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Measurement of thermal carrier de-trapping in double-layer organic light-emitting diodes by electric-field-induced optical second-harmonic generation

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Abstract

By using electric-field-induced optical second-harmonic generation (EFISHG) measurement, we have been studying carrier transport mechanism in organic light-emitting diodes (OLEDs), and showed that excess carriers are accumulated at interfaces during EL radiation. However, we have not yet studied energetics of trapped carriers at interfaces. In this study, we directly probe holes thermally being de-trapped from double-layer interfaces of IZO/α-NPD/Alq3/Al OLEDs (IZO: indium-zinc-oxide, α-NPD: N,N'-di [(1-naphthyl)-N,N'-diphenyl]-(1,1'-biphenyl)- 4,4'-diamine, Alq3: tris(8-hydroxyquinolinato) aluminum(III)) by using the EFISHG. Results show that de-trapping of holes is thermally activated at around T_d= 280 K, indicating that hole depth is 0.49 eV. We conclude that the EFISHG measurement is available for analyzing energetics of trapped carriers at interfaces in organic thin film devices.

1. Introduction

Organic thin film devices such as organic light-emitting diodes (OLEDs), organic solar cells (OSCs), organic transistors (OFETs), have attracted much attention in electronics for the past several decades [1]. New organic materials and advanced device techniques have been developed to realize these high performance organic devices. Nevertheless, understanding of the carrier behavior is still insufficient for further advancing device performance. Consequently, direct probing of carrier transport in device is helpful. However, this is not an easy task, owing to (1) complex multilayer structure of these devices, (2) presence of electrons and holes, and (3) very thin layer < 100 nm in organic devices. We have been developing electric-field-induced optical second-harmonic generation (EFISHG) measurement that can visualize carrier motions in organic materials and devices [2-4]. The EFISHG measurement has many advantages: (1) Direct probing of electrons and holes is possible, individually. (2) By choosing probing laser wavelength appropriately, carrier motion in one of layers in a multilayer device is allowed to be selectively probed. However, these are no longer sufficient. To make further clarify carrier transport in organic devices, it is very important to get information on energetics of carriers and trapped carriers that dominantly contribute to organic device performance. Experiments using thermal heating will be helpful. Thermally stimulated current (TSC) and thermally stimulated surface potential (TSSP) measurements are well known as techniques for evaluating trap energies in organic materials [5-7], by measuring short-circuit current or open-circuit voltage during heating. However, these are indirect methods, and we must estimate carrier motions from the trace of TSCs and TSSPs.

In this study, we developed a modified EFISHG measurement system that allows carrier motions during heating to be directly probed. By using the modified EFISHG system, we studied thermally stimulated de-trapping process in IZO/α-NPD/Alq3/Al OLEDs. Results showed that holes trapped at the α-NPD/Alq3 interface is thermally de-trapped at T_d=280 K, suggesting that hole depth is 0.49 eV. We conclude that our developed EFISHG system is useful to measure energy state of trapped carriers in multi-layered organic thin film devices.

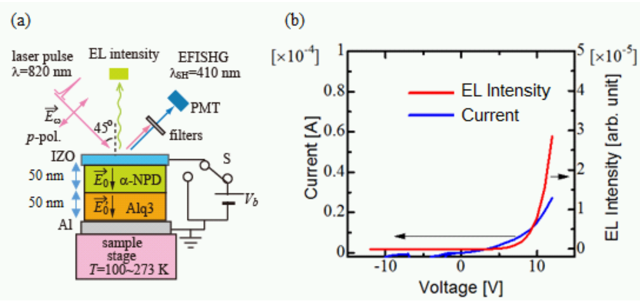

Figure 1: (a) Experimental setup for EFISHG measurements. (b) *I-V-L* characteristics of IZO/α-NPD/Alq3/Al OLEDs used here.

2. Experimental

Figure 1a illustrates the modified EFISHG measurement system which equips with a temperature variable stage for thermal heating. In the EFISHG measurement, *p*-polarized pulsed laser beam was supplied from an optical parametric oscillator (OPO) excited by the third-harmonic light of neodymium-doped yttrium-aluminum-garnet (Nd:YAG) laser, and used as a probing light. In organic device, carriers accumulate at the multilayer interface due to the Maxwell-Wagner effect, and they are working as a source of electrostatic field $\vec{E}_0$ [8]. The electrostatic field $\vec{E}_0$ deforms electron clouds of molecules. As a result, the second-harmonic polarization $\vec{P}_{2\omega}$ is induced by an electromagnetic coupling of $\vec{E}_0$ and vibrating electric field of the probing light $\vec{E}_\omega$. The light intensity $I_{2\omega}$ produced by $\vec{P}_{2\omega}$ is given as

$$I_{2\omega} \propto \left|\vec{P}_{2\omega}\right|^2,\ \vec{P}_{2\omega} = \varepsilon_0 \chi^{(3)} : \vec{E}_0 \vec{E}_\omega \vec{E}_\omega, \qquad (1)$$

where ε_0 is vacuum permittivity, $\chi^{(3)}$ is the third-order susceptibility tensor of molecules. The $\chi^{(3)}$ specifies material property, and results in the activation of EFISHG signal, accordingly. As the result, we can probe carriers in a selected layer of multilayer device. In the measurement, we used a probing light with a wavelength of 820 nm (SHG wavelength, 410 nm), and probed electric field formed in the α-NPD layer [2]. The carrier Q_s accumulated at the interface is a source of the electrostatic field $\vec{E}_0$. In a double-layer device, $E_0 = |\vec{E}_0|$ is

$$E_0 = \frac{1}{d_i}\frac{Q_s}{C_1+C_2}\ , \qquad (2)$$

where d_i and C_i is the thickness and capacitance of a layer (i=1, 2 for α-NPD and Alq3), respectively.

The carrier Q_s is thermally de-trapped at the interface, on following the rate equation [5-7]

$$\frac{dQ_s}{dt} = -\frac{Q_s}{\tau}, \qquad (3)$$

with $\tau = \nu^{-1}\exp(H/kT)$, and $T = T_0 + \beta t$

Here ν is an attempt to escape frequency, H is an activation energy for carriers being de-trapped, k is Boltzmann constant, T is temperature ($T = T_0$ at t=0), β is a heating rate. Analysis of Eq. (3) shows that de-trapping process is mainly activated at the temperature T_d given by [5]

$$\nu^{-1}\exp(H/kT_d) = \frac{kT_d^2}{\beta H} \qquad (4)$$

Eq. (4) is not trivial to solve, and it is known that H [eV] is approximately given as a linear function of T_d as [9]

$$H = \left[1.92\log_{10}\frac{\nu}{\beta} + 3.2\right] \times 10^{-4} T_d - 0.015 \qquad (5)$$

Using Eq. (5), trap energy H is evaluated by measuring temperature T_d.

3. Results

We measured de-trapping process of holes in IZO/α-NPD/Alq3/Al double-layer OLEDs (see Fig. 1). The OLED samples were prepared using vacuum evaporation technique. The thickness of α-NPD/Alq3 layer was 50 nm/50 nm and active device area was 3.1 mm^2. The trap-filling and de-trapping processes were designed as illustrated in Fig. 2a-c. A positive external voltage (V_b=+12 V) was applied to the IZO electrode in reference to the Al electrode grounded at room temperature (T_b=+293 K). The OLED emits green light due to recombination at Alq3 molecules (Fig. 1b), while excess holes (~10^{-7} C/cm^2) is being accumulated in a manner as we reported previously [2]. Then OLEDs were quickly cooled to T_0=100 K. After that, we electrically connected the IZO and Al electrodes to short-circuit the OLED, and heated the sample. During the heating, de-trapping process is expected to be activated at a temperature T_d satisfying Eq. (4). Figure 2d shows the EFISHG measurement during heating. The solid curve is measured after voltage application at V_b=+12 V, and dotted curve is measured without voltage application V_b=0 V. For V_b=+12 V, holes accumulated at the sample, and they were de-trapped at T_d=280 K. Using Eq. (5) with β=2 K/min, ν=10^{12} s^{-1}, activation energy H=0.49 eV was obtained for holes trapped at the α-NPD/Alq3 interface.

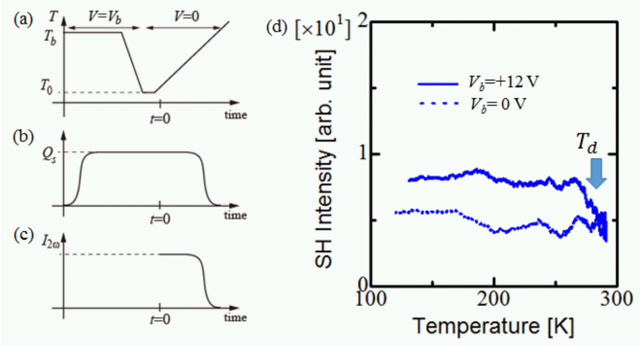

Figure 2: Experimental sequence for the modified EFISHG measurement. (a) External voltage, (b) excess carriers trapped at α-NPD/Alq3 interface, (c) Expected EFISHG signal during thermal heating. (d) EFISHG result during heating: V_b=+12 V (solid curve) and V_b= 0 V (dotted curve).

4. Conclusions

We modified our EFISHG system to analyze carriers energetically. The system was used to measure energy state of holes accumulated at the double-layer interface of IZO/α-NPD/Alq3/Al OLEDs. During heating, we probed the change of EFISHG response, due to de-trapping of holes, and determined the trap depth as 0.49 eV. We conclude that the system is useful for analyzing energy state of carriers in thin film electronic devices.

Acknowledgements

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