PAPER *Special Issue on Recent Progress in Organic Molecular Electronics*

Study on the Conduction Mechanism of Organic Light-Emitting Diode Using One-Dimensional Discontinuous Model

Takuya OGAWA[†a)], ***Student Member***, **Don-Chan CHO**[††], **Kazue KANEKO**[†], **Tatsuo MORI**[†], ***and*** **Teruyoshi MIZUTANI**[†], ***Nonmembers***

SUMMARY We proposed the conduction mechanism of organic light-emitting diode (OLED) using a one-dimensional discontinuous model. We assumed that each emitting molecule corresponds to a hopping site according to the actual charge transfer between adjacent molecules. Both carrier mobility of Alq3 and barrier heights for each carrier were derived from experimental data. We calculate transient behavior of carrier, field, and exciton distribution. Both carrier injections assumed the Schottky injection. In the previous results, when we assumed that calculated current density fit the experimental one in the current density field curve, calculated light-emission intensity did not fit the experimental one in the light-emission field curve. Furthermore, the slope of the calculated light emission-field curve is too small to fit the experimental one. In the previous study, hopping distance was assumed to be 1 nm. In this study, it is assumed to be 1.7 nm. We consider that field dependence of electron injection is too weak to explain only the Schottky emission. When the electron injection is assumed to be both Schottky emission and Fowler-Nordheim emission calculated light-emission field as well as the current-density field curves were fit to the curve of each experimental characteristics.

key words: *organic light-emitting diode, hopping conduction, field distortion, carrier injection, Fowler-Nordheim emission*

1. Introduction

An organic light-emitting diode (OLED) using an organic fluorescent dyes as an emitting material is an emitting device. The device has many advantages: low operating voltage, low power consumption, flat shape, light weight, wide angle view, short response time, and so on. Therefore, OLED displays will increasingly take the place of liquid-crystal displays. Device performance progress has been remarkable since the first report of the Tang and Vanslyke [1]. In Japan, OLED is used as a color display for mobile phones in 2001.

Although the structure of the device in which organic layers are sandwiched between two electrodes is simple, light-emitting mechanisms of the device are quite complicated. These mechanisms may be roughly divided into three processes: the carrier injection process from each electrode, the carrier transport process, and the emission process via excitons generated by electron-hole recombination. For example, many researchers tried to explain the carrier injection mechanism of OLED from the viewpoint of experimental current-voltage characteristics. However, such external information is insufficient to explain the injection mechanism. Clarification of each process will ease improvement of current performance of the device.

When we improve on the device performance, it is important to discuss the balance between electron and hole injections. Rate of electron-hole recombination, field, and space-charge distributions in the device are also important. However, it is impossible to obtain and evaluate these parameters experimentally because these parameters are "internal" OLED parameters. In the present work, we assumed a simple model and attempted to calculate carrier behavior in OLED devices in order to clarify OLED light-emitting mechanisms.

2. The Model of Simulation

Many groups have attempted to simulate I-V characteristics of devices [2], [3]. Calculations were carried out using a "continuous model" in which conduction current density is explained by carrier drift and carrier diffusion. Davids et al. assumed that initial hole distribution followed Maxwell-Boltzmann statistics [2]. They treated only holes. However, Tsutsui et al. pointed out that the main factor of current in organic film is not always an equilibrium carrier density [4]. In general, space-charge-limited current (SCLC) is used to explain conduction of organic thin films such as OLED. In this model, the injection field becomes zero, so that carrier density is infinite at the interface. However, this density never becomes infinite since sites are limited in organic films.

We proposed a one-dimensional discontinuous model for simulation as shown in Fig. 1. Simulation of carrier behavior in an insulator is based on the hopping model proposed by Iwamoto and Hino [5]. Although carrier density is not limited in continuous models, the carrier number accepted by a molecule is limited in our model. Because the carrier transport between organic molecules is regarded as an intermolecular redox re-

Manuscript received October 25, 2001.

[†]The authors are with the Department of Electrical Engineering, Nagoya University, Nagoya-shi, 464-8601 Japan.

[††]The author is with the Venture-Business Laboratory, Nagoya University, Nagoya-shi, 464-8603 Japan.

a) E-mail: t_ogawa@echo.nuee.nagoya-u.ac.jp

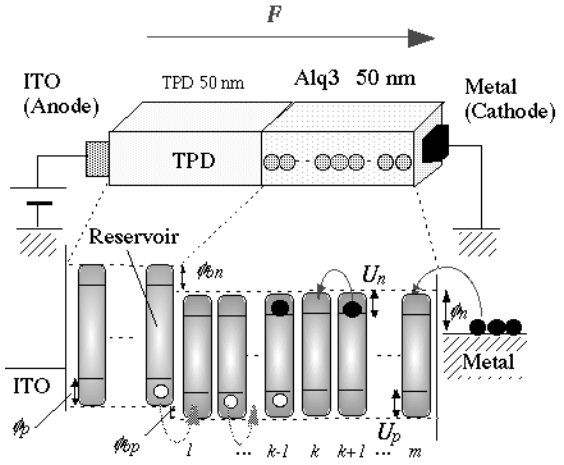


Fig. 1 One-dimensional hopping model.

action, our model approximates carrier behavior more accurately than conventional continuous models. In continuous models, the carrier number accepted by a molecule was not limited.

We assumed a bilayer OLED of ITO/TPD/Alq3/Al, where ITO, TPD, and Alq3 are indium-tin-oxide, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine, and hydroxyquinoline aluminum, respectively. Thickness of each organic layer is 50 nm. Since an Alq3 molecule is represented by a sphere of 0.8 nm diameter, we approximate that these molecules are arranged with average distance of 1.73 nm in an electric field. The number of sites is 30. Molecular stacking is not considered. Maximum carrier density per unit area is $10^{18}\,\mathrm{m}^{-2}$ $[(10^9)^2]$.

Most parameters obtained by experiments can be found in our previous papers [6]. The carrier conduction process is assumed as follows: (i) a molecule is a hopping site, (ii) a site can be occupied by an electron or a hole at most, (iii) carriers move only to adjacent sites, and (iv) the hopping rate depends on not only to carrier density, but also to the rate of unoccupied adjacent sites. Conduction currents from the kth site to the adjacent $(k+1)$th site for hole ($J_{p(k,k+1)}$) are represent as Eqs. (1)–(4).

$$\begin{aligned} J_{p(k,k+1)} &= \nu'_p q p_k \left[\frac{N-p_{k+1}-r_{k+1}}{N}\right] \exp\left[\frac{qaF_{(k,k+1)}}{2k_BT}\right] \\ &\quad - \nu'_p q p_{k+1} \left[\frac{N-p_k-r_k}{N}\right] \exp\left[\frac{-qaF_{(k,k+1)}}{2k_BT}\right] \\ &\quad (k=1,2,\ldots,m) \end{aligned} \tag{1}$$

$$\left(\nu'_p = \nu \exp\left[-\frac{U'_p}{k_BT}\right]\right), \tag{2}$$

and those for electron ($J_{n(k,k+1)}$) are

$$\begin{aligned} J_{n(k,k+1)} &= \nu'_n q n_k \left[\frac{N-n_{k+1}-r_{k+1}}{N}\right] \exp\left[\frac{qaF_{(k,k+1)}}{2k_BT}\right] \\ &\quad - \nu'_n q n_{k+1} \left[\frac{N-n_k-r_k}{N}\right] \exp\left[\frac{-qaF_{(k,k+1)}}{2k_BT}\right] \\ &\quad (k=1,2,\ldots,m-1) \end{aligned} \tag{3}$$

$$\left(\nu'_n = \nu \exp\left[-\frac{U'_n}{k_BT}\right]\right), \tag{4}$$

where N represents the maximum site density for a molecular layer ($=10^{18}$ m^{-2}); p_k, n_k, and r_k (m^{-2}) are densities of the hole, electron, and exciton of the kth site, respectively; $F_{(k,k+1)}$ is an electric field between the kth and $(k+1)$th sites; and U'_p and U'_n (eV) are hopping barriers for holes and electrons, respectively. Also, ν (s^{-1}) is the attempt-to-escape frequency; m shows site numbers for Alq3; and T, k_B, and q are temperature, the Boltzmann constant, and elementary charge, respectively. The hopping distance a is assumed to be 1.73 nm, which is the average distance between the two centers of adjacent molecules. U_p and U_n were calculated using the equation for conventional hopping transport from experimental carrier mobility, m_p, and m_n [7]. Electron mobility is about 100 times higher than hole mobility in Alq3; hole mobility in the TPD bulk is about five orders of magnitude higher than that in the Alq3 bulk [9]. We use U_p (0.27 eV) as U'_p and U_n (0.15 eV) as U'_n respectively in Alq3. At the TPD/Alq3 interface, U'_p and U'_n are $U_p+\phi_{bp}$ and $U_n+\phi_{bn}$, where ϕ_{bp} (0.26 eV) and ϕ_{bn} (0.83 eV) are barrier heights for the hole and the electron, respectively. Since ϕ_{bn} is so high that electrons are almost blocked at the TPD/Alq3 interface, electron behavior can be ignored in the TPD bulk. We use both Schottky emission and Fowler-Nordheim emission for electron injection from the cathode. Electron current density passing between the Alq3 and the cathode interface, $J_{n(m,m+1)}$, is assumed as

$$\begin{aligned} J_{n(m,m+1)} &= \left[\frac{N-n_m-r_m}{N}\right] \left[A_n T^2 \exp\left[\frac{-\phi_n}{k_BT}\right] \right. \\ &\quad \times \exp\left[\frac{q}{k_BT}\sqrt{\frac{qF_{(m,m+1)}}{4\pi\varepsilon_r\varepsilon_0}}\right] \\ &\quad \left. + \rho \frac{qF^2{}_{(m,m+1)}}{8\pi h\phi_n} \exp\left[\frac{-8\pi\sqrt{2m^*{\phi_n}^3}}{3qhF_{(m,m+1)}}\right]\right] \\ &\quad - \nu'_n q n_m \exp\left[\frac{-qaF_{(m,m+1)}}{2k_BT}\right], \end{aligned} \tag{5}$$

where ϕ_n (eV) is the barrier height for electron injection from the cathode to an Alq3 molecule and is estimated to be 0.67 eV, and A_n, ε_0, and ε_r are initial parameters based on the Richardson-Dushman constant for electrons, vacuum permittivity, and relative permittivity of

Alq3 bulk, respectively. Hole injection from an anode is assumed to be due to Schottky emission. The hole current density passing through the TPD/Alq3 interface, $J_{p(0,1)}$, is assumed to be the same at the ITO/TPD interface because a space charge density is negligible in the TPD bulk except for the site adjacent to the Alq3. Thus, the interface is assumed to be a hole reservoir as shown in Eq. (6). As holes are accumulated in the TPD site closest to the TPD/Alq3 interface, we can regard this site as a reservoir for holes. Hole density is represented as p_{res}, that is, $p_0 = p_{res}$ [8]. Therefore, the hole conduction current passing through the TPD/Alq3 interface is obtained by substituting p_{res} into Eq. (1):

$$\begin{aligned} J_{p(0,1)} &= \left[\frac{N - p_{res}}{N}\right] A_p T^2 \exp\left[\frac{-\phi_p}{k_B T}\right] \\ &\quad \times \exp\left[\frac{q}{k_B T}\sqrt{\frac{qF_{(0,1)}}{4\pi\varepsilon_r\varepsilon_0}}\right] \\ &\quad - \nu_p' q p_1 \left[\frac{N - p_{res}}{N}\right] \exp\left[\frac{-qaF_{(0,1)}}{2k_B T}\right]. \end{aligned} \tag{6}$$

Barrier height, ϕ_{bp}, for hole injection from the TPD molecule to Alq3 is estimated to be 0.26 eV. Current density flowing in an external circuit consists of the hole conduction component Eq. (7), and the electron conduction one Eq. (8), both of which are derived from the continuity equation under dc field, J_p is hole current density; $J_{p(0,1)}$, $J_{p(m,m+1)}$, $wJ_{p(0,1)}$ and the sum of $J_{p(k,k+1)}$ are hole current densities flowing in the TPD/Alq3 interface, the Alq3/Al interface, the TPD bulk, and the Alq3 bulk, respectively.

$$\begin{aligned} J_p &= \left[\frac{1}{2}\{J_{p(0,1)} + J_{p(m,m+1)}\} + wJ_{p(0,1)} \right. \\ &\quad \left. + \sum_{k=1}^{m-1}\{J_{p(k,k+1)}\}\right]. \end{aligned} \tag{7}$$

In the equation above, J_n is electron current density; $J_{n(0,1)}$, $J_{n(m,m+1)}$, and the sum of $J_{n(k,k+1)}$ are flowing the TPD/Alq3 interface, the Alq3/Al interface, and the Alq3 bulk. Electron mobility in the TPD bulk is very low and electron current is negligible.

$$\begin{aligned} J_n &= \left[\frac{1}{2}\{J_{n(0,1)} + J_{n(m,m+1)}\} \right. \\ &\quad \left. + \sum_{k=1}^{m-1}\{J_{n(k,k+1)}\}\right]. \end{aligned} \tag{8}$$

Here, w is the number of sites in TPD. Time variation of hole density is shown in Eq. (9) and that of electron density is shown in Eq. (10).

$$\frac{dp_k}{dt} = \frac{1}{q}\{-J_{p(k,k+1)} + J_{p(k-1,k)}\} - Rn_k p_k \tag{9}$$

$$\frac{dn_k}{dt} = -\frac{1}{q}\{-J_{n(k,k+1)} + J_{n(k-1,k)}\} - Rn_k p_k, \tag{10}$$

where R is an electron-hole recombination coefficient for Alq3 molecules. Fields are expressed as Eqs. (11)–(13), which are derived from the Poisson equation.

$$\begin{aligned} &F_{(k,k+1)} \\ &= \frac{-qa}{\varepsilon_r\varepsilon_0 d}\left[\sum_{s=1}^{k}\left(s - \frac{1}{2}\right)(p_s - n_s)\right] \\ &\quad + \frac{qa}{\varepsilon_r\varepsilon_0 d}\left[\sum_{s=k+1}^{m}\left(m - s + \frac{1}{2}\right)(p_s - n_s)\right] \\ &\quad - \frac{V_a}{d}, \end{aligned} \tag{11}$$

$$\begin{aligned} F_{(0,1)} &= \frac{-qa}{\varepsilon_r\varepsilon_0 d}\left[\sum_{s=k+1}^{m}\left(m - s + \frac{1}{2}\right)(p_s - n_s)\right] \\ &\quad - \frac{V_a}{d}, \end{aligned} \tag{12}$$

$$\begin{aligned} F_{(m,m+1)} &= \frac{-2qa}{\varepsilon_r\varepsilon_0 d}\left[\sum_{s=1}^{m}\left(s - \frac{1}{2}\right)(p_s - n_s)\right] \\ &\quad - \frac{V_a}{d}, \end{aligned} \tag{13}$$

in those equations, d and V_a are thickness and applied voltage V_a of the device. When L is the length of exciton diffusion and τ is the fluorescence lifetime in Alq3, the diffusion coefficient, D, is shown by Eq. (14).

$$D = \frac{L^2}{\tau} \tag{14}$$

Time variation of exciton density is shown by Eq. (15).

$$\begin{aligned} \frac{dr_k}{dt} &= Rn_k p_k + D(N - p_k - n_k - r_k)\frac{d^2 r_k}{dk^2} \\ &\quad + Dr_k\frac{d^2}{dk^2}(N - p_k - n_k - r_k) - \frac{r_k}{\tau}. \end{aligned} \tag{15}$$

Electroluminescence (EL) intensity is assumed to be proportional to the sum of $Rn_k p_k$ in the Alq3 layer (k: from 1 to m),

$$EL \propto \frac{1}{\tau}\sum_{k=1}^{m} Rn_k p_k. \tag{16}$$

3. Results and Discussion

3.1 Carrier Behaviors

In this simulation, the carrier (electron and hole) distribution and field distribution as well as current density and EL intensity are calculated when DC step voltage

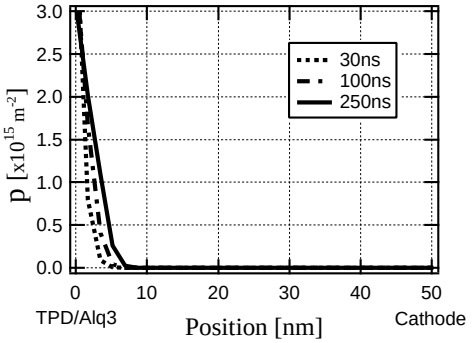


Fig. 2 Distribution of hole density.

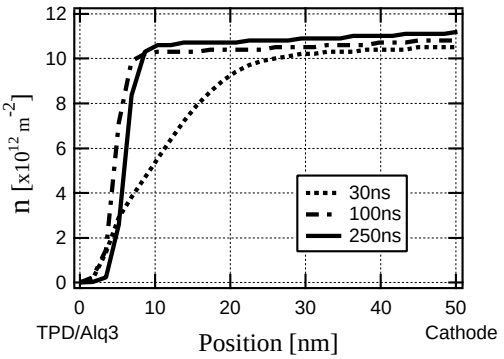


Fig. 3 Distribution of electron density.

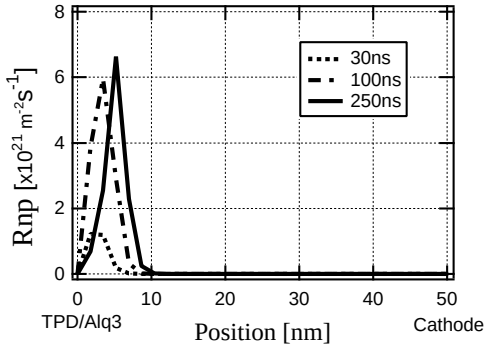


Fig. 4 Distribution of generated exciton density.

is applied.

Distributions of hole density, electron density, and exciton generation density are shown in Figs. 2–4, respectively. In these calculations, recombination rate, $R = 1.0 \times 10^{-5}\,\mathrm{m^2 s^{-1}}$, is used to calculate exciton generation distribution.

Holes are accumulated near the TPD/Alq3 interface, as shown in Fig. 2. Hole density decreases with distance from the TPD/Alq3 interface. Holes are accumulated within 10 nm distance from the interface (Fig. 2) because of low hole mobility in the Alq3 layer. In the emission layer (Alq3), electrons injected from a cathode move to the TPD/Alq3 interface. Electrons are comparatively uniformly distributed in Alq3 bulk

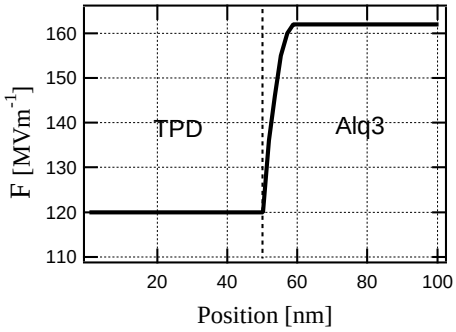


Fig. 5 Distribution of electric field at $F_a = 140\ \mathrm{MVm^{-1}}$.

($10 \leq$ position ≤ 50), and decrease near the TPD/Alq3 interface. Electron density near the TPD/Alq3 interface is lower than that near the cathode, as shown in Fig. 3. Distribution of hole density differs from that of electron density because electron mobility is 100 times faster than hole mobility in the Alq3 layer. Figure 4 shows distribution of generated exciton density after 30, 100, and 250 ns. Exciton generation due to recombination occurs near the TPD/Alq3 interface. Distribution of exciton generation depends on the product of hole and electron densities. The electron density rapidly decreases near the interface because of the recombination of electron and hole, resulting in generating excitons near the TPD/Alq3 interface. Exciton generation density achieves a maximum value and it moves from the interface with time. Since electron density is lower than hole density, all electrons are considered to recombine with holes before reaching the TPD/Alq3 interface.

Figure 5 shows the field distribution in both organic layers at an average field, $F_a = 140\,\mathrm{MVm^{-1}}$. Field distortion in TPD bulk is little observed at $F_a = 140\,\mathrm{MVm^{-1}}$ where OLED shows strong luminance over $600\,\mathrm{cdm^{-2}}$. Our one-dimensional discontinuous calculation model suggests that conduction in OLED cannot be explained by a typical SCLC conduction model since field distortion is not observed near both cathodes in organic layers.

3.2 Transient Response Characteristics

Figures 6 and 7 show calculated time dependence of current density and EL intensity at $F_a = 140\ \mathrm{MVm^{-1}}$. Hole current density, J_p, of 100 ns decreases until it reaches 90% of 30 ns. Since distribution of hole density spreads into the Alq3 bulk over time, as shown in Fig. 2, accumulation of electrons results in inducing field relaxation near the interface (Fig. 5). Also, the amount of injected electrons decreased. In 30 ns, electron current density is 90% of 100 ns and saturated. Thus, electron current density appears to be saturated after 100 ns. It has a turning point in 30 ns; after which EL begins to increase. Amounts of injected electrons and recombined electrons equalize due to exciton gener-

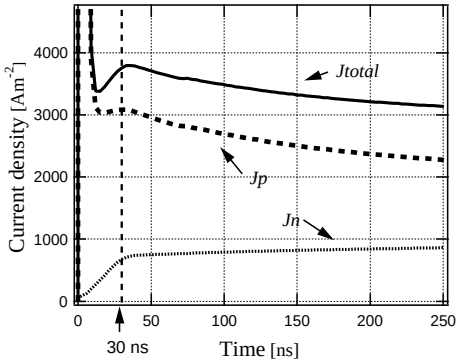


Fig. 6 Time dependence of current densities at $F = 140\,\mathrm{MVm}^{-1}$.

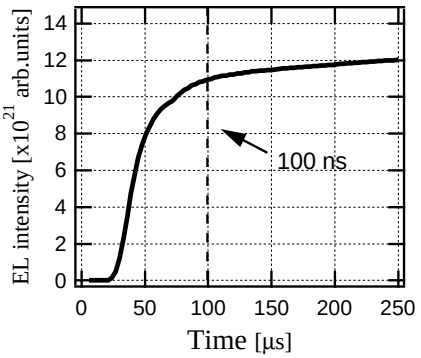


Fig. 7 Time dependence of EL intensity at $F_a = 140\,\mathrm{MVm}^{-1}$.

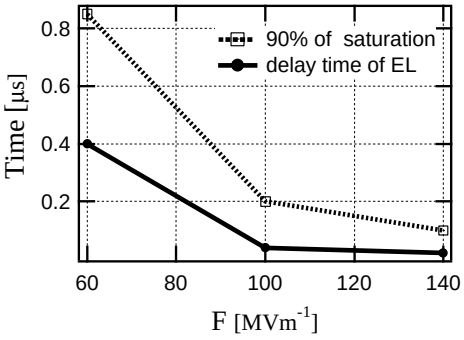


Fig. 8 Field dependence of delay time for luminance.

ation near the TPD/Alq3 interface. When an applied electric field is small, ($F_a < 100$ MVm^{-1}), the delay time of EL (solid line) and 90% of EL value at 250 ns (dashed line) is longer than when a high electric field is applied in Fig. 8.

3.3 Field Dependence of Current Density and Luminance

Figure 9 the calculated current densities flowing in an external circuit. The calculated current density normalized by the current density at F_a =100 MVm^{-1} are used to calculate at other F_a. The curves of calculated (solid line) agree to those of experimental (dashed line), as shown in Figs. 9 and 10. In our previous work, we considered only Schottky emission as electron injection mechanism. EL intensity did not agree with experimental values at low electric field although calculated density agreed with experimental data [11]. After considering both Fowler-Nordheim emission and Schottky emission into electron injection mechanism, Fowler-Nordheim emission is dominant in high fields, as shown in Fig. 11.

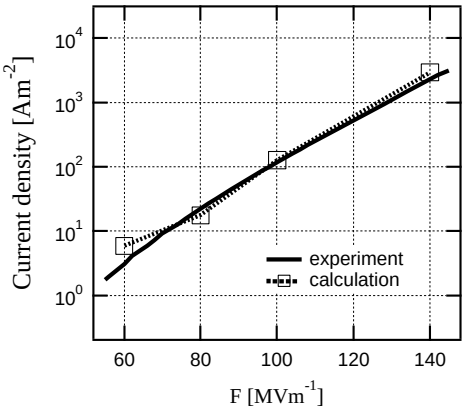


Fig. 9 Field dependence of current density.

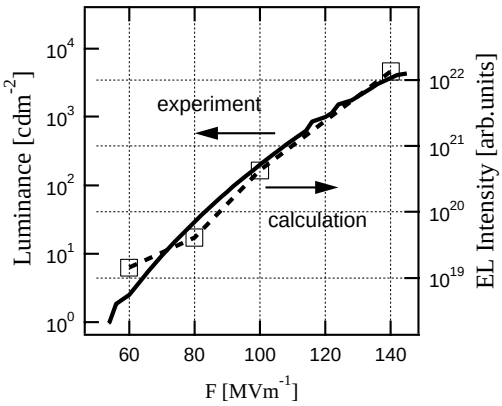


Fig. 10 Field dependence of luminance.

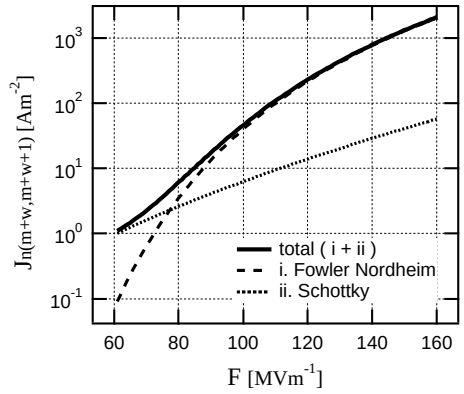


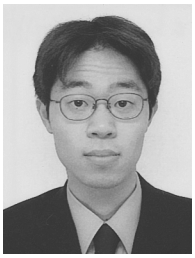
Fig. 11 Field dependence of electron injection.

4. Conclusions

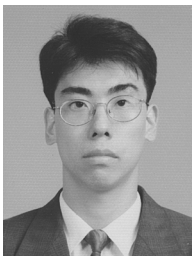
We assume a one-dimensional hopping conduction model for the OLED: each emitting molecule corresponds to a hopping site simulating actual charge transfer between adjacent molecules. Time dependence of carrier, exciton and EL intensity, and distributions of field and carrier density are calculated. Hole and electron densities decrease near the TPD/Alq3 interface. As a result, the density of exciton generation achieves its maximum within 10 nm from the TPD/Alq3 interface. Field distribution due to the space charge effect is not apparent in the TPD bulk. These results suggest that the conduction mechanism in bilayer OLED cannot be explained by a typical SCLC conduction model. This model accommodates Fowler-Nordheim emission as an electron injection mechanism. As a result, behavior of current density and EL intensity agree with measured current density and luminance. From above results, a simple bilayer and discontinuous model is effective for investigating OLED carrier behavior.

References

[1] C.W. Tang and S.A. Vanslyke, "Organic electroluminescent diodes," Appl. Phys. Lett., vol.51, p.913, 1987.
[2] P.S. Davids, I.H. Campbell, and D.L. Smith, "Device model for single carrier organic diodes," J. Appl. Phys., vol.82, p.6319, 1997.
[3] P.W.M. Brom, M.J.M. de Jong, and M.G. van Munster, "Electron and hole transport in poly (p-phenylene vinylene) devices," Appl. Phys. Lett., vol.68, p.3308, 1996.
[4] T. Tsutsui, C.P. Lin, and S. Saito, "Charge injection, transport, recombination and generation of neutral excitations in multilayer-dye electroluminescent diodes," Mol. Cryst. Liq. Cryst., vol.256, p.63, 1994.
[5] M. Iwamoto and T. Hino, "A method for the numerical analysis of the ionic transient current by hopping model and its application for the measurement of physical quantities," IEE Trans. Jpn. A, vol.100, p.291, 1980.
[6] T. Mori, K. Imaizumi, K. Kaneko, and T. Mizutani, "Analysis of EL mechanisms in TPD/Alq3 double layer organic light-emitting-diode by bipolar hopping conduction," Jpn. J. Appl. Phys., vol.41, no.1, p.366, 2001.
[7] R.G. Kepler, P.M. Besson, S.J. Jacobs, R.A. Anderson, M.B. Sinclair, V.S. Valencia, and P.A. Cahill, "Electron and hole mobility in tris (8-hydroxyquinolinolato-N1,O8) aluminum," Appl. Phys. Lett., vol.66, p.3618, 1995.
[8] K. Imaizumi, K. Kaneko, T. Mori, and T. Mizutani, "Simulation of carrier and exciton behavior with discontinouous model in doublelayer organic light-emitting diode," ISOME, p.13, Nagoya, Jpn, 2000.
[9] Y. Takeshita, S. Tokito, T. Tsutsui, and S. Saito, Rep. Prog. Polym. Phys. Jpn., vol.30, p.503, 1987.
[10] C. Hosokawa, H. Tokailin, H. Higashi, and T. Kusumoto, "Transient behavior of organic thin film electroluminescence," Appl. Phys. Lett., vol.60, p.1220, 1992.
[11] K. Imaizumi, K. Kaneko, T. Mori, and T. Mizutani, "Analysis of carrier behavior in organic light-emitting-diode by computer simulation on the basis of hopping conduction [2]," IEE Trans. Jpn. A, vol.121, p.337, 2001.

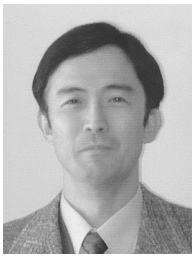


Takuya Ogawa was born on July 11, 1978. He received B.S. degree in Electrical Information Engineering from Nagoya University, in 2001. He is presently working toward the M.S. degree at Nagoya University, Japan. He is a member of the Japan Society of Applied Physics.

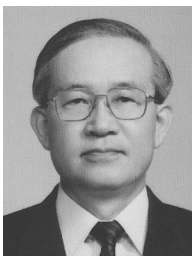


Don-Chan Cho was born on April 15, 1970. He received D.S. degree in Electrical Engineering from Nagoya University, in 2001. He is presently working a researcher of Venture Business Laboratory at Nagoya University, Japan. He is a member of the Japan Society of Applied Physics, the Institute of Electrical Engineers of Japan and the Institute of Electrical and Electronics Engineers.

Kazue Kaneko was born on September 1, 1951. She received B.S. degree in Physics from Nara Women's University, in 1974. She is presently working at Nagoya University, Japan. She is a member of the Institute of Electrical Engineers of Japan and the Japan Society of Applied Physics.



Tatsuo Mori was born on January 17, 1962. He received D.S. degree in Electrical Engineering from Nagoya University, in 1990. He is presently working as an associate professor at Nagoya University, Japan. He is a member of the Japan Society of Applied Physics, the Society of Polymer Science of Japan and the Institute of Electrical Engineers of Japan.



Teruyoshi Mizutani was born on May 9, 1941. He received D.S. degree in Electrical Engineering from Nagoya University, in 1969. He is presently working as a professor at Nagoya University, Japan. He is a member of the Japan Society of Applied Physics, the Society of Polymer Science of Japan, the Institute of Electrical Engineers of Japan and the fellow of the Institute of Electrical and Electronics Engineers.