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Detection of Pre-electrical Breakdown of IZO/α-NPD/Alq3/Al Light-emitting Diodes by Electric-field-induced Optical Second-harmonic Generation Measurement

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Abstract

By using the electric-field-induced optical second-harmonic generation (EFISHG), we measured the EFISHG-time (EFISHG-*t*) characteristics to study pre-electrical breakdown of indium-zinc-oxide (IZO)/ N,N'-di [(1-naphthyl)-N,N'-diphenyl]-(1,1'-biphenyl)- 4,4'-diamine (α-NPD)/ tris(8-hydroxy-quinolinato)aluminum(III) (Alq3)/Al organic light-emitting diodes (OLEDs). A series of EFISHG pulses were identified as a pre-electrical breakdown phenomenon, before OLEDs were electrically broken. Analyzing the results revealed the additional negative charge accumulation at the α-NPD/Alq3 interface which caused by the generation of EFISHG pulses. We concluded that the EFISHG-*t* measurement is available as a method for detecting

pre-electrical breakdown phenomena of OLEDs.

1. Introduction

Organic light-emitting diodes (OLEDs) are being intensively studied for practical use as displays in electronics [1], where device life time is one of main research subjects. A variety of mechanisms that govern the life time have been proposed, on the basis of luminescence-time (*L*-*t*) characteristics [1, 2], optical-microscopic observation, and so forth. In the field of electrical insulating engineering, “Electro-luminance (EL)” from non-luminescence insulators is well-known as one of pre-electrical breakdown phenomena [3-5], and the detection of this EL is used to estimate the life time of insulating layers of power cables [6-10]. Noteworthy that the EL emission from non-luminescence insulators, e.g., polyethylene, is very weak, but the EL emission spectra evidently reflect the presence of carrier traps, which are energetically distributed and can be origins of space charge field formation. As a result, probing spectroscopic EL emission from insulators being subjected to an external electric field is helpful to identify the origins of electrical breakdown. Similarly, detection of such EL emission will be helpful to study “electrical breakdown of OLEDs” [11, 12], but ordinary emitted light from the EL materials of OLEDs is strong and the identification of such EL emission is quite a task. Actually, our previous study using indium-zinc-oxide (IZO)/ N,N'-di

[(1-naphthyl)-N,N'-diphenyl]-(1,1'-biphenyl)- 4,4'-diamine (α-NPD)/ tris(8-hydroxy-quinolinato)aluminum(III) (Alq3)/Al diodes showed that EL is generated from Alq3 layer via intrinsic EL process by applying AC voltages, but could not see any spectroscopic EL emission activated via interface states though the presence of interface charge accumulation at the double-layer interface was verified [13, 14]. Accordingly, it is necessary to find a way that is available for detecting pre-electrical break down phenomena. As a promising technique for the detection, we are paying attention to the electric-field-induced optical second-harmonic generation (EFISHG) measurement [15-19], which can directly probe carrier motions in OLEDs as well as interfacial charge accumulation in terms of charging and discharging via interfacial states [20-24]. In our previous paper, we observed carriers that are injected from electrodes and then conveyed to the interface states followed by charge accumulation, by applying a step AC voltage to double-layer EL diodes [25-27]. On the other hand, our interest here is charging and discharging into interface states during device operation, under applying DC voltage to EL diodes. Therefore, the trace of EFISHG-time (EFISHG-*t*) characteristics is our main interest.

In this study, using IZO/α-NPD/Alq3/Al OLEDs, we measured the EFISHG-*t* characteristics, and revealed that a series of EFISHG pulses is observed as a pre-breakdown phenomenon of the OLEDs. Analyzing the results showed that additional negative charge is accumulated at the

α-NPD/Alq3 interface, in prior to the electrical breakdown. We propose that the EFISHG-*t* measurement is available as a method for detecting pre-electrical breakdown phenomena of OLEDs.

2. Experimental methods

Figure 1(a) illustrates a device structure of IZO/α-NPD/Alq3/Al OLED used here. The diode was prepared by using the vacuum evaporation method. A glass substrate with patterned IZO electrodes was cleaned in a UV/ozone cleaning apparatus, onto which α-NPD, Alq3, and Al were deposited. The thickness of α-NPD layer and Alq3 layer was 50 nm, and the thickness of Al electrode was 100 nm. These prepared samples were encapsulated in a glass bottle with desiccant to avoid degradation. Figure 1(b) shows current-voltage (*I*-*V*) and EL intensity-voltage (*L*-*V*) curves of the prepared sample. These curves exhibit a typical diode-like behavior that well agreed to our previous study [17].

The EFISHG measurement was used for detecting carrier behavior related to the pre-electrical breakdown phenomena. Figure 1(a) illustrates optical setup for the EFISHG measurement which was the same as that used in our previous study [17]. A laser pulse generated from the third-order harmonic light of a Nd-doped yttrium aluminum garnet

(Nd:YAG) laser coupled with an optical parametric oscillator was used as an optical probe (average power 1 mW, repetition rate 10 Hz, duration 4 ns). The EFISHG intensity $I_{2\omega}$ radiated from the layer is given by [15-17]

$$I_{2\omega} \propto \left|\vec{P}_{2\omega}\right|^2 = \left|\varepsilon_0 \chi^{(3)} \vdots \vec{E}_0 \vec{E}_\omega \vec{E}_\omega\right|^2 = A|E_0|^2, \qquad (1)$$

where $\vec{P}_{2\omega}$ is the second-order nonlinear polarization, ε_0 is vacuum permittivity, $\chi^{(3)}$ is the third-order susceptibility tensor, $\vec{E}_0$ is a local DC field, and $\vec{E}_\omega$ is electric field of the laser pulse. In other words, EFISHG intensity is in proportion to the square of electrostatic field $\vec{E}_0$ with proportionality constant *A*. For the EFISHG measurement, the laser beam was *p*-polarized, and irradiated from the IZO electrode side at an incident angle of 45°. This optical arrangement allows electromagnetic coupling of the laser beam with local field $\vec{E}_0$ formed in film thickness direction of OLEDs. The wavelength of the laser beam was set at 820 nm (the wavelength of EFISHG at 410 nm) to selectively probe the electric field in the α-NPD layer [17]. At this wavelength, the EFISHG intensity from IZO, Alq3, and Al is negligibly small. The incident laser beam reflection by the OLEDs with a fundamental wavelength λ, i.e., with an angular frequency of ω was removed by using optical filters and a spectrometer, and only the EFISHG signals generated with an angular frequency of 2ω were collected by the photomultiplier tube (PMT). The EFISHG intensity was measured by using a digital multi-meter equipped with a gated integrator. The spot size of the laser beams irradiated on the OLEDs was about 100 μm in diameter, and was smaller than the active OLED device area (3.1 mm^2).

The electrostatic field E_0 $(= |\vec{E}_0|)$ in the α-NPD layer is described as sum of an external field by charges $\pm Q_m$ on electrodes and a space charge field formed by charges Q_s accumulated at α-NPD/Alq3 interface [17, 26]. That is, modeling the IZO/α-NPD/Alq3/Al diodes as a double-layer dielectric system, the electric field in the α-NPD layer is derived as

$$E_0 = \frac{Q_m}{\varepsilon_1 \varepsilon_0} - \frac{1}{d_1} \frac{Q_s}{C_1 + C_2}, \qquad (2)$$

where ε_1 is the relative dielectric constant of the α-NPD layer, d_1 is the layer thickness, and C_1 (C_2) is the capacitance of the α-NPD (Alq3) layer. The interfacial charge Q_s is the Maxwell-Wagner effect charge, and it is given as $Q_s = I(\tau_2 - \tau_1)$ in steady state. Here, I is a conduction current flowing across the double layer interface, and τ_1 and τ_2 are dielectric relaxation times of α-NPD and Alq3 layer, respectively [15, 28]. As described in our previous study [25], Q_m is the charge induced on electrodes due to electrode charging with a response time of τ_{RC} ~10^{-7} s, and the response time of interface Maxwell-Wagner-type charging is on the order of τ_{MW}= 10^{-3} s. By using the EFISHG intensity probed, we directly measured the electric field given by Eq. (2). Note that the EFISHG intensity was normalized to determine the electric field, using the response at t ~ t_{RC} in the time-resolved EFISHG measurement [25] as follows: in the time-resolved EFISHG measurement, we applied AC square voltage V (10 Hz) to the IZO electrode of OLEDs with reference to the Al electrode, and measured the EFISHG intensity as a function of delay time t_d with respect to the applied AC square voltage [25]. Two relaxations were observed in the EFISHG-time curves, corresponding to the electrode charging and the Maxwell-Wagner type charging. After the first relaxation due to electrode charging, charge $Q_m = CV$ ($C = \frac{C_1 C_2}{C_1 + C_2}$) is induced on electrode, and the electric field $E_{0,Qm}$ ($= \frac{Q_m}{\varepsilon_1 \varepsilon_0}$) given by the first term in Eq. (2) is formed. Consequently, the EFISHG intensity was nearly constant $I_{2\omega,Qm} \left(= A\left|E_{0,Qm}\right|^2\right) = A|\frac{CV}{\varepsilon_1 \varepsilon_0}|^2$, until the second relaxation due to the Maxwell-Wagner type charging was initiated. By using the linear relationship between the EFISHG intensity $I_{2\omega,Qm}$ and the electric field $E_{0,Qm}$, and the $I_{2\omega,Qm}$ and V, we normalized the EFISHG to estimate the electric field.

Our interest here is the detection of interfacial charging whilst the IZO/α-NPD/Alq3/Al OLED is being operated with DC biasing voltage. Therefore, we are monitoring the EFISHG with elapsed time (EFISHG-*t*), under application of DC voltage. On the other hand, Q_s will change with time due to interfacial charging which is relevant to pre-electrical breakdown. However, this charging happens occasionally. In other words, Q_s is supposed to change as $Q_s + Q'_s\delta(t - t_i)$. Here, t_i is the time when interfacial charging happens due to pre-electrical breakdown. As such, we could see the generation of positive EFISHG pulse at $t = t_i$ in the EFISHG-*t* characteristics if Q'_s is negative, while the generation of negative pulse if Q'_s is positive [see Eqs.(1) and (2)]. In the EFISHG-*t* measurement, we applied a DC forward voltage of V = 25 V or 15 V to the IZO electrode with respect to the Al electrode grounded, and monitored the EFISHG-t characteristics. Results showed totally different electrical breakdown behaviors for V = 25 V and 15 V; the OLEDs were electrically broken-down within 15 min under DC voltage application of 25 V, whereas the OLEDs were not electrically broken for more than 1 hour under the voltage of 15 V. To clarify the electrical breakdown behaviors, we also recorded currents flowing across the OLEDs and the EL intensity generated, during the EFISHG-t measurement.

3. Results and discussion

Figures 2(a) and 2(b) show the current and EL intensity after applying DC voltage at t = 0, respectively. Results showed that the current and EL intensity decayed shortly and almost saturated at t = 50 s, and suddenly EL emission stopped at around t = 800 s due to electrical breakdown. Note that optical microscope observation showed traces of discharge path on the IZO electrode after the electrical breakdown, indicating that the organic layer was destructively broken. Until the time OLED was electrically broken down, the current and EL were stable, and no signal relevant to the pre-electrical breakdown was seen. On the other hand, Fig. 2(c) displays the EFISHG intensity with time after the DC voltage application. The magnitude of

EFISHG intensity is nearly constant, but a series of positive EFISHG pulses is seen at time $t = t_i$ (380, 510, 600, 650 s) as indicated by arrows. After DC voltage was applied to the OLED, electrode charging and interfacial charging proceed in a short time (<10^{-3} s), and made balance for electron-hole recombination with EL. As the result, EFISHG intensity is constant during the EL is generated. The appearance of additional positive EFISHG pulses revealed that electrons occasionally injected to interface states at the α-NPD/Alq3 interface. That is, the charging related to pre-electrical breakdown phenomena is seen. The electric field change $\Delta \mathrm{E}_0$ at the EFISHG pulse was about 1.0 MV/cm and this field corresponds to the electrical breakdown strength of many of organic materials [29, 30]. Further, using the relation $\Delta E_0 = -\frac{1}{d_1}\frac{Q'_s}{C_1+C_2}$ (d_1=50 nm, C_1=5.5×10^{-8} F/cm^2, C_2=7.4×10^{-8} F/cm^2), the electron density was calculated as Q'_s= -6.7×10^{-7} C/cm^2. Taking account of these results, we argue carrier processes which lead to electrical breakdown as follows: in steady state, holes are accumulated at the α-NPD/Alq3 interface to make balance electron-hole recombination, in a manner as we reported previously [23], and electrons additionally but occasionally injected to the interface states that are relevant to electrical breakdown. Figure 3 shows the results of the EFISHG-*t* measurement under the DC voltages 25 V and 15 V. We can see that the spike-like EFISHG signals are produced from OLEDs for *V* = 25 V. On the other hand, the EFISHG-*t* of OLEDs for *V* = 15 V is nearly constant and spike-like EFISHG pulses never appear. As mentioned in Sect. 2, the OLEDs for 25 V were electrically broken down shortly after the DC voltage application, whereas the OLEDs for 15 V were free from electrical breakdown over 1 hour. These results also support our argument that a series of pulse-like EFISHG is an identification of pre-electrical breakdown phenomenon of OLEDs. Noteworthy that the EL spectrum never changed until the EL emission suddenly stopped due to electrical breakdown. That is, the EL due to normal electron-hole recombination is remarkable, making difficult to analyze the electron injection into interface states in terms of electrical breakdown. On the other hand, the EFISHG measurement is a promising method that is available for directly probing pre-electrical breakdown phenomena in OLED devices. Finally we should note that we carried the same experiments by using other samples, and similar results were obtained. Therefore, we can carry the above discussion on the experimental results of EFISHG without loss of generality.

4. Conclusions

By using the EFISHG-*t* measurement, we revealed the electron injection to interface states relevant to electrical breakdown of double-layer (IZO/α-NPD/Alq3/Al) OLEDs. After DC voltage was applied, holes accumulated at the α-NPD/Alq3 interface to make carrier balance for electron-hole recombination, while electrons additionally injected to interface states that trigger electrical breakdown. In conclusion, EFISHG measurement is available as a method for detecting carrier behavior as a pre-electrical breakdown phenomenon.

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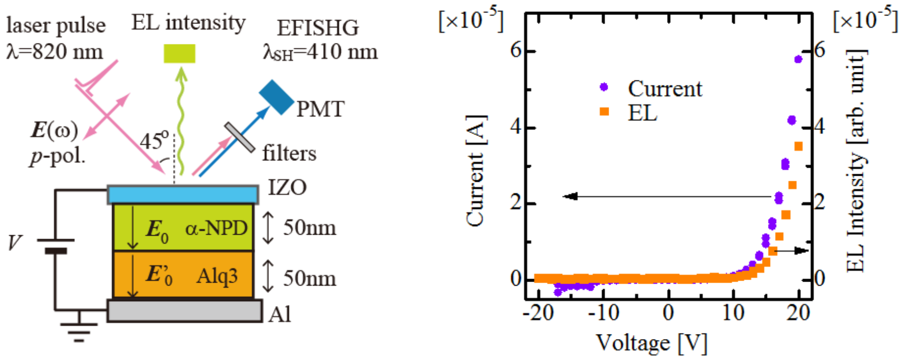
Figure captions

Fig. 1: (a) Optical arrangement of the EFISHG measurement and IZO/α-NPD/Alq3/Al OLEDs. (b) Current-voltage and luminance-voltage curves of the OLED.

Fig. 2: (a) Current, (b) EL intensity, and (c) EFISHG intensity (EFISHG-*t*) after DC voltage (V = 25 V) was applied to the OLED at t = 0. Arrows “a”-“d” in the Fig. 2(c) indicate EFISHG enhancement due to unstable electron accumulation. See the text for details.

Fig. 3: EFISHG-*t* measurement under voltage application V=15 V and 25 V to IZO electrode in reference to Al electrode grounded. Arrows “a” and “b” correspond to the peak-like EFISHG signals in Fig. 2(c).



(a) (b)

Figure 1: D. Taguchi et al.

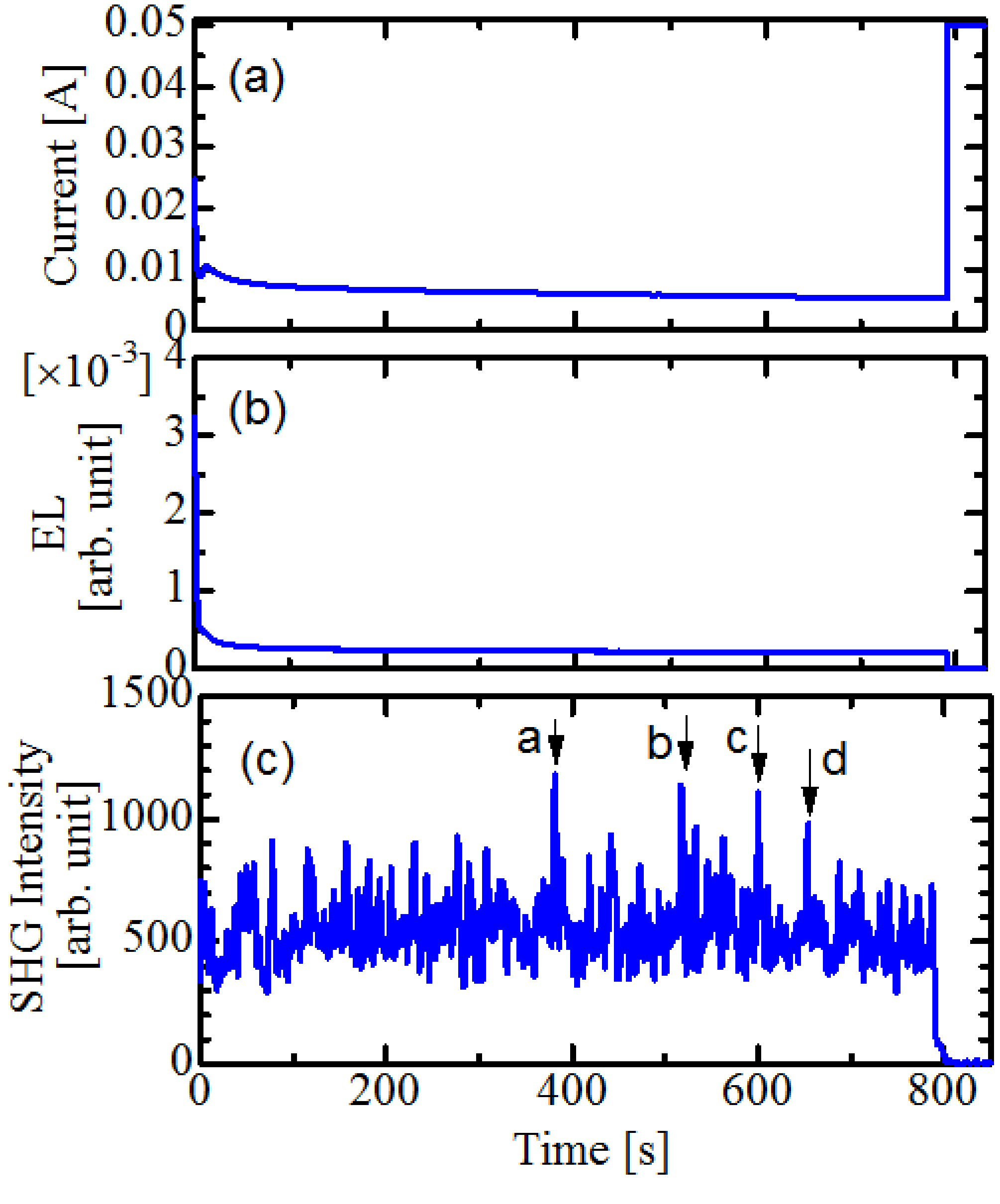


Figure 2: D. Taguchi et al.

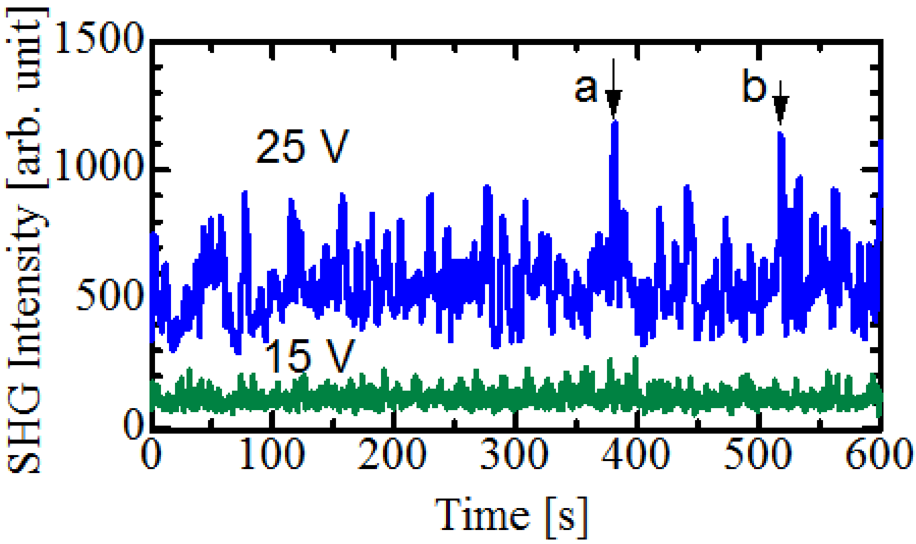


Figure 3: D. Taguchi et al.