

## Bright Luminescence from Organic EL Thin Films by Electron Beam Irradiation

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We propose that organic electroluminescent (EL) materials are suitable for a phosphor of Field Emission Display (FED). Tris-(8-hydroxyquinolino) aluminum ( $\text{Alq}_3$ ), 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl ( $\alpha$ -NPD) and copper phthalocyanine (CuPc) is an emitting layer, a hole transporting layer and a hole injecting layer, respectively. In the specific structure, electron beam excited luminescence was obtained from the  $\text{Alq}_3$  layer without electrons injected from a metal cathode. The luminescence revealed a large enough intensity but was quenched within 1 sec. The films were investigated with X-ray diffraction (XRD), atomic force microscope (AFM), and X-ray photoelectron spectroscopy (XPS). From the analysis by XPS, the C1s peaks of  $\text{Alq}_3$  and CuPc at the  $\alpha$ -NPD interface shifted to the higher binding energy after the electron beam irradiation. The distance between the emitter and the anode was ca. 30 mm and the electric field was very weak in the organic layered films. Then the carriers were accumulated at the  $\alpha$ -NPD interface to decrease the luminescence. The initially observed bright luminescence suggested that the the luminescence efficiency or the lifetime will be improved by adopting the specific structure which increases the electric field in the films.

Key words: luminescence, OLED, FED,  $\alpha$ -NPD,  $\text{Alq}_3$

### 1. INTRODUCTION

Recently organic light emitting displays (OLED) and field emission displays (FED) have been investigated aggressively as the next generation displays.<sup>1-5)</sup> OLED and FED have the advantages of ultra thin, low-power consumption, and high luminescence etc, in comparison with LCD and PDP. A sulfide phosphor often used in a cathode ray tube (CRT) is, however, degraded by electron beam bombardment in the configuration of low voltage driving FED.<sup>6-7)</sup> A Tris-(8-hydroxyquinolino) aluminum ( $\text{Alq}_3$ ) is expected to be suitable material for the phosphor of low voltage driving FED with highly effective luminescence and materials stability. Figure 1 shows the specific device structure proposed here. The organic EL thin films is irradiated by electron beams emitted from the emitter through vacuum, and a recombination of electrons and holes takes place at the light emitting layer.

The specific structure has two advantages. As the first advantage, the light emitting efficiency is improved due to the difference of the reflectance between a vacuum and the film. As the second, the lifetime and materials stability of the organic EL films are improved because of elimination of a cathode metals film.

In this work, we investigated the luminescence properties of  $\text{Alq}_3$  / 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl ( $\alpha$ -NPD) / copper phthalocyanine (CuPc) multilayered structure by irradiating electron beam. The characterizations of the films before and after the electron beam irradiation were also carried out by AFM,

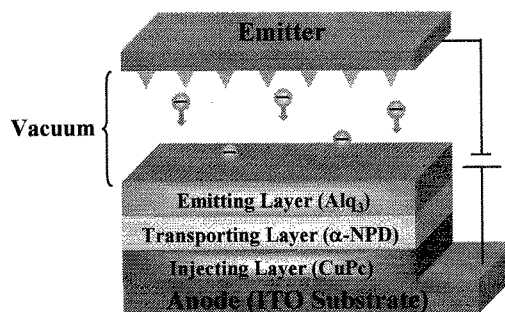


Fig. 1. The schematic structure of the proposed novel FED

XRD, and XPS measurements.

### 2. EXPERIMENTAL

Indium tin oxide (ITO) substrates were loaded on the vacuum chamber after cleaning in acetone ultrasonically. Figure 2 shows evaporation chamber equipped with evaluation system of luminescence. The pressure during films deposition was  $1.4 \times 10^{-4}$  Torr. The evaporation rate of all materials was  $1.7 \text{ \AA/s}$ . The thickness of organic materials was monitored by a quartz microbalance. Luminescence properties are measured immediately sample holder and multilayered organic thin films were successively deposited by thermal evaporation from the

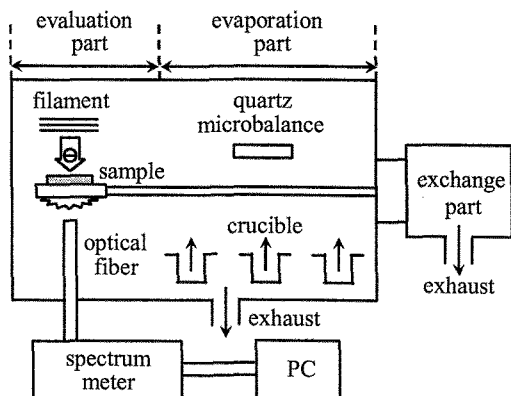


Fig. 2. The schematic diagram of the evaporation chamber equipped with the *in-situ* evaluation system of luminescence.

each crucible. For the luminescence measurement thermal electrons are emitted from the filaments, which have been used in a Vacuum Fluorescence Display. The distance between the emitter and anode was fixed to ca.30mm. The obtained luminescence light was led to the spectrum meter (PMA-1; HAMAMATSU PHOTONICS) through the optical fiber and was analyzed with a personal computer. The acceleration voltage and the current density of the electron beam was 200V and 3.75 mA/cm<sup>2</sup>, respectively.

### 3. RESULTS AND DISCUSSION

Figures 3 show (a) the luminescence spectrum observed initially and (b) the change of luminescence in the Alq<sub>3</sub> (30nm) /  $\alpha$ -NPD (30nm) / CuPc (15nm) // ITO structure. The intensity of luminescence was normalized by the initial value. The lifetime was investigated by the characteristic luminescence peak of Alq<sub>3</sub> around 550nm. The lifetime, defined as the period in which the luminescence intensity becomes 50 % of the initial value after electron beam irradiation, was about 1 sec.

As the mechanism of the short life the surface damage by electron beam irradiation was doubtful. Then the properties of the film were investigated with XRD, AFM and XPS.

Figure 4 shows XRD pattern of ITO substrate and Alq<sub>3</sub> (30nm) /  $\alpha$ -NPD (30nm) / CuPc (15nm) // ITO before and after the electron beam irradiation. Figure 5 shows AFM image of Alq<sub>3</sub> (20nm) // ITO before and after the irradiation. A definite change of the surface morphology was not observed. The results of XRD and AFM suggested that the crystallization of the organic layers did not take place by electron irradiation.

Figure 6 shows the depth profile of the C1s spectra of (a) Alq<sub>3</sub> layer and (b) CuPc layer by etching the Alq<sub>3</sub> (30nm) /  $\alpha$ -NPD (30nm) / CuPc (15nm) // ITO multilayered films. The upper figures show the C1s spectra without irradiation and the lower the spectra with irradiation. The numbers indicated at the right hand of each figure show the number of etching operation. As

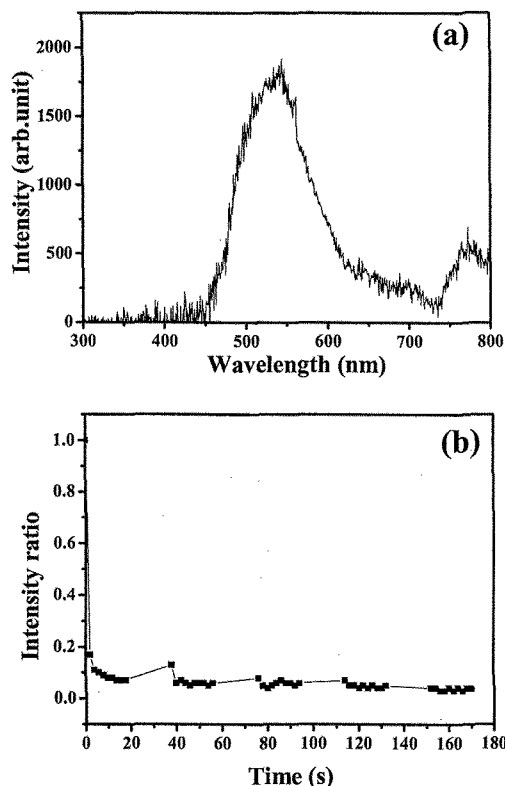


Fig. 3. Luminescence properties of Alq<sub>3</sub> (30nm) /  $\alpha$ -NPD (30nm) / CuPc (15nm) multilayered structure: (a) the luminescence spectrum observed initially and (b) the time dependence of luminescence intensity normalized by the initial value.

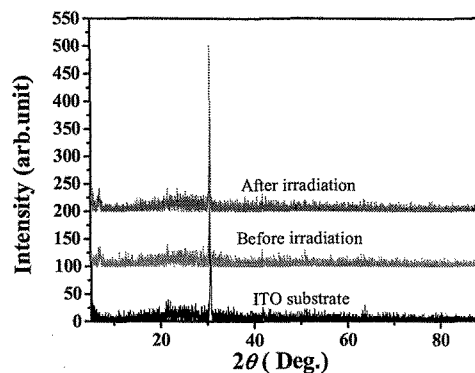
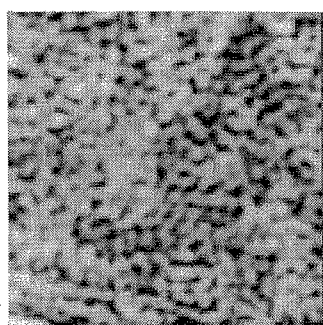
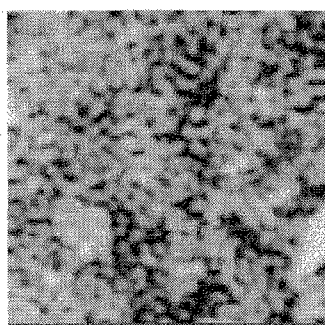


Fig. 4. XRD patterns of the ITO substrate and the sample before and after electron beam irradiation.

the etching condition Alq<sub>3</sub> and CuPc layers were etched by the thickness of 15nm and 2.5 nm by one etching operation, respectively. In the case of without irradiation any peak shift was not observed. The peak of the Alq<sub>3</sub> contacting with the  $\alpha$ -NPD layer shifted



(a) Before electron beam irradiation

2  $\mu$  m  $\square$  Ra = 1.83nm

(b) After electron beam irradiation

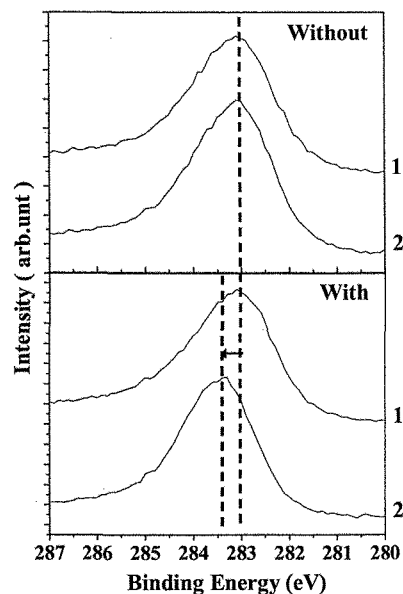
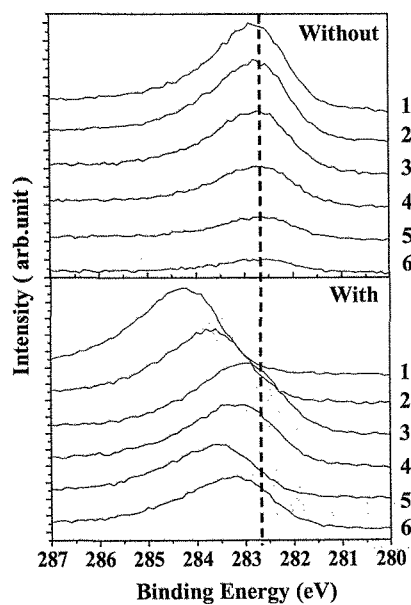
2  $\mu$  m  $\square$  Ra = 1.87nm

Fig. 5. The 2  $\mu$  m  $\square$  AFM images of Alq<sub>3</sub> (20nm) // ITO before electron beam irradiation (a), and after electron beam irradiation (b).

towards higher binding energy by about 0.5 eV after electron beam irradiation. The position of the peaks of the CuPc near the  $\alpha$ -NPD layer was also fluctuated.

The peak shift of the each film took place near the interface of  $\alpha$ -NPD. In case of the Alq<sub>3</sub> film, the peak of second etched layer is shifted. In the CuPc film, the peak of first etched layer revealed the definite shift. From these results it was considered that electrons and holes were accumulated at the interface of  $\alpha$ -NPD and the excess carriers varied the binding energy of C1s of organic molecules at the interface.

In this experiment we fixed the distance between the emitter and the anode ca.30mm and applied voltage was 200V. Then the average electric field between the electrodes was 10<sup>2</sup> Vcm<sup>-1</sup> at most in this experimental structure. In the case of a conventional OLED the distance between the anode and cathode films is the order of few tens nm and an electric field applied to organic films is the order of 10<sup>6</sup> Vcm<sup>-1</sup>. In the comparison electric field in this experiment was too small, about 10<sup>-4</sup> times. Since the carrier mobility in organic films is proportion to the applied electric field by Gill's empirical equation<sup>8)</sup>, the luminescence might be quenched rapidly due to the electrons which were not sufficiently compensated by the holes transported by

(a) Alq<sub>3</sub> (C 1s)

(b) CuPc (C 1s)

Fig. 6. The depth profile of XPS C1s core level spectra of the Alq<sub>3</sub> film on the  $\alpha$ -NPD layer (a) and the CuPc film under the  $\alpha$ -NPD layer (b) with and without irradiation as a function of etching operation.

hopping and were accumulated at Alq<sub>3</sub> layers near the injection barrier of  $\alpha$ -NPD.

The positively charge up at the surface after the deposition of Alq<sub>3</sub> layers was reported by Ito *et al.*<sup>9)</sup>. The initial bright luminescence observed may be caused by the recombination of irradiated electrons and surface

positive charges.

#### 4. CONCLUSION

We propose the specific structure of FED with organic EL materials films as the phosphor. It was found that the Alq<sub>3</sub> layer emitted luminescence light by electron beam excitation. The observed luminescence revealed high intensity initially but was quenched within 1 sec. The EL films were investigated with, XRD AFM, and XPS before and after electron irradiation. It was found that the crystallization of the organic layers did not occur even after irradiation. The observed XPS spectra indicated, however, the C1s peak in Alq<sub>3</sub> and CuPc layers shifted toward the higher binding energy near the interface of  $\alpha$ -NPD. Therefore we concluded that the short lifetime of the luminescence was due to the accumulation of electrons in the emitting Alq<sub>3</sub> layer near the  $\alpha$ -NPD layer. On the other hand, the initial luminescence may be caused by the recombination of irradiated electrons and the surface positive charges.

From considering of the bright initial luminescence the organic EL thin films will be available as the phosphor of FED if we can apply strong enough electric field to the films in the proposed structure.

#### 5. REFERENCES

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