Quantification of temperature rise in unipolar organic conductors during short voltage-pulse excitation using electrical testing methods

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A B S T R A C T

To quantify the rise in device temperature caused by Joule heating during short voltage-pulse excitation at high current densities (>10 A/cm^2), the device temperatures of unipolar organic conductors were measured using electrical testing methods. For a maximum voltage amplitude of 59 V at a current density of ~300 A/cm^2, temperature rose over 145 °C within a pulse duration of 5 μs in an N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD)-based single-carrier organic conductor. This result is in reasonable agreement with numerically calculated values. These findings indicate that suppressing the effects of Joule heating by carefully adjusting pulse width, substrate and organic materials, and device configuration is important to achieve further carrier injection in the ultra-high current density region (>1 kA/cm^2).

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1. Introduction

The realization of electrically-pumped organic semiconductor laser diodes (OSLDs) is highly desired since OSLDs have the potential for low-cost fabrication and flexible tuning of their lasing wavelength [1]. Thus, they can be applied as alternative light sources for applications such as data communications, compact chemical sensors, and spectroscopic measurements of biological systems. Despite recent intense research on organic semiconductors, OSLDs still have yet to be realized [2—4]. To achieve lasing action in an organic semiconductor, the accumulation of a large number of excitons in an organic gain media to attain population inversion is required. Thus, under electrical pumping, recombination of a large number of holes and electrons injected at high current densities (J) is necessary [1]. However, during high J injection into the organic thin film, device breakdown often occurs because of a significant temperature rise caused by Joule heating.

To achieve high J without device breakdown, short operation times are commonly used by applying square-voltage pulses with short pulse widths ($\tau_P < 10$ μs), i.e., pulse-voltage operation [3—11]. Although heat generation is expected to be minimized under short pulse-voltage operation, Joule heating during short pulse operation was found to affect J and external electroluminescence (EL) quantum efficiency in organic light-emitting diodes (OLEDs) in our previous study [12]. In addition, the OLED response was observed to depend on the thermal conductivity (k) of the substrates. Based on these results, an increase of J during device operation was concluded to originate from an increase of device temperature and subsequent enhancement of charge carrier mobility (μ). However, the temperature change (ΔT) under very high J has not yet been quantified.

There are several studies reporting the measurement of ΔT in OLEDs during device operation. While some groups have directly examined ΔT in OLEDs using an infrared camera [13,14], others have used methods such as Raman spectroscopy [15,16] and analysis of the temperature dependence of the EL spectrum [17]. In particular, L. Y. Bing et al. proposed a technique for evaluating ΔT in OLEDs by using the temperature dependence of electrical conduction [18]. However, they only examined ΔT in the low J (< 10 A/cm^2) region with long τ_P (several seconds), and ΔT at higher J (> 10 A/cm^2) with short pulse widths ($\tau_P < 10$ μs) has not been deeply studied. Such an investigation is very important for the basic understanding of the effect of Joule heating on carrier transport behavior in organic semiconductors and the realization of OSLDs.

In this study, the time evolution of ΔT during the application of square voltage pulses with various pulse amplitudes (V_P) and fixed

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τ_P of 5 μs is examined by using the temperature dependence of the current-density–voltage (J–V) characteristics. The validity of the results are discussed by comparison with numerically calculated values.

2. Experimental

In this study, unipolar organic conductors, *i.e.*, hole-only devices, were investigated [19] using the device structure in Fig. S1. First, following a standard cleaning procedure and UV/ozone treatment, chromium (Cr, 5 nm) and Au (200 nm) were deposited on glass substrates as electrodes to minimize the contribution of the wiring resistance (R_W) to total device resistance (R_{tot}), which is the sum of the active layer resistance (R_D) and the R_W originating from our device architecture as discussed in a previous report [12]. As shown in Fig. S2, the R_W estimated from a device excluding the organic layer was negligible compared to R_{tot} for complete devices. Next, the device active area was precisely defined to a diameter of 226 μm using an insulating photoresist layer (Toray Industries, Inc., DL-1000) coated on the anode layer and patterned by a conventional photolithography technique [20]. For efficient hole injection, a layer of molybdenum trioxide (MoO$_3$) with a thickness of 0.5 nm was then evaporated on the Au surface. Next, a neat *N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine (α-NPD) layer with a thickness of 200 nm was deposited as the active layer. Subsequently, a 10-nm-thick neat layer of MoO$_3$ was deposited as an electron block-ing layer. Finally, an Al electrode with a thickness of 100 nm was deposited as the cathode. During the evaporation processes, the vacuum pressure was kept below 10^{-3} Pa. The film thicknesses were monitored during deposition using quartz crystal microbal-ances, and the evaporation rates were about 0.1–0.3 nm/s. All of the devices were encapsulated in a dry nitrogen atmosphere shortly after fabrication.

The J-V characteristics were measured in a vacuum chamber equipped with a temperature controller. In the chamber, device temperature (T_D) was adjusted by changing the temperature of the sample stage (T_S), which was in contact with the glass side of the device substrate. A high thermal conductivity grease with $k = 0.126$ W/cm °C (Jou Jye computer GmBH, Nano diamond grease OverClock7) was used between the sample stage and device sub-strate for good thermal contact. Using this setup, T_S could be varied from −120 °C to 25 °C. For pulsed operation, a wave function generator (NF, WF1974), a high speed amplifier (NF, HSA4101), and an oscilloscope (Agilent, DSO5034A) were used. During the mea-surements, V_P was varied to investigate the heat generation effects. The J flowing through the device was obtained from the voltage drop (V_S) across a termination resister ($R_S = 95$ Ω) connected in series with the device using the relationship $J = V_S/(S \times R_S)$, where S is the device area, *i.e.*, $S = 4 \times 10^{-4}$ cm^2. The voltage drop across the device active layers (V_D) was obtained by subtracting V_S from V_P, *i.e.*, $V_D = V_P - V_S$. During the experiments, transient J was found to exhibit a time dependency because of heat generation. To eliminate cumulative heat effects and device degradation [17], the pulse repetition rate was kept low (<1 Hz). In addition, for better statis-tics, J-V_D characteristics were obtained by averaging several points around each time t_P after pulse voltage application, as explained later.

To check the validity of the experimental data, numerical cal-culations were performed using the numerical calculation software Marc®. For the calculations, layers of glass, Au, α-NPD, and Al, with thermal conductivities (k), specific heat capacities (C), and densities (ρ) as summarized in Table 1 [21–26], were stacked in a cylindrical shape with radii of 200 μm and thicknesses (d) of 100 μm, 200 nm, 200 nm, and 100 nm, respectively. Here, the d of the glass substrate was reduced compared with its actual thickness ($d = 700$ μm) to

reduce calculation time. Because of the short τ_P examined here, only a small fraction of the substrate should contribute to the heating phenomenon (<10 μm from the Au surface along the axis normal to the substrate surface; see Fig. S3). Thus, the reduction of d for the glass substrate should be reasonable. However, we note that, for higher k substrates or longer τ_P, larger or actual d values must be used. In addition, the MoO$_3$ and Cr layers were eliminated because their thermal properties could not be obtained and their thicknesses are small compared with the other layers ($d \le 5$ nm). The temperature dependencies of k, C, and ρ were ignored because of a lack of complete data for all of the used materials.

For the Au, α-NPD, and Al layers, each layer was divided into 200×100 parts along the directions parallel and perpendicular to the substrate surface, respectively. On the other hand, the glass substrate was divided into 200×1000 parts along the directions parallel and perpendicular to the substrate surface, respectively, considering its larger thickness compared to other layers. Heat sources were placed in the organic layer filling a 113-μm radius from the center axis to reproduce the heat generation during the operation and simulate the thermal diffusion in a direction parallel to the substrate surface, *i.e.*, to the region not under operation. Here, for simplicity, we assumed Joule heating was produced only in the organic layer and with a uniform distribution. This assumption is discussed more in Section *3.5*. The production rate per unit volume of Joule heating in the device during the application of square voltage pulses (Q_{Joule}) was estimated by using Eq. (1):

$$Q_{Joule}(t) = \frac{J(t) \times V_D(t)}{d_{Org}}, \tag{1}$$

where $J(t)$ and $V_D(t)$ are the current density and device voltage at time t and d_{Org} is the thickness of the organic layer, 200 nm. Experimentally obtained $J(t)$ and $V_D(t)$ were used for the calcula-tions. Radiation with an emissivity of $\varepsilon = 0.04$ for Al and thermal convection to the atmosphere with a thermal convection coeffi-cient of 3×10^{-3} W/cm^2 °C from the top Al surface in vacuum were also considered. The initial temperature of all layers was set to −120 °C, which is the same as the experimental conditions.

3. Result and discussion

3.1. Principle of temperature measurements

Fig. 1 shows a schematic illustration of the method for transient temperature measurement using electrical conduction. The basic method is similar to electrical testing methods that were reported for not only inorganic LEDs [27] but also OLEDs [18]. First, J-V_D characteristics were measured at various T_S using square-voltage pulses with $\tau_P = 500$ ns and analyzed at probing times shorter than the pulse ($t_P < \tau_P$) to minimize ΔT increases during operation so that $T_D = T_S$ can be reasonably assumed. Next, at certain stage temperatures (T_{S-ini}), square-voltage pulses with various τ_P and V_P were applied to the device. During operation, J increases with time because of an increase of ΔT caused by Joule heating as mentioned earlier, leading to a decrease in V_D. By plotting $J(t_P)$ and $V_D(t_P)$ of the transient measurements with the T_S-dependent J-V_D characteristics measured with short τ_P of 500 ns, the transient device temperature $T_D(t_P)$ could be estimated for t_P where $J(t_P)$ and $V_D(t_P)$ fall on one of the T_S-dependent J-V_D characteristics as the corresponding T_S. Setting $T_D(0)$ to T_{S-ini} and plotting the estimated $T_D(t_P)$ against t_P, the time evolution of T_D during operation was obtained, with $\Delta T(t_P) = T_D(t_P) - T_{S-ini}$.

At high T_D (>+70 °C), enhancement of device degradation [28,29] or device failure [30,31] is expected, making accurate temperature dependencies of the J-V_D characteristics difficult to