peak is found not to be shifted. If this emission derives from the energy transfer from the lowest vibrational level of first singlet excited state to the lowest vibrational level of ground state, the increase in high energy component will suggest that the energy state of exciton produced by an electron-hole recombination depends on generating concentration of exciton. The authors are investigating the EL mechanism in detail.

The authors tried to improve EL performance of BALq LED using electron transport/injection layer. Figure 6 shows the maximum external quantum efficiency vs. thickness of Alq3 layer. The

authors fabricated the devices of ITO/CuPc[30nm]/NPD[50nm]/BAIq[50-xnm]/Alq3[xnm]/LiF[0.6nm]/Al, $x=0, 10, 20, 25, 30, 40, 50$. $x=0$ nm means only BAIq emission layer and $x=50$ nm means only Alq3 emission layer.

Fig. 6 The maximum external quantum efficiency vs. thickness of Alq3 layer: ITO/CuPc[30nm]/NPD[50nm]/BAIq[50-x nm]/Alq3[x nm]/LiF[0.6nm]/Al, $x=0, 10, 20, 25, 30, 40, 50$.

Fig. 7 The EL spectra of BAIq(50-x)/Alq3(x nm) LEDs: $x=0, 10, 25, 40$.

Figure 7 shows the EL spectra of BAIq LED with Alq3 electron transport layer. It is very difficult to separate Alq3 from BAIq in all EL spectra of various BAIq/Alq3 LEDs. The authors conclude that the emission of BAIq/Alq3 LEDs is due to only emission from BAIq. If the decrease in EL efficiency of BAIq LED was caused by lower electron injection and lower conductivity, the EL efficiency of BAIq/Alq3 LED should increase with

decreasing the thickness of BAIq. However, since it has an optimal thickness of BAIq as shown in Fig. 6, a factor causing efficiency loss is implied to exist. Especially, the diffusion length of Alq3 exciton is reported to be ~ 20 nm[2,11]. The lifetime of Alq3 exciton is comparatively long and 12~16ns[2,11]. When the thickness of BAIq layer is thinner than the diffusion length of BAIq, BAIq exciton migrating at the interface is thought to be disassociated and then the concentration of radiative deactivation will reduce.

As you know, in the case that OLDE consists of hole transport layer and conventional emission layer, the recombination zone is located near the interface between hole transport layer and emission layer[2]. Therefore, the authors investigated the EL mechanism of BAIq/Alq3 LED by means of dye doping method.

Fig. 8 The structure of doped emission layer and chemical structures of typical guest dyes.

Fig. 9 Energy diagram of dyes.

Figure 8 shows the doping location in emission layer and chemical structure of typical guest dyes. DCM and C540 are popular laser dyes. The emission color of DCM is orange and that of C540 is deeper green than that of Alq3. In order to check the spectrum change, DCM is thought to be suitable of the two. However, DCM dye in Alq3 acts as an electron trap center since DCM has deeper LUMO than Alq3 as shown in figure 9. The EL from C540 cannot be observed in the Alq3 LED whose C540-doped layer is located at 30nm-far from the interface between a hole transport layer and Alq3. Therefore, the authors selected C540 as doping dye. In addition, the authors doped 1mol%-C540 in Alq3 layer 30nm-far from the interface not to disturb recombination process in BAq.

Figure 10 shows the EL spectra of ITO/CuPc/NPD/BAq/C540-doped Alq3/Alq3/LiF/Al and ITO/CuPc/NPD/C540-doped Alq3[50nm]/LiF/Al. If the main recombination zone is located near the interface between NPD and BAq, it is thought that the emission from C540 cannot be observed in EL spectrum of doping device. However, the EL spectrum of doping device almost agrees with that of C540-doped Alq3 LED.

Fig. 10 The EL spectra of ITO/CuPc/NPD/BAq/C540-doped Alq3/Alq3/LiF/Al and ITO/CuPc/NPD/C540-doped Alq3[50nm]/LiF/Al ($J=50\text{mA/cm}^2$).

Figure 11 shows the applied current density dependence of EL spectra of C540-doping device. The high energy emission component increases with increasing current density. This emission is due to BAq.

These results suggest that the recombination zone of BAq is located near the interface between BAq and C540-doped Alq3. Although the model that recombination zone is near the interface between NPD and BAq and BAq has a long diffusion length of exciton with more than 30nm

may also be thought, this model is unrealistic since the emission from BAq could be observe during migration under a reactivation probability.

Fig. 11 Applied current density dependence of EL spectra of C-540-doping device.

That is, our proposed model requires to think that the emission from C540 ought to occur after the energy transfer from BAq3 to C540. The increase in the EL from BAq can be explained by the diffusion of BAq exciton into BAq layer toward NPD. When the number of BAq exciton is small, it is enough to transfer energy to C540 at the interface between BAq and C540-doped Alq3. On the other hand, when the generating rate of BAq exciton exceeds above the quenching rate of C540 molecules, superfluous BAq excitons are thought to migrate BAq toward the interface between BAq and NPD.

However, it cannot explain why the energy transfer from BAq to Alq3 does not occur. But, if Alq3 acts as nonradiative quencher to BAq, our experimental results can be explained by the quencher model. The authors try to investigate the EL mechanism of BAq LEDs in details.

4. Conclusions

Since the emission color of BAq is light blue, BAq is not appropriate for blue emitting material. However, it is very effective for hole-blocking material. The authors clarified the EL mechanism of BAq LED. BAq LED has lower EL performance than Alq3 LED because of lower electron injection. The introduction of Alq3 electron injection layer improved EL performance and an optimal Alq3 thickness was 25nm. The authors clarified by doping method that the recombination zone of BAq/Alq3 LED is located near the interface between BAq and Alq3 and Alq3 may act as quencher to BAq. However, the authors

have to investigate the detailed carrier transport of BAq in order to observe recombination of BAq and quencher action of Alq3.

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References

1. C.W. Tang and S.A. VanSlyke, *Appl. Phys. Lett.* **51** (1987) 913.
2. C. W. Tang, S.A. VanSlyke and C. H. Chen, *J. Appl. Phys.* **65** (1989) 3610.
3. S. A. VanSlyke, P. S. Bryan, C. W. Tang, *Inorganic and Organic Electroluminescence/ EL96* Berlin, p195 (1996).
4. S. Kawami, K. Nanamura, T. Wakimoto, T. Miyaguchi, T. Watanabe, *PIONEER R&D* **11**, 13 (2000)[in Japanese].
5. R.C. Kwong, M. R. Nugent, L. Michalski, T. Ngo, K. Rajan, Y.-J. Tung, M. S. Weaver, T. X. Zhou, M. Hack, M. E. Thompson, S. R. Forrest, J. J. Brown, *Appl. Phys. Lett.* **81**, 162 (2002).
6. S. Tokito, T. Iijima, T. Tsuzuki, F. Sato, *Appl. Phys. Lett.* **83**, 2459 (2003).
7. M. Suzuki, S. Tokito, M. Kamachi, K. Shirane, F. Sato, *J. Photopolym. Sci. Technol.* **16**, 309 (2003).
8. S. Tokito, M. Suzuki, F. Sato, *Thin Solid Films* **445**, 353 (2003).
9. T. Mori, K. Obata, T. Inagaki, T. Kubuki, T. Mizutani, *Trans. IEEJ.* **116-A**, 30 (1996) [in Japanese].
10. M. Matsumura and Y. Jinde, *Appl. Phys. Lett.*, **73**, 2872 (1998).
11. T. Mori, K. Obata, K. Miyachi, T. Mizutani, Y. Kawakami, *Jpn. J. Appl. Phys.*, **36**, 7239, (1997).