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Direct Probing of Carrier Behavior in Electroluminescence IZO/α-NPD/Alq3/LiF/Al Diode by Time-Resolved Optical Second-Harmonic Generation

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1. Introduction

Organic light-emitting diodes (OLEDs) have been intensively studied for practical use in electronics [1]. In order to improve the device performance with its lifetime, understanding carrier mechanism is of great importance, i.e., carrier injection, transport, and accumulation at the multi-layer interface. In OLEDs, electrons and holes recombine to emit light. Hence transient electroluminescence measurement (TEL) [2] is available for exploring carrier behaviors, though it cannot probe carrier behavior prior to electroluminescence (EL). On the other hand, electrical measurements [2,3], e.g., time-of-flight (TOF) method [4], have been utilized for investigating carrier transport across a film sandwiched between two facing electrodes. However, multi-layer structure and multi-species (electrons and holes) carrier transport complicate our understanding. A new probing technique that enables us to directly probe carrier behavior in multi-layer OLED is thus needed. Recently, we have developed a time-resolved optical second-harmonic generation measurement (TRM-SHG) [5] that can visualize carrier motion in organic devices, e.g. field-effect transistors (OFETs).

In this study, we employed TRM-SHG and TEL measurements for studying transient carrier behaviors leading to EL in double-layer OLEDs. Results showed EL is enhanced while excess charge is accumulated at the interface. We explain this charge accumulation on the basis of Maxwell-Wagner (MW) effect model. The accumulated charge $Q_s(\infty)$ at the interface was nearly independent of voltage, but a space charge field from this charge contributed to make balance electron and hole injection from facing electrodes, and resulted in continuously EL enhancement. The response time of EL was dependent on applied voltage, while the EL decayed in a same way after switching-off. We also explained these results using a simple model with consideration of MW effect charge accumulation.

2. Experimental

A double-layer OLED (see Figure 1a) was prepared using vacuum evaporation. N,N'-di-[(1-naphthyl)-N,N'-diphenyl]-(1,1'-biphenyl)-4,4'-diamine (α-NPD, 150nm) and tris(8-hydroxy- quinolinato) aluminum (III) (Alq3, 50nm) were deposited on the cleaned surface of indium-zinc-oxide (IZO)-coated glass substrate. Finally, LiF (0.5 nm) and Al were evaporated and used as top-electrodes. All measurements were carried out in dry nitrogen atmosphere. Figure 1a portrays the experimental arrangement for EFISHG measurements. Repeating laser pulses at 10 Hz (duration, 4 nsec; average power, 1 mW) were produced from a Nd:YAG laser equipped with third-harmonic generator and optical parametric oscillator. *p*-polarized laser pulse impinged onto the sample surface at an incident angle of 45°. EFISHG is generated in the presence of electric field $E(0)$ as [6]

$$I(2\omega) \propto |\chi^{(3)} \vdots E(0)E(\omega)E(\omega)|^2 . \qquad (1)$$

Here $\chi^{(3)}$ is the third order susceptibility, and $E(\omega)$ is electric field of the laser pulse. $\chi^{(3)}$ is a material dependent parameter with ω. By setting the laser wavelength at λ_ω=820 nm (EFISHG at $\lambda_{2\omega}$=410 nm), electric field in α-NPD E_1 (see Fig.1) was selectively probed [7]. Here, $E_1 = E_m - E_s$. E_m and E_s are Laplace field by charges Q_m on electrode and space charge field generated by charges Q_s accumulated at the interface. In other words, EFISHG directly probes Q_m and Q_s. Transient EL was monitored using oscilloscope with photomultiplier tube.

Figure 1b illustrates an equivalent circuit based on the Maxwell-Wagner effect model. Organic transport layers are modeled as a set of parallel capacitance C and conductance G. Charging Q_m on electrodes takes a relaxation time $\tau_{RC} = R_s C$ ($C = C_1 // C_2$). On the contrary, charging Q_s at the double-layer interface takes a relaxation time $\tau_{MW} = (C_1 + C_2)/(G_1 + G_2)$ ($\tau_{RC} \ll \tau_{MW}$). After the equivalent circuit analysis, we obtain E_1 for charging process of Q_m as

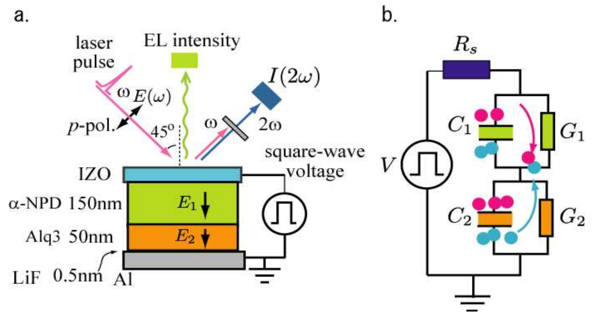

Fig. 1 (a) OLED (IZO/α-NPD/Alq3/LiF/Al) structure and experimental arrangement for EFISHG measurements. (b) Equivalent circuit model for OLED based on the Maxwell-Wagner effect.

$$E_1(t) = \frac{Q_m}{\varepsilon_1 \varepsilon_0} \quad (2)$$

with $Q_m = CV_{ex}(1 - \exp(-t/\tau_{RC}))$,

and of Q_s, $$E_1(t) = \frac{CV_{ex}}{\varepsilon_1 \varepsilon_0} - \frac{1}{d_1} \frac{Q_s}{C_1 + C_2} \quad (3)$$

with $Q_s = Q_{MW}(1 - \exp(-t/\tau_{MW}))$,

where $Q_{MW} = \frac{G_1 G_2}{G_1 + G_2} V_{ex} (\frac{C_2}{G_2} - \frac{C_1}{G_1})$

and d_1 is α-NPD thickness. Similarly, we obtain E_1 for discharging process of Q_m as

$$E_1(t) = \frac{Q_m}{\varepsilon_1 \varepsilon_0} - \frac{1}{d_1} \frac{Q_{MW}}{C_1 + C_2} \quad (4)$$

with $Q_m = CV_{ex} \exp(-t/\tau_{RC})$,

and of Q_s, $$E_1(t) = -\frac{1}{d_1} \frac{Q_s}{C_1 + C_2} \quad (5)$$

with $Q_s = Q_{MW} \exp(-t/\tau_{MW})$.

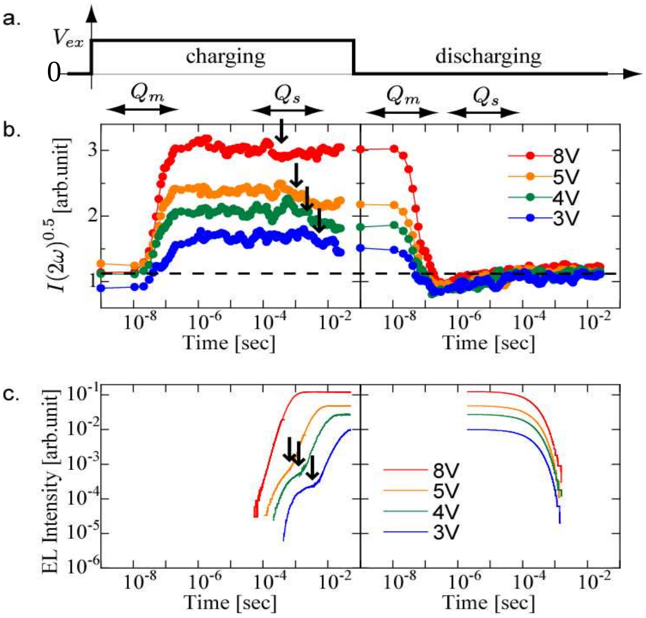

Fig.2 (a) Square-wave voltage applied for OLED. (b) EFISHG transient $I(2\omega)^{0.5}$ proportional to electric field in α-NPD layer E_1 only. (c) Transient EL measurements.

3. Results and Discussion

Transient EFISHG and EL were obtained at voltages V_{ex} = 3 V to 8 V. EFISHG signal reflected both charging/discharging of Q_m and Q_s. For charging process, EFISHG increased with increase of Q_m. The experimental relaxation time τ_{RC} agreed well with the expected value $\tau_{RC} = R_s C$, and it was independent of V_{ex}. On the other hand relaxation time τ_{MW} exhibited voltage dependence (indicated by arrows in Fig.2b). Similar dependence was obtained for the response of transient EL (see Fig.2c), and it corresponded well to the τ_{MW} for charging Q_s (see Fig.2b). After short-circuited (discharging), charge on electrodes Q_m disappeared in a manner similar to that in the charging process. On the other hand, Q_s remained and formed a space charge field, giving rise to EFISHG. As shown in Fig.2b, transient behavior of Q_s was the same for V_{ex}. Correspondingly, EL (Fig.2c) decayed in a similar manner. Figure 3 shows EL decay process plotted in semi-log scale. All transients were with a same slope, i.e., relaxation time τ_{EL} =0.25 ms. This result indicated that discharging process was responsible for the EL decaying. As we described in previous study [8], space charge field made a contribution to assist electron injection during discharging process, and prolonged recombination until discharging of Q_s completed. Results showed that engineering of excess charges is essential to realize fast switching performance for OLEDs.

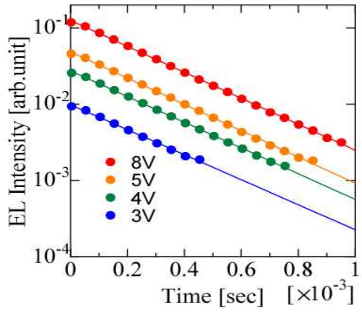

Fig.3 Semi-log plots of EL decay after shot-circuited. Voltage applied for charging was indicated.

4. Conclusions

Time-resolved EFISHG measurements were carried out with transient EL measurements to examine carrier transient in a double-layer OLED. Results showed that EL enhanced with accompanying carrier (hole) accumulation at the α-NPD/Alq3 interface. The charging time of carriers decreased with increase of applied voltage. In accordance with the charging time, the response time of EL enhancement became shorter. By contrast, discharging time and EL decay were independent of applied voltage, indicating that discharge process is responsible for the EL decay time.

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