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# Time resolved luminescence properties of Al<sub>q3</sub> for spin-injection into organic semiconductor

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## Abstract

The electroluminescence and conduction properties of organic light emitting devices(OLEDs) with Al<sub>q3</sub> emissive layer and with Fe cathode were investigated. The relative luminescence intensity for the device became lower than that with Al cathode. Time resolved photoluminescence of Al<sub>q3</sub> was measured to investigate the electronic state of the interface between Fe and Al<sub>q3</sub> layer of OLEDs. The difference of luminescence intensities of OLEDs could not be explained only due to the work functions, but also due to the essential increase of quenching centers. © 2001 Elsevier Science. All rights reserved.

**Keywords:** Electroluminescence; Time resolved photoluminescence; Organic semiconductor

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Recently, spin-polarized electroluminescence(EL) due to spin-injection into inorganic light-emitting devices were observed[1]. Also, the study related with spin-injection into organic semiconductor attracts much attention[2], although spin-polarized EL using the organic molecule as an emitter has not been observed. In investigations of OLEDs, no ferromagnetic electrode has been used except for Ref. [3]. Because ferromagnetic metal(ex. Fe, Co, Ni) have relatively high work function, it causes decrease of luminescent efficiency of OLEDs[4]. In this work, EL and electronic conduction properties of OLEDs with Fe cathodes as a spin injector were investigated. Also, in order to investigate electronic states of the interface between cathode and emissive layer of OLEDs, time resolved photoluminescence(PL) properties of *tris*-(8-hydroxyquinolino)-aluminum(Al<sub>q3</sub>) thin films deposited on Fe films were measured.

The stacking structure of our OLEDs was glass-substrate/ITO(thickness: 20 or 40 nm)/TPD(45 nm)/Al<sub>q3</sub>(45, 55 or 65 nm)/Al-oxide(Al-O: 1.0 nm)/M(M = Al or Fe: 20 nm)/Al(120 nm). For the sake of comparison, the devices with non-magnetic electrode Al were also investigated. ITO(In<sub>2</sub>O<sub>3</sub> + SnO<sub>2</sub> 10 wt%) transparent anode was

deposited on glass substrates by conventional magnetron sputtering. TPD(Tri-Phenyl-Diamine) as a hole transport layer, Al<sub>q3</sub> as an emissive layer and Al for the making of Al-O insulator were made by conventional evaporation without breaking vacuum. Pots for TPD and Al<sub>q3</sub>, and an electron gun for Al were used. After Al thin film deposition, the evaporation chamber was leaked for the making of Al-O layer for five minutes. Then, the cathode M(M = Al or Fe) was evaporated using an electron gun. They were deposited as slow as possible monitoring their thickness by quartz-resonator. The current-voltage and EL properties of OLEDs were measured at room temperature.

For the time resolved PL measurements, Al<sub>q3</sub> films(thickness: 10 nm) were deposited on M(M = Al or Fe) films(20 nm) using evaporation without breaking vacuum. The samples with the Al-O layer between Al<sub>q3</sub> and M were also made. Total thickness of Al-O layer(5 nm) and M films(15 nm) was 20 nm. In the case of making Al-O layer, the evaporation system was leaked at atmosphere before Al<sub>q3</sub> deposition. The spectra were plotted by using a streak camera equipped with a mode-lock Ti-sapphire laser at room temperature.

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Fig.1 shows current-voltage properties of OLEDs with  $M = \text{Al}$  and with  $M = \text{Fe}$  in the absence of applied magnetic fields. Threshold voltage of OLEDs with  $M = \text{Al}$  and that of OLEDs with  $M = \text{Fe}$  were about 6.5 V and 10 V, respectively. The efficiency of electron injection from Fe cathode into  $\text{Alq}_3$  layer through Al-oxidized layer should become low essentially because of the high work function of Fe. The inset in Fig.1 shows EL spectra of the OLEDs with  $M = \text{Al}$  and with  $M = \text{Fe}$ . Applied current density for their measurements is 25.0  $\text{mA}/\text{cm}^2$  that is enough to be luminous. While the difference of the peak position between their devices was little, the relative luminescence intensity for OLEDs with  $M = \text{Fe}$  was about 1/40 of those with  $M = \text{Al}$ . The difference of intensities could not be explained only due to the work functions. One possible reason is that the changes of the molecular conformation at the interface between Fe and  $\text{Alq}_3$  cause more quenching sites. No effects of an applied magnetic field until 0.12 T was observed on the EL measurements.

Fig.2 shows the analyses of time resolved PL spectra near 520 nm wavelength of  $\text{Alq}_3$  on various underlayers. The time resolved PL intensity shows a relatively fast monotonous decay. In order to consider the fast decay, the signal intensity ( $I$ ) was decomposed into two components with an exponential decay of an ordinary lifetime  $\tau_2$ , of 10 ns[5] and an unusual lifetime  $\tau_1$ , for the lowest unoccupied molecular orbital(LUMO) of  $\text{Alq}_3$  using the following equation,

$$I = a_1 \times \exp(-t/\tau_1) + a_2 \times \exp(-t/\tau_2). \quad (1)$$

The estimated  $\tau_1$  for  $\text{Alq}_3$  on Fe was 69 ps, which is half of that for  $\text{Alq}_3$  on  $\text{SiO}_2$ -substrate;146 ps. Interestingly, the lifetime became longer by inserting Al-oxide(Al-O) layer between the  $\text{Alq}_3$  and Fe layers;116 ps. It should be noticed that the proportional coefficient of the part of unusual lifetime  $a_1$ , is larger than the part of ordinary lifetime  $a_2$ , in the case of  $\text{Alq}_3$  on Fe compared with the case of  $\text{Alq}_3$  on Al. From FT-IR analysis,  $\text{Alq}_3$  molecular structure on Fe was found to become different in comparison with  $\text{Alq}_3$  on  $\text{SiO}_2$ -substrate or on Al, while the change was little for the molecule on Fe/Al-O. This must come from the transformation of the chemical bonding at interface between  $\text{Alq}_3$  and Fe, resulting in a change of electronic states of the LUMO of  $\text{Alq}_3$  on Fe and the unusual short lifetime. Neither changes of the chemical bonding nor changes of the unusual lifetime were observed for  $\text{Alq}_3$  on Al films. Consequently, one possible reason that the relative luminescence intensity for OLEDs with  $M = \text{Fe}$  was weaker than that with  $M = \text{Al}$  might be that the changes of the molecular conformation at the interface between Fe and  $\text{Alq}_3$  leads to an increase of the number of quenching centers, then OLEDs with  $M = \text{Fe}$  might need higher current density for luminescence than that with  $M = \text{Al}$ . Effects of lowering temperature on the PL and EL

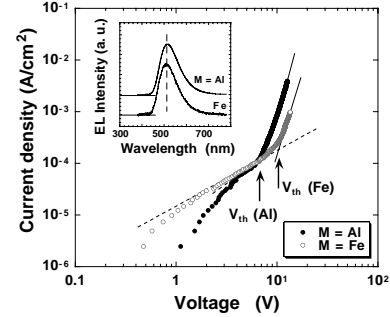


Fig. 1 Current density-voltage curves and EL spectra(inset) of OLEDs with  $M = \text{Al}$  and with  $M = \text{Fe}$ .

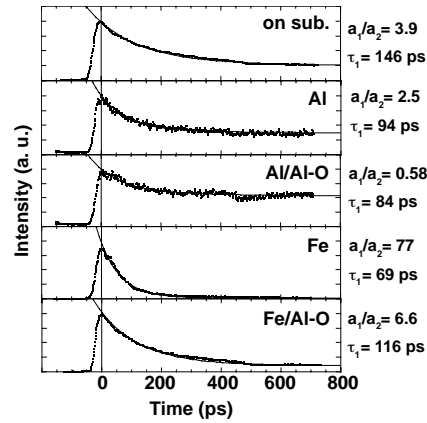


Fig.2 Time resolved PL spectra of  $\text{Alq}_3$  thin films on various underlayers. Data were fitted by the equation (1).

properties will be investigated in the future in order to find out details of the excited states of  $\text{Alq}_3$ .

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