Mitigation of Roll-off Property in OLED by Accumulated Electron Reduction at Emission/Electron-Transport Layer Heterojunction Interface

Masahiro Minagawa[†], Yusuke Tsuchida[†], Katsuya Takahashi[†],
Akira Takahashi[†]

Abstract The dependence on the roll-off property of carrier accumulation at the heterojunction interface between the emission layer (EML) and carrier transport layers was investigated in organic light-emitting diodes (OLEDs). The roll-off property was mitigated in an OLED having an indium tin oxide (ITO, 145 nm, anode)/40 wt%-molybdenum(VI) trioxide (MoO₃)-doped 9,10-diphenyl-anthracene (DPA, 30 nm)/DPA (10 nm)/5 wt%-5,6,11,12-tetraphenyl-naphthacene (rubrene)-doped DPA (40 nm)/DPA (20 nm)/14 wt%-cesium (Cs)-doped DPA (20 nm)/aluminum (Al, 100 nm, cathode) structure, although a conventional OLED having an ITO (145 nm, anode)/N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl)-4,4'-diamine (α -NPD, 20 nm)/5 wt%-rubrene-doped DPA (42 nm)/tris(8-hydroxyquinoline) aluminum (Alq₃, 20 nm)/lithium fluoride (LiF, 0.5 nm)/Al (100 nm, cathode) structure exhibited a typical roll-off property. This difference can be attributed to a decrease in the electron accumulation at the interface between the EML and electron transport layer (ETL), following a reduction in the distinct heterojunction structures at the interface in the OLED.

Key words: Organic Light-Emitting Diodes, Roll-Off Property, Carrier Accumulation, Exciton Annihilation.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted significant interest since the first report on high-intensity OLEDs was published by Tang *et al.* in 1987¹⁾. In recent years, several breakthroughs in both device structure^{2)–5)} and materials^{6)–8)} have led to significant improvements in OLED performance. However, a reduction in the roll-off property, which refers to the emission efficiency degradation in response to increased driving current density, is required for the development of high-brightness and high-efficiency applications. Previous reports have attributed this property to carrier accumulation at the heterojunction between the stacked organic layers in the devices^{9)–11)}. Moreover, the authors of these earlier studies have also suggested that the emission efficiency in an OLED decreases because the exciton energy in the emission layer (EML) is transferred to the carriers at the interface, once a sufficient number of carriers have accumulated at the heterojunction. Therefore, it is thought that the roll-off prop-

erty can be mitigated by reducing the number of carriers accumulating at the heterojunction interface in an OLED.

In this study, we investigated the underlying mechanism of the roll-off property by determining which type of carrier accumulation (holes or electrons) was dominant during a decrease in emission efficiency, and by determining the dependence of the emission efficiency on the interface structure at the EML and carrier transport layer heterojunction. Moreover, we also fabricated an OLED with no distinct heterojunction interface and then investigated its roll-off property.

2. Experimental Method

The fabricated OLED device structures are shown in **Fig. 1**. Device A (in Fig. 1(a)) is the reference device, with a structure of indium tin oxide (ITO, 145 nm, anode)/N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4'-diamine (α -NPD, 20 nm, hole transport layer (HTL))/5 wt%-5,6,11,12-tetraphenyl-naphthacene (rubrene)-doped 9,10-diphenyl-anthracene (DPA, 42 nm, (EML))/tris(8-hydroxy-quinoline) aluminum (Alq₃, 20 nm, electron transport layer (ETL))/lithium fluoride (LiF, 0.5 nm)/aluminum (Al, 100 nm, cathode). Further, we also fabricated Device B, shown in Fig. 1(b), in

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[†] Department of Electronic Control Engineering, National Institute of Technology, Nagaoka College
(Niigata, Japan)

order to investigate the relationship between the roll-off property and the interface structure of the EML/ETL heterojunction. Device B has an ITO layer (145 nm) as the anode; α -NPD (20 nm) as the HTL; 5 wt%-rubrene-doped DPA (42 nm) as the EML; 2,4,6-tripyrindyl-s-triazine (TPTZ) as the ETL (20 nm); a LiF layer (0.5 nm); and an Al layer (100 nm) as the cathode. We note that a TPTZ ETL has a higher electron affinity than one made of DPA or Alq₃. Moreover, we also fabricated an OLED having the structure ITO (145 nm)/ α -NPD (20 nm)/5 wt%-rubrene-doped DPA (42 nm)/Alq₃ (x nm, ETL1)/TPTZ (20 - x nm, ETL2) [which has a higher electron mobility than one of Alq₃]/LiF (0.5 nm)/Al (100 nm), as Device C, and we investigated the effects of the electron mobility of the ETL on the roll-off property mitigation by varying the thicknesses of the Alq₃ layer and the TPTZ layer. The following characteristics were measured for Devices A, B, and C: current density versus driving voltage (J - V), current density versus the external quantum efficiency (J - η_{ext}), and the electroluminescence (EL) spectrum. Here, the η_{ext} of an OLED is defined as

$$\eta_{\text{ext}} = \frac{N_p}{N_e} \times 100 \quad (\%), \quad (1)$$

where η_{ext} is the external quantum efficiency, N_p is the number of photons emitted from the OLED, and N_e is the number of carriers injected into the OLED.

Fig. 1 Schematics of OLEDs fabricated in this study. (a) Conventional OLED having stacked organic layers between the anode and cathode electrodes. Heterojunctions exist between each pair of organic layers. (b) OLED in which a tris(8-hydroxyquinoline) aluminum (Alq₃) layer was substituted for a 2,4,6-tripyrindyl-s-triazine (TPTZ) layer, in order to reduce the barrier height for electron transfer between the emission layer (EML) and electron transport layer (ETL).

Furthermore, we also fabricated Devices D1 and D2, which were OLEDs with no distinct heterojunction interfaces, and investigated their roll-off properties. Device D1 had an ITO (145 nm, anode)/40 wt%-molybdenum(VI) trioxide (MoO₃)-doped DPA (30 nm)/DPA (10 nm)/5 wt%-rubrene-doped DPA (42 nm)/Alq₃ (40 nm)/LiF (0.5 nm)/Al (100 nm, cathode) structure. This was specifically fabricated to investigate the relationship between the interface structure at the HTL/EML heterojunction and the roll-off property. Similarly, D2 had an ITO (145 nm, anode)/ α -NPD (40 nm)/5 wt%-rubrene-doped DPA (42 nm)/DPA (20 nm)/14 wt%-cesium (Cs)-doped DPA (20 nm)/Al (100 nm, cathode) structure, which was fabricated in order to investigate the relationship between the interface structure at the EML/ETL heterojunction and the resultant roll-off property. MoO₃ and Cs were used as dopants to aid carrier injection and transport in the DPA layers. The J - V and J - η_{ext} characteristics for Devices D1 and D2 were measured and compared with those for Device A. Each device was fabricated using a vacuum evaporation method, and all measurements were performed in darkness under a nitrogen atmosphere at room temperature. In addition, a homojunction OLED, having no heterojunction interface, was also constructed and evaluated.

3. Results and Discussion

The J - η_{ext} characteristics of Device A are shown in **Fig. 2(a)**. It is apparent that the efficiency decreased with increasing current density. According to some studies^{12)–16)}, the roll-off property mechanism may be explained by accumulated carriers at the heterojunction interface functioning as a polaron, and thus being conducive to exciton energy annihilation. This would then result in a decrease in emission efficiency [singlet-polaron annihilation (SPA)]^{10), 12), 17), 18)}. It has also been proposed that the roll-off property due to the SPA model could be described as

$$\frac{\eta_{\text{ext}}}{\eta_0} = \frac{1}{1 + (J/J_e)^{1/(m+1)}}, \quad (2)$$

where η_0 is the external quantum efficiency without SPA, J_e is the current density at an η_{ext} value equal to $\eta_0/2$, and m is the fitting parameter. The experimental properties of Device A, as illustrated in **Fig. 2(a)**, show an almost perfect fit with the SPA model at $m = 1.7$. Therefore, it is proposed that the SPA model describes the dominant roll-off property mechanism for Device A.

Further, the Device A emission spectrum, driven by a 1000-mA/cm^2 current density, is shown in Fig. 2(b). An emission peak and shoulder can be observed at approximately 560 nm and 600 nm, respectively, originating from the rubrene in the emission layer. In addition, low-intensity emission attributable to the Alq_3 layer, which was used as the ETL, can also be observed at approximately 510 nm, although a similar feature, attributable to the $\alpha\text{-NPD}$ layer, was not observed. Therefore, it is supposed that the emission zone expanded toward the ETL and that electron accumulation at the EML/ETL heterojunction interface is a dominant factor leading to the decrease in emission efficiency.

Figs. 3(a) and 3(b) show the J - V and J - η_{ext} properties for Devices A and B, respectively. Device B has a TPTZ-ETL, the electron affinity energy level of which is higher than that of the EML. Therefore, it is estimated

Fig. 2 (a) J - η_{ext} characteristics of Device A. The roll-off property in Device A agreed with the calculated characteristics, which were based on singlet-polaron annihilation (SPA). (b) Emission spectrum of Device A, driven by a current density of 1000 mA/cm^2 . Evidence of a small extra emission peak caused by the Alq_3 layer can be observed near a wavelength of approximately 510 nm.

that the number of accumulated electrons in Device B is smaller than that in Device A, resulting in the driving voltage reduction observed in Device B, as shown in Fig. 3(a). Further, mitigation of the roll-off property was observed in Device B at current densities greater than 100 mA/cm^2 , although η_{ext} decreased (as shown in Fig. 3(b)). It was not possible to fit the SPA model to the J - η_{ext} property in Device B. Hence, it is supposed that the influence of the SPA is decreased in Device B, and that the roll-off property can be mitigated by optimizing the structure at the EML/ETL heterojunction in the OLED. Further, the emission efficiency decreased at current densities below 100 mA/cm^2 . This behavior

Fig. 3 (a) J - V characteristics of Devices A and B. The driving voltage of Device B changed markedly such that it was less than that of Device A. (b) J - η_{ext} characteristics of Devices A and B. Mitigation of the roll-off property in Device B was observed, although the emission efficiency decreased.

was attributed to the fact that, at the current densities in the device, the numbers of electrons in the EML became larger than the number of holes as a result of substituting a TPTZ layer for an Alq₃ layer.

However, TPTZ layers are known to have higher electron mobilities than Alq₃ layers¹⁹⁾, and it is unclear whether it was the improvement of the interface structure at the EML/ETL heterojunction or the higher electron mobility in the ETL layer that was dominant in mitigating the roll-off property. Therefore, we also in-

vestigated the effects of varying the Alq₃ and TPTZ layer thicknesses on the roll-off property mitigation in Device C, as shown in the inset of **Fig. 4(a)**. **Fig. 4(a)** shows the J - V characteristics for these devices under variation of the ETL1 and ETL2 layer thicknesses ($x = 0, 5, 10, 15$, and 20 nm). The device with no Alq₃ layer (i.e., the device with $x = 0$ nm) exhibited a lower voltage compared to the other OLEDs. However, the J - V characteristics depended weakly on the thickness of the TPTZ layer but strongly on the structure of the interface between the EML and ETL layers. This may be because the electron transport energy barrier between the DPA and Alq₃ layers is decreased by the substitution of the TPTZ for the Alq₃, as TPTZ has a lower electron affinity (2.7 eV) compared to the Alq₃ layer (3.0 eV), and the number of accumulated carriers then decreases at the interface.

Fig. 4(b) shows the J - η_{ext} characteristics of the devices with different ETL1 and ETL2 layer thicknesses. It is apparent that these characteristics changed markedly when the thicknesses of the ETL1 and ETL2 layers were varied, and those characteristics exhibited poor fits with the SPA model. Therefore, it is supposed that the influence of the SPA decreases in Device C, except in the device with the 20-nm-thick Alq₃ layer (i.e., Device A). Further, it was observed that the device with the thinnest Alq₃ layer exhibited the lowest η_{ext} . This result is attributed to the fact that the carrier balance (i.e., the balance between the numbers of holes and electrons) will become uneven in the EML as a result of thickness variations of the ETL1 and ETL2 layers in the device. Furthermore, only the device having both an Alq₃ and a TPTZ layer (along with Device A) exhibited the typical roll-off property, although mitigation of the roll-off property was observed in the device with no Alq₃ layer (Device B) at current densities greater than 100 mA/cm^2 . This result is attributed to the fact that the roll-off property depended on the interface structure at the heterojunction between the EML and ETL.

The J - η_{ext} properties for Devices D1 and D2 are shown in **Fig. 5**. The device structures of D1 and D2 are also given in the inset. The roll-off property was observed in Device D1 (which had no distinct interface at the HTL/EML heterojunction), and its properties were similar to those exhibited by Device A. Actually, Device D1 showed a good fit with the SPA model. Reduction of the distinct heterojunction interface was expected to decrease the number of accumulated carriers

Fig. 4 (a) J - V characteristics of Device C having two kinds of ETL (ETL1 and ETL2). The device structure, ITO/ α -NPD (40 nm)/5 wt%-rubrene-doped-DPA (42 nm)/Alq₃ (x nm)/TPTZ (20 - x nm)/LiF (0.5 nm)/Al, is also shown in the inset. (b) J - η_{ext} characteristics of Device C having two kinds of ETL (ETL1 and ETL2). Mitigation of the roll-off property was only observed in the OLED with no Alq₃ layer.

Fig. 5 J - η_{ext} characteristics of Devices D1 and D2. Schematics of each device structure are also shown in the inset. Mitigation of the roll-off property was only observed in Device D2. However, the emission efficiency decreased, in a way that was similar to that seen in the results for Device B.

at the heterojunction interface. Therefore, the accumulated holes at the HLT/EML had a weak effect on the roll-off property. However, mitigation of the roll-off property was also observed in Device D2, which had no distinct interface at the EML/ETL heterojunction. Moreover, Device D2 showed a poor fit with the SPA model. Hence, we surmised that the roll-off property is mitigated because the number of electrons accumulated at the interface between the EML and ETL decrease in response to a reduction in the distinct heterojunction structures. However, the emission efficiency decreased at current densities below 100 mA/cm^2 . This behavior was attributed to the fact that the numbers of electrons in the EML became larger than the number of holes at the current densities as a result of doping the device with Cs. These results are supported by Fig. 4(b). Furthermore, the J - η_{ext} characteristics of Device D2 exhibited lower values of η_{ext} than those of Device A. This result is also attributed to the fact that the carrier balance will become uneven in the EML as a result of variations in the interface structure between the EML and ETL.

Therefore, we attempted to control an OLED structure having no heterojunction interface (that is, a homojunction OLED), in order to improve the roll-off property at the high current densities. **Fig. 6** shows the J - η_{ext} properties of both the homojunction OLED and Device A. The homojunction OLED we fabricated in this study has an ITO (145 nm)/40 wt%-MoO₃-doped DPA (30 nm)/DPA (10 nm)/5 wt%-rubrene-

Fig. 6 J - η_{ext} characteristics of Device A and the homojunction OLED. Mitigation of the roll-off property and improvement of the emission efficiency were observed in the controlled homojunction OLED.

doped DPA (42 nm)/DPA (20 nm)/14 wt%-Cs-doped DPA (20 nm)/Al (100 nm) structure, as shown in the inset of Fig. 6. It was found that the roll-off property was almost completely absent in the homojunction OLED. This result was attributed to the fact that the carrier accumulation was decreased by a reduction in the distinct heterojunction interface and, therefore, the influence of the SPA became small. Moreover, the emission efficiency was found to be higher than that of Device A at current densities greater than approximately 50 mA/cm^2 . This result was attributed to the fact that the carrier balance became even in the EML at those current densities as a result of the controlled concentrations of MoO₃ and Cs dopants in the device. However, a decrease of the emission efficiency was observed at current densities below approximately 50 mA/cm^2 . This was attributed to the fact that the carrier balance became uneven in the EML in this current density range, and the fact that the condition of the concentrations for the mitigation of the roll-off property was not appropriate for the improvement of emission efficiency at these current densities.

4. Conclusions

In this study, we investigated the dominant mechanism underlying the roll-off property in an OLED by attempting to mitigate this property. We found that the roll-off property depended on the interface structure between the EML and ETL in the heterojunction OLED. Further, the roll-off property depended weakly on the number of accumulated holes at the HLT/EML

interface but strongly on the number of accumulated electrons at the heterojunction interface between the EML and ETL. Moreover, we fabricated a homojunction OLED which had no distinct heterojunction between each pair of organic layers, and we investigated the effect of a reduction of the heterojunction interface for mitigation of the roll-off property. We found that the roll-off property could be mitigated by reducing the heterojunction interface, and the emission efficiency could be improved by controlling the concentrations of MoO₃ and Cs dopants in the homojunction OLED. However, it was also found that there was a trade-off between the mitigation of the roll-off property and the improvement of emission efficiency at low current densities in a homojunction OLED. Hence, we concluded that the homojunction OLED, which allows for a reduction in the number of accumulated carriers and control of the carrier balance in the EML, is an effective device for mitigation of the roll-off property, although solutions for improvement of emission efficiency at low current densities are necessary. The results obtained in this paper should be very useful for the development of a high-brightness OLED application.

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Masahiro Minagawa received M.E. and Ph.D. degrees in Electronic Engineering from Niigata University in 2000 and 2007, respectively. From 2001 to 2010, he worked at Nippon-Seiki Co., Ltd., studying durable OLED displays. He is currently an Associate Professor at the Department of Electronic Control Engineering, Nagaoka National College of Technology. Dr. Minagawa is a member of the Japan Society of Applied Physics.

Yusuke Tsuchida received an Associate Degree in Electrical Engineering from Nagaoka National College of Technology in 2012, and a B.E. degree from the National Institution for Academic Degrees and University Evaluation (NIAD-UE) in 2014. He is currently working at Nippon Seiki Co., Ltd. His research interests include the mitigation of the roll-off property in OLEDs.

Katsuya Takahashi received an Associate Degree in Electrical Engineering from Nagaoka National College of Technology in 2012, and a B.E. degree from the National Institution for Academic Degrees and University Evaluation (NIAD-UE) in 2014. He is currently working at Kuraray Co., Ltd. His research interests include the mitigation of the roll-off property in OLEDs.

Akira Takahashi received B.E., M.E. and Ph.D. degree in Information Engineering from Niigata University, Japan, in 1991, 1993, and 1997, respectively. He is now an Associate Professor at the Department of Electronic Control Engineering, Nagaoka National College of Technology, Japan. His current research interests are computer vision and artificial reality. Dr. Takahashi is a member of the Institute of Electronics, Information and Communication Engineers.