Time-Of-Flight Technique to Examine Carrier Blocking Nature in Organic Light Emitting Diode

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In organic light emitting diodes, carrier-blocking property at organic hetero interfaces is one of important factors to get better performance, but the factor have not been well investigated experimentally. In this study, we proposed a new usage of time-of-flight (TOF) technique to quantitatively examine the carrier behavior in operating device. The measurement was demonstrated for ITO|α-NPD|Alq3|Al device. TOF signal was successfully observed under the influence of actual current flow. For hole transport from ITO to Al electrode, delayed-transport and blocking nature at α-NPD/Alq3 was clearly observed. In contrast, for electron transport in the same direction, no delayed transport was detected. This result was consistent with the possible energy barrier at the interface, indicating the feasibility of this technique to examine carrier blocking nature in electronic devices. The method to analyze the TOF in detail will be discussed. [DOI: 10.1380/ejssnt.2012.315]

Keywords: Organic Electronic device; Charge carrier behavior; Time of Flight; Displacement current measurement; Organic Light Emitting Diode; Carrier Blocking

I. INTRODUCTION

Organic electronics have attracted much attention in recent years due to their multiple advantages such as high flexibility, easy processing, low fabrication cost, and large area fabrication. These unique advantages make them highly promising for organic solar cells [1], organic thin film transistors [2], organic light emitting diodes [3], and so forth. Among the different classes of organic electronic devices, organic light-emitting diodes (OLEDs) are the most matured and developed, but further improvement of the device performance is still required. To do that, the understanding of its operation mechanism should be clarified. Especially, charge carrier transport and blocking at the organic hetero interface is essential to the exciton formation and charge balance in OLED, but experimental study has been limited so far. This is because experimental technique to probe carrier behavior was limited.

As a tool to probe carrier behavior, capacitance-voltage measurement has been applied to various OLEDs. Recently our group demonstrated that carrier behavior in OLED is measured under a triangular voltage scan [4–7]. For ITO|α-NPD|Alq3|Al device, which is one of the most widely-investigated standard OLED, DCM revealed the hole blocking nature at α-NPD/Alq3 [4, 5]. It was examined, only for low voltage region without actual current or light emission. This limitation is because large actual current tends to hinder displacement current. Also, in high voltage region with light emission, holes and electrons are transporting and being blocked. So, in DCM, we cannot separate carrier blocking nature of each carrier. To understand OLED operation, we need another method to investigate carrier blocking nature of the device in operation.

In this study, as a possible approach to examine the carrier transport and blocking nature in operation condition, we propose a new usage of time-of-flight (TOF) method. TOF has been applied to various electronic materials to measure the carrier mobility by using single-layer device structure. We have applied this technique to ITO|α-NPD|Alq3|Al double-layer device with organic-organic hetero interfaces. We will demonstrate that the obtained TOF curves include rich information about carrier transport and blocking in operating OLED.

II. PRINCIPLE OF TIME-OF-FLIGHT MEASUREMENT

In TOF measurement, a flash of laser light generates charge carriers in a thin sheet near one boundary of a sample layer, and an applied electric field sweeps them through the layer. With this technique, carriers are often generated well within the sample layer because of the penetration depth of the light [8]; the laser might penetrate a
distance of a few hundred nanometers into the sample [9]. Therefore, in order to have a well-defined flight distance, the thickness of the sample should be at least ten times larger the penetration depth of the laser [9] and minimum gusableh film thickness are about 0.5-1 \( \mu \text{m} \) [10, 11].

A. Traditional TOF

The traditional TOF method is applied to single layer device without carrier injection to determine the carrier mobility as shown in Fig. 1(a). In this method carrier blocking layer is used to disallow the injected actual current; only photo carrier is allowed. If there is no trap, the carrier travels smoothly and at transit time \( \tau \), photo current drops suddenly as shown in Fig. 1(b). We can calculate the mobility \( \mu \) as

\[
\mu = \frac{d^2}{V \tau},
\]

where \( V \) is the voltage across the device, \( d \) is the thickness of the organic layer, and \( \tau \) is the transit time. If we generate too much photo-carrier by using high intensity laser beam, the curve shows the peak structure [red line of Fig. 1(b)] due to space charge effect of excess photo-carriers [12]. So, laser intensity should be adjusted to remove the space charge effect. If there are traps, the photo current drops slowly and it is difficult to clearly determine the transit time. After making a log-log plot, we can determine the transit time \( \tau \) as in Fig. 1(c). The photocurrent roughly indicates the carrier velocity. Thus the integration of the current in relation to time reflects the travel distance of the carrier as follows. The current integration from \( t = 0 \) to \( \tau \) gives the total charge of photo carriers \( Q_0 \) created in the whole device. The integration up to any time \( t \) reflects the averaged travel distance of the photo carrier \((\langle x \rangle)\) at \( t \) as shown in the next equations.

\[
\int_0^t I(t') \, dt' = Q_0, \tag{2}
\]

\[
\int_0^t \frac{I(t') \, dt'}{Q_0} = \frac{\langle x \rangle}{d}. \tag{3}
\]

This equation is useful to analyze the movement and distribution of carriers.

B. TOF for double layer device in operation

We propose to apply TOF measurement to a double layer OLED device with actual current flow. In contrast to traditional TOF, our device is not single-layer device and photo-carrier is affected by other carriers injected from the electrode (Fig. 2(a)). In this case, carrier blocking layer to suppress injection is not used to allow the injected actual current. We measure the AC component through the coupling condenser to isolate the photocurrent from the actual current. By using AC mode detection, the photo-current can be detected by oscilloscope.
For a device consisting of layer 1 and layer 2 without carrier blocking at the organic/organic interface, TOF curve should be expected as shown in Fig. 2(b). At first, we observe the current \( I_1 \) due to carrier travel in the first layer \( L_1 \) and the current decays at \( \tau_1 \) when the carrier reaches the \( L_1/L_2 \) interface. After \( \tau_1 \), we observe the current \( I_2 \) due to carrier travel in second layer \( L_2 \), and transit time at \( \tau_2 \) when the carrier reach the counter electrode. For this situation,

\[
\frac{I_1}{I_2} = \frac{\mu_1}{\mu_2}
\]

holds, here \( \mu_1 \) and \( \mu_2 \) denote the mobility of the layer 1 and 2, respectively. Therefore, the current integral \( 0 \sim \tau_1 \) and \( \tau_1 \sim \tau_2 \) should be expressed by the following equations.

\[
\int_0^{\tau_1} i(t) dt = \frac{L_1}{L_1 + L_2} Q_0, \quad (5)
\]

\[
\int_{\tau_1}^{\tau_2} i(t) dt = \frac{L_2}{L_1 + L_2} Q_0. \quad (6)
\]

In summary, if there is no carrier blocking, we see two rectangular structures. The current ratio should be equal to that of mobility and the area ratio to that of layer thickness. For TOF measurement of double layer structure, if we observe the deviation from this double-rectangular shape, it should be ascribed to carrier blocking. Thus we expect this method as a good measure of carrier blocking.

**III. EXPERIMENTAL**

The indium tin oxide (ITO) coated glass substrate was purchased from Q-lights Co. Ltd. The thickness of an ITO film was 150 nm with a sheet resistivity of 50 \( \Omega/\square \). The substrates were initially degreased by scrubbing with detergent and deionized water and then cleaned by ultrasonic agitation successively with detergent diluted with deionized water (once, 10 min), deionized water (four times), acetone (twice), and isopropyl alcohol (twice) for 5 min each unless explicitly stated. The substrate was then dried with \( N_2 \) blow and finally UV-ozone treated for 20 min. After the surface treatment, the substrates were immediately transferred to the deposition chamber. The structure of the device is indium-tin oxide (ITO)\( /\alpha\)-NPD(1100 nm)\( /Alq_3(60 \text{ nm})/Al(100 \text{ nm}) \) as shown in Fig. 3, where the active area (A) is 4.0 mm\(^2\). The organic films and the Al electrode were deposited successively at rates within 0.1–0.12 and 1–1.2 nm/s, respectively with a working pressure of \( 2.8 \times 10^{-4} \sim 4.8 \times 10^{-4} \text{ Pa} \). The thicknesses of the organic layers and the Al electrode were measured in situ with a quartz crystal sensor and devices were fabricated under dark conditions. Following the evaporation, the device was transferred to the glovebox under \( N_2 \) atmosphere and encapsulated with a glass lid and a getter, and removed from the glovebox for testing. DCM and Current-Voltage-Luminance (\( I-V-L \)) measurements were performed in the dark condition at room temperature. Our experimental setup and procedure of DCM and \( I-V-L \) were described elsewhere [4, 13].

We performed Time-Of-Flight (TOF) measurement, and the experimental setup is shown in Fig. 4. Our TOF measurement were performed using a \( N_2 \) pulsed laser (\( \lambda = 337.1 \text{ nm}, \text{ pulse width}=600 \text{ ps} \)) as the light source to generate photocarriers. The laser beam was directed from the ITO side of the multilayer OLED device in operating state to create photo-carriers (hole or electron) near the ITO/organic interface. The laser intensity was adjusted using neutral density (ND) filter to avoid space charge effect. A DC power supply was used to provide the positive bias voltage \( V \) for hole measurement and negative bias voltage \( V \) for electron measurement. A current sensing resistor \( R \) in series with the sample device was used to detect the AC component of the photocurrent. The value of \( R \) (100 \( \Omega \) -10 K\( \Omega \)) was chosen so that the time constant \( RC \) was at least 20 times less than the carrier transit time [9] because the \( RC \) time constant of the sample must be kept much shorter than the transit time [8]. A digital oscilloscope, TDS3032C (frequency =300 MHz, sample rate =2.5 GS/s, Tektronix Inc.) was used to measure the voltage across \( R \).

**IV. RESULTS AND DISCUSSION**

**A. \( I-V-L \) and DCM results**

Figure 5 shows the typical \( I-V-L \) curve of the device. With increasing bias current, the current increases with the light emission above 13 V. For the negative bias, very small current was observed. The device worked well as OLED although the \( \alpha\)-NPD layer is too thicker than conventional OLED.

Next, we investigated the carrier behavior in the device by using DCM. The current measured in DCM (\( I_{\text{DCM}} \)) can be described as the sum of the actual current \( I_{\text{act}} \) and the displacement current proportional to the effective capacitance of the device (\( C_{\text{eff}} \)).

\[
I_{\text{DCM}} = I_{\text{act}} + \alpha C_{\text{eff}}. \quad (7)
\]

where \( \alpha \) is the sweep rate (= \( dV/dt \)).

Figure 6 shows the DCM curve for \( V = -15 \text{ V} \sim +3 \text{ V} \). The sweep rate was 1 V/s. Vertical axis is the current density divided by the ramp rate, corresponding to \( C_{\text{eff}} \) of the device with unit area. The change of the current in the forward scan (\( dV/dt > 0 \)) can be explained for the three voltage regions as follows. In region (I), a constant current was observed. Since the effective capacitance calculated from the current corresponds to that of \( \alpha\)-NPD and \( Alq_3 \) layers, it indicated that no carrier is injected for this bias region. In region (II), a sudden increase of current was observed at \( V = V_{\text{inj}} \). This means that the hole injection from the ITO to the \( \alpha\)-NPD layer starts. Since the effective capacitance is similar to that of \( Alq_3 \) layer, injected holes are blocked and accumulated at the \( \alpha\)-NPD/\( Alq_3 \) interface. In region (III), the current shows further increase at \( V = V_{\text{th}} \). This means that hole injection from \( \alpha\)-NPD to \( Alq_3 \) layer starts. The component of the actual current becomes dominant, and it is difficult to separate the displacement current due to hole blocking at the interface.
FIG. 3: OLED device (a) structure and (b) top view of the device.

B. Analysis of TOF curves

We measured the TOF of the device with light emission under high positive bias. In this polarity, the transport of photo-induced holes was recorded. Figure 7 shows the TOF signals in μs scale. The sharp peak around 0 s is due to the travel of photo-created electrons into ITO electrode. After the peak, other broader peak appears. The peak time decreased with increasing voltage, suggesting that this is due to the travel of holes in α-NPD layer. By assuming the peak corresponds to transit time when the leading edge of the photo-induced holes reaches the α-NPD/Alq3 hetero-interface, we can roughly evaluate the hole mobility ($\mu_h$) in operating condition as $2.7 \times 10^{-4}$ cm$^2$/Vs. This is very close to the value of α-NPD layer.
With increasing voltage and current, the peak became clearer and the intensity increased. As mentioned in Section 2, the peak structure is characteristics of space charge effect. To check this point, the light intensity dependence was observed. For the reduced laser beam, such peak structure was still observed (not shown), indicating the space charge effect is due to not excess photo carriers but injected carrier for actual current. This result suggests that TOF measurement is a good tool to examine the carrier behavior of operating device.

Figure 8 shows the signal for +20 V in wide time scale. The current signal shows a peak structure at the transit time $\tau_1 = 2.4 \mu s$. As discussed above, the $\tau_1$ roughly corresponds to the time when the photo-holes reach the interface. The second kink at $\tau_2$ is expected as the transit time when the holes travel through the Alq$_3$ layer and reach the Al electrode. The overall line shape of the signal was much different from the double rectangular structure expected for the case without carrier blocking as mentioned in the proceeding section.

Next let us discuss the TOF results for negative bias condition, where photo-created electrons travel from ITO to Al. Figure 9 shows the log-log plot of TOF for high negative voltage ($-20 V$) in the scale of millisecond region. In contrast to positive bias condition, only single transit time was observed. The observed transit time ($\tau_1 = 0.7 \mu s$) corresponded to the time when the electrons arrived at $\alpha$-NPD/Alq$_3$ interface, because the electron mobility of $\alpha$-NPD estimated from the $\tau_1$ ($9.6 \times 10^{-4} \text{cm}^2/\text{Vs}$) is similar to that in literature ($6 - 9 \times 10^{-4} \text{cm}^2/\text{Vs}$ [14]). The second transit time when the electron should reach the Al electrode may be smeared out due to trap effect.

The observed difference between positive and negative bias can be explained by carrier blocking nature as follows. Figure 10 shows the energy diagram of $\alpha$-NPD|Alq$_3$ layer. For negative bias, no blocking of electrons occurs because there is no barrier across the interface. But at the positive bias, blocking of holes occurs due to the barrier ($0.3 \text{eV}$) between $\alpha$-NPD and Alq$_3$ layers. The quantitative analysis based on Eqs. (4)-(6) also revealed the difference. For positive bias, the integral of current up to $\tau_1$ is only 0.02% of the whole photo carriers. This value is much smaller than the ratio of film thickness (95%). This value means that, when the leading edge of holes reaches the interface, most holes still locate near ITO in average, suggesting that charge blocking at the hetero-interface retards the flow of the photo-holes. Similar effect can be concluded from the difference in current between $\tau_1$ and $\tau_2$: the difference ($I_1/I_2$) was about 8. Taking into account the mobility difference, $I_1/I_2$ is expected as $5 \times 10^2$ for the case of no blocking.

In the case of negative bias. The integration of the photocurrent form $t = 0$ to $\tau_1$ corresponds to ca. 9% of the total photo-induced charge. The order of magnitude is comparable to the ratio of film thickness. Also, the current ratio between at $\tau_1$ and $\tau_2$ ($I_1/I_2$) is roughly one order of magnitude. This is close to the ratio of electron mobility of $\alpha$-NPD to Alq$_3$ [$\mu_e (\alpha$-NPD)/$\mu_e (\text{Alq}_3)=10^2$]. This correspondence suggests that electron is not blocked at this interface. Therefore, our proposed way of analysis is good measure to examine the carrier blocking nature in
real device under operation.

V. CONCLUSIONS

We demonstrated the possibility of time of flight technique as a tool to examine carrier behavior in multilayer device in operation. For ITO/α-NPD/Alq3/Al OLED device, the observed TOF signal gave us useful information about carrier behavior. The peak structure observed for operating OLED with light emission and high current density is due to space charge effect by actual current. This demonstrated that TOF can probe practical environment of carrier surrounded by other carriers. The analysis of integrated current is a good method to examine carrier blocking nature at organic-organic interfaces. This technique can be applied to not only OLED but also other organic devices such as organic transistors and solar cells.

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