Electrical Conduction of Organic Light-Emitting Diodes Using Self-Assembled Monolayer-Modified Indium Tin Oxide Electrode

Tatsuo Mori, Masato Imanishi* and Takao Nishikawa**

Department of Electrical Engineering, Aichi Institute of Technology, 1247 Yachigusa, Yakusa-cho, Toyota, Aichi 470-0392, Japan
*Department of Electrical Engineering and Computer Science, Nagoya University, Furo-cho, Chikusa, Nagoya, Aichi 464-8603, Japan
**Center for Regional Collaboration in Research and Education, Iwate University 4-3-5 Ueda, Morioka, Iwate, 020-8551, Japan

The introduction of fluorinated self-assembled monolayer (FSAM) as a hole-injection layer increased the work function of ITO and decreased the driving voltage of Alq3-based organic light-emitting diodes (OLED). We discussed carrier transport of Alq3-based OLED with or without FSAM and LiF as an electron-injection layer. The current amount depends on hole injection and the emission depends on electron injection. We proposed the method comparing between two ratios of current density and luminance and clarified the leakage of hole current through Alq3 layer with low hole mobility in the low voltage region.

Keywords : Organic light-emitting diodes, Self-assembled monolayer, Carrier injection, Carrier transport, Carrier balance

1. Introduction

Organic light-emitting diodes (OLEDs) consisting of multi-layer structure are reported by Tang and Van Slyke in 1987[1]. OLEDs are one of injection luminescent devices as inorganic LEDs. The carrier transport from electrodes to a recombination zone plays an important role of high efficiency performance. In general, since most organic materials show an insulating property, it is not easy to inject electrons and holes from electrodes. In OLEDs, enough carriers are injected and provided into the recombination zone with comparative ease by means of incorporating hole injection, hole transport, electron injection and electron transport layers. The EL efficiency of OLEDs depends on light out-coupling factor, PL quantum efficiency, exciton factor, and carrier balance factor. However, the light out-coupling factor, PL quantum efficiency and exciton generation factor are determined by a device structure, an intrinsic material performance and a quantum-chemical mechanism, respectively. Only the carrier balance factor can be artificially controlled by tuning various organic materials, layer thickness and carrier injection. For example, we showed the EL and conduction properties for the OLEDs consisting of a naphthyl-substituted diamine derivative (α-NPD) and a blue-emitting aluminum quinoline (BAIq)[2]. In this case, it was found that the recombination zone is shifted and extended by the thickness ratio of α-NPD/BAIq. We try to control the carrier balance by changing the condition of carrier injection but not organic materials. Using a fluorinated self-assembled monolayer (FSAM), we have already reported the stability of film structure of hole transport layer[3], the enhancement of hole injection[4] and the improvement of device lifetime[5]. In this paper, we discuss the carrier balance of OLEDs with or without FSAM-modified indium tin oxide (ITO).

2. Experimental

We used N,N’-di(1-naphthyl)-N,N’-diphenyl-1,1’,1’-diphenyl-1,4’-diamine (α-NPD) as a hole-transport material and 8-hydroxyquinoline aluminum (Alq3) as an emission material from Nippon Steel Chemical Co. We used (heptadeca...
fluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane (FSAM) as a SAM material.

Organic thin films were prepared on a glass substrate with an ITO transparent electrode (anode). The organic thin films were prepared using the vacuum deposition at a pressure of 0.8 ~1x10^{-3} Pa at room temperature. We carried out a vacuum-deposition with EO-5 (EIKO Co.).

Absorption spectra were measured by spectrophotometer (U-3000; Hitachi Co., Ltd.). Photoluminescence (PL) spectra were measured using a spectrophotometer (FP-777; JASCO Corp.). The work functions of ITO and FSAM-modified ITO are measured with the photoemission yield spectroscopy in air (AC-2, Riken Keiki Co.). Luminance-current-voltage characteristics were measured using a source measure unit (Keithley 2400 Source Measure Unit) and a luminance meter (TOPCON BM-8). The measurements of luminance-current-voltage characteristics were carried out under vacuum of ~0.1 Pa.

3. Results and Discussions

3.1. Contact angles and work functions of FSAM on ITO substrates

While the ITO’s surface is hydrophilic, the surface of FSAM on Si is hydrophobic and its contact angle is ~110° because of fluorine atoms[6]. As shown in Fig. 2, since the surface of ITO is the aggregate of crystals, it is very rough and different from the smooth surface of Si. Its arithmetic mean deviation of the profile (Ra) is ~1.2 nm. FSAM molecules are combined with OH groups on ITO via hydrolysis. FSAM domains are thought to extend during linking with neighbor molecules. The formation of FSAM cannot smooth the asperity of ITO.

Fig. 1 Chemical structures of organic materials.

Fig. 2 Typical profile of ITO substrate.

Fig. 3 The contact angles and work function of FSAM-modified ITO substrates vs. deposition time of FSAM.

Fig. 3 shows the contact angle and work function of ITO with a keeping time. When the covering of FSAM on ITO is not enough, the contact angles of the partially uncovered ITO substrates are smaller than that of whole covered ITO substrate, 110°[5]. The contact angle increases steeply with the attachment of FSAM molecules at short time and then increases gradually.

The work function of FSAM-modified ITO increases with a keeping time. The work function of FSAM-modified ITO with the saturated contact angle is estimated to be 5.5 eV. The difference between the work function of the FSAM-modified ITO and the ionization potential of α-NPD, 5.5 eV, becomes smaller with increasing the work function. The ionization potential of FSAM cannot be estimated by AC-2 and AC-3 which has a more widely measurable range than AC-2. It is thought that the change of work function is caused by the strong polarization of FSAM molecules. Ishii et al. have already reported the effect of interface dipole layer on the metal-organic interface[7].

The molecules of FSAM are polarized natively at alkyl-group side and positively at silole side in terms of the strong electronegativity of fluorine atom. The value of polarization is almost estimated to be 3 D. In Fig. 4, the direction of
interface dipole is toward α-NPD side for a left model and it is toward ITO side for a right model. In the former, since the interface dipole layer lowers the vacuum level of α-NPD side (the work function of ITO including a dipole layer become smaller), the difference between the work function of ITO and the ionization of α-NPD is extended. On the other hand, in the latter, since the interface dipole layer increases the vacuum level of α-NPD side (the work function of ITO including a dipole layer is shrunk), the difference is smaller. Although the difference is not always equal to the barrier height of hole injection between ITO and α-NPD, it is related to the barrier height without occurring a pinning phenomenon due to interface states. The increase in work function of FSAM-modified ITO can be explained by the above interface dipole model[8].

3.2. Initial properties of OLEDs with or without FSAM

Fig. 5 shows the initial conduction characteristics for OLEDs with or without FSAM. The current density curve is shifted to low voltage region by the introduction of FSAM. Since only the hole-injection condition is changed, it is thought that the hole injection is enhanced and the increase in hole current leads to the increase in the current of device. However, since an emission is obtained by an electron-hole recombination, only an excess carrier current component will increase if only a carrier component increases as compared with a counter carrier. Consequently the emission per current efficiency will decrease.

Fig. 5 The FSAM deposition time dependence of the current density – voltage curves for OLEDs using FSAM-modified ITO: ITO/w/ or w/o FSAM/α-NPD(50nm)/Alq3(50nm)/LiF/Al.

But, as shown in Fig. 6, the luminance efficiency per current density for the OLED with FSAM does not decrease by the introduction of FSAM and equal to that for the OLED without FSAM. Strange as it may look to you, the phenomenon can be understood by the law of current continuity. For OLEDs, when emissions are observed, both electrons and holes flow in a device. In a single layer device, the device consists of an organic material. Since electrons and holes flow in the layer simultaneously, the electron amount does not always agree with the hole amount. However,
for Tang’s type device that consists of multilayer including hole transport and electron layers etc., the carrier balance (current balance), which is the ratio of a recombination current density to a total current density, can be controlled by selecting organic materials and layer structures. Therefore, the carrier balance will be a unity for multi-layer devices. In our case, α-NPD and Alq3 layers are regarded as hole and electron transport layers, respectively. Therefore, the electron and hole currents are determined by the shared voltage of α-NPD and Alq3 layers. If electrons can be provided (injected) from an anode, the electron current can keep pace with the increase in hole current. Consequently, it is thought that the luminance efficiency per current density does not change by the enhancement of hole injection due to the introduction of FSAM. In fact, luminance is proportional to current density as reported by Kao and Hwang [9]. They pointed out that if one carrier is minor to the counter carriers, luminance increases as the square of current density[6].

![Graph](image1.png)

**Fig. 7** The current density – voltage curves for OLEDs using FSAM-modified ITO and/or LiF: ITO/w/o FSAM/α-NPD (50nm)/Alq3(50nm) /w/o LiF/Al.

3.3. Effect of LiF electron injection

Figs. 7, 8 and 9 show the initial conduction properties for OLEDs with or without FSAM and LiF. Henceforth, the sample names are called FSAM/LiF, FSAM/Al, ITO/LiF and ITO/Al. It is well-known that an electron injection is enhanced by inserting ultra thin layer of halides and oxides of alkali and alkali earth metals[10]. We use 0.6-nm-thick LiF layer as an electron injection layer. If it is not used, OLEDs without LiF layer show high driving voltage and low EL efficiency. In Fig.7: current density vs. voltage, the current density of FSAM/LiF is the highest of 4 specimens.

![Graph](image2.png)

**Fig. 8** The luminance - current density curves for OLEDs using FSAM-modified ITO and/or LiF: ITO/w/o FSAM/α-NPD (50nm)/Alq3(50nm) /w/o LiF/Al.

![Graph](image3.png)

**Fig. 9** The luminance - voltage curves for OLEDs using FSAM-modified ITO and/or LiF: ITO/w/o FSAM/α-NPD (50nm)/Alq3(50nm) /w/o LiF/Al.

The ITO/Al is the worst and two other specimens are same.

In Fig. 8; luminance vs. current density, the specimens without LiF (FSAM/Al, ITO/Al) are poorer than the specimens with LiF (FSAM/LiF, ITO/LiF). Especially, the former luminance is proportional to the square of current density in the low current region and the gradient approaches to a unity with increasing current. When the device has a LiF layer, the luminance is proportional to current density even if FSAM is not introduced. This suggests that enough electrons are not provided to a recombination zone for the specimens without LiF and the current through the device is hole-rich.

In Fig. 7, there is not one order difference of current density at a voltage between ITO/LiF and
FSAM/Al. On the other hand, in Fig. 9: luminance vs. voltage, there is two order difference of luminance at a voltage between the two specimens. This suggests that the electron current density of ITO/LiF is higher than that of FSAM/Al under almost same current flowing through an external circuit.

In the above conduction model proposed by Kao and Hwang, when luminance \( L \) is proportional to current density \( J \), luminance is derived from prompt electroluminescence. When luminescence is proportional to the square of current density, luminescence is derived from delayed electroluminescence.

\[ L = a J + b J^2 \]

where \( a \) and \( b \) are proportionality constants. When electron-hole recombination occurs, a singlet \( S_1, \ldots, S_n \) and a triplet \( T_1, \ldots, T_n \) are stochastically produced according to the ratio of 1 : 3. The prompt electroluminescence occurs by the direct deactivation from a singlet state \( S_1 \) to a ground state \( S_0 \) (Eq.(2)) and is the same as fluorescence. On the other hand, a phosphorescence occurs by the direct deactivation from a triplet state \( T_1 \) to the ground state \( S_0 \) (Eq.(3)). The decay time of phosphorescence is much longer than that of fluorescence because of the spin-forbidden transition of \( T_1 \) to \( S_0 \). The delayed electroluminescence also occurs by the deactivation from \( S_1 \) to \( S_0 \) but emits after a singlet is reproduced through the triplet-triplet annihilation (eq.(4-6)).

\[ \begin{align*}
S_1 & \rightarrow S_0 + h\nu \\
T_1 & \rightarrow S_0 + h\nu' \\
T_1 + T_1 & \rightarrow S_1 + S_0 \rightarrow 2S_0 + h\nu
\end{align*} \]

where \( h\nu \) mean an emission, \( h \) is the Plank constant, \( \nu' \) is a frequency. The quantitative production process of the singlet state due to the triplet-triplet annihilation is shown as the follows[11]:

\[ \begin{align*}
8T_1 & \rightarrow S_1 + 3T^* \\
8T_1 & \rightarrow S_0
\end{align*} \]

Since the triplet-triplet annihilation depends on the density of triplet, it is thought to be dominant in the high current density region. Therefore, the Kao’s model is applied to this case because the gradient of luminance – current density curve approaches to a unity. If luminance is proportional to current density in the whole current region, Fig. 9 should show the same behavior as Fig. 7. It is clarified that the threshold voltage of luminance is controlled by hole injection and the increase behavior of luminance depends on electron injection.

Fig. 10 shows the ratio of current density and luminance of ITO/LiF to FSAM/Al. The ratio of current density is at most 3 in the voltage region of 4-11 V. Especially it is almost unity above 6 V and both current densities are same. On the other hand, the ratio of luminance is 100 at 4 V and it decreases rapidly with increasing voltage. Above 8 V, it is a little over 2. The region that the ratio of luminance is above 10 corresponds to the region that the luminance is proportional to the square of current density. That is, it is suggest that the electron current flowing in the device is minor and the hole current is major in the voltage region. For the Alq3-based OLEDs consisting of hole transport layer and Alq3 layer, the recombination zone exists in the Alq3 layer near the hole transport layer. Because the hole and electron mobilities are estimated to be \( 10^{-5}-10^{-6} \text{ cm}^2/\text{V}s \) and \( 10^{-8} \text{ cm}^2/\text{V}s \), respectively[12]. For the specimen without LiF, it is suggests that hole current flows through Alq3 layer in the current region of <10 \( \mu \text{A/cm}^2 \) and electron current is a half of hole current in the current region of \( \geq 10 \text{ mA/cm}^2 \). Therefore, it is found that the recombination zone does not exist around the \( \alpha \)-NPD/Alq3 interface but it exists at the Alq3 layer near a cathode. For the case that electrons are provided from the cathode, the recombination zone is near the \( \alpha \)-NPD/Alq3 interface below 10 \( \mu \text{A/cm}^2 \). The hole current injected into the Alq3 layer will leak to the cathode when enough electrons are provided from the cathode.

**4. Conclusions**

We fabricated OLEDs with different carrier injection conditions by means of deposition of FSAM and LiF. The introduction of FSAM as a hole injection layer lowered the driving voltage but...
did not reduce the carrier balance factor. Designing carrier injection conditions, we realized the OLEDs which showed a same current density and different luminance. Consequently we proposed the method comparing between two ratios of current density and luminance and clarified the leakage of hole current through Alq3 layer with low hole mobility in the low voltage region.

**References**