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Enhanced stability of organic light-emitting devices fabricated under ultra-high vacuum condition

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Abstract

Studies on the intrinsic degradation of organic light-emitting devices (OLEDs) based on tris(8-hydroxyquinolinolato) aluminum (III) (Alq_3) revealed that the operation stability of the OLEDs depends on the process pressure during device fabrication. Lowering of the pressure resulted in stable devices. In sharp contrast, differences in the initial device characteristics were marginal in all devices. Analyses with a quadrupole mass spectrometer indicated that the primary difference in the pressure during device fabrication was attributable to the amount of residual water. The results show that the degradation of OLEDs is associated with the electrochemical reaction of Alq_3 with water.

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1. Introduction

Organic light-emitting devices (OLEDs) are attractive for display applications. The efficiency and reliability of OLEDs have improved significantly over the years since Tang reported the efficient OLEDs based on tris(8-hydroxyquinolinolato) aluminum (III) (Alq_3) as an emitting material [1]. However, their operation lifetimes, thousands of hours, are sufficient only for a limited range of applications.

Degradation in OLEDs appears essentially in the form of a decrease in luminance in time. The degradation phenomena in OLEDs can be classified in three modes: dark-spot formation, catastrophic failure, and intrinsic degradation. Among these modes, intrinsic degradation, where the brightness of the emissive area of a device gradually decreases without any obvious change in device appearance, is the largest obstacle to be overcome for further expansion of the application range of OLEDs. A number of the degradation mechanisms have been proposed for Alq_3-based OLEDs, including migration of mobile ions [2], reorientation of molecular dipoles [3], formation of fluorescence quenchers by the cationic species of Alq_3 [4], and positive charge accumulation at the interface of a hole transport layer and Alq_3 layer [5]. It has also been proposed that Alq_3 would be decomposed by the reaction with H_2O at elevated temperature [6]. However, there has been no direct experimental evidence for the last mechanism in working OLEDs.

In general, OLEDs are fabricated by the vacuum deposition of organic layers and metal electrodes under high vacuum conditions, where the pressure ranges from 10^{-5} to 10^{-7} Torr. At this vacuum level, residual gas such as H_2O and O_2 may affect the device performance as traps for electron transport. It has indeed been reported that trap-free space charge limited current (SCLC) can be solely observed in the Alq_3-based “electron-only devices” fabricated under ultra high vacuum (UHV) conditions with great care [7]. This result suggests that intrinsic electric properties of Alq_3 can be seen in the device fabricated under UHV conditions.

In this letter, we report the stability of the Alq_3-based OLEDs fabricated under different pressures during device fabrication. Fabrication of devices under UHV condition brought about stable devices. We discuss the intrinsic degradation mechanism of the Alq_3-based OLEDs in terms of the electrochemical reaction of Alq_3 with water.

2. Experimental

Devices were fabricated on a glass substrate coated with indium–tin–oxide (ITO) electrode. The thickness of ITO was 150 nm and the sheet resistance was 8.2 V/sq. Devices consisted of copper phthalocyanine (CuPc) as a hole injection layer (HIL), *N,N'*-di-[(1-naphthaleyl)-*N,N'*-diphenyl]-1,1'-biphenyl-4,4'-diamine (α-NPD) as a hole transport layer (HTL) and tris(8-hydroxyquinolinolato) aluminum (III) (Alq_3) as emission and electron transport layers (EML and ETL). High purity materials of CuPc, a-NPD and Alq_3 were provided by Nippon Steel Chemical Co., Ltd. and were used without further purification. Thicknesses of the layers of CuPc, a-NPD and Alq_3 were 10, 50 and 65 nm, respectively. Lithium fluoride (LiF) and aluminum (Al) were used for cathodes. The use of a very thin LiF layer (0.5 nm) between the Alq_3 layer and the Al electrode enhances electron injection from Al to Alq_3 layer [8]. The fabrication procedure was as follows.

An ITO substrate in a load-lock chamber was transferred to a growth chamber, where the base pressure was set in the range of 10^{-7} to 10^{-9} Torr. All organic layers and cathode layers were successively fabricated by vacuum evaporation in the growth chamber. The base pressure was adjusted by the baking condition of the growth chamber. For instance, after the exposure to ambient atmosphere (23 °C, 13 % RH) for 10 h, the growth chamber was baked at 120 and 180 °C and was left for 12 h to cool the chamber. Pressure was measured with a cold cathode gauge (Pfeiffer Vacuum: IKR 270). The residual gas component was analyzed with a quadrupole mass spectrometer (ANELVA: AQA-360). Four pieces of ITO substrates were used in one experiment. Eight active devices were fabricated on the substrate, and the active area of the device was 2×2 mm^2.

Devices were characterized in a measurement chamber attached to the growth chamber. The base pressure of the measurement chamber was below 5.0×10^{-10} Torr when the devices were transferred to this chamber. The current density (J), voltage (V), and luminance (L) of the devices were measured with a source measure unit (Keithley 2400) and a luminance meter (Topcon, BM-9). A PC-base software for OLED characterization was kindly provided by Keithley Instruments K.K. Japan.

Stability measurements of OLEDs were performed in the measurement chamber filled with an ultra-high purity nitrogen ($O_2 < 0.1$ ppm, $H_2O < 0.5$ ppm) to be consistent with the measurement environment that has been generally achieved in the OLED community. No difference was observed in the initial J-V-L characteristics of the devices measured under UHV or a nitrogen atmosphere.

2. Result and discussion

Initial characteristics of devices

Table 1 summarizes the pressure and residual gas components observed during device fabrication. The base pressure was measured before heating evaporation sources. The process pressure and the residual gas components were measured during device fabrication. The process pressure was slightly higher than the base pressure for devices B and C because of the outgas from heated evaporation sources. Analysis of residual gas pointed out that the dominant gas components during device fabrication were water for device A, water/nitrogen for device B, and nitrogen for device C.

Figure 1 shows the initial *J*-*V*-*L* characteristics of the devices fabricated under different process pressures. As shown in Fig. 1(a), the *J*-*V* characteristics are almost identical such that the driving voltages at 10 mA cm^{-2} were within the range of 8.05 ± 0.15 V. Such a small variation in the voltage was observed among the eight devices fabricated on the same substrate. Figure 1(b) shows the *L*-*J* characteristics of the devices. All data are overlapped on a single line, suggesting that initial device characteristics are independent of the process pressure.

The transition from trap-controlled charge-limited current (TCLC) to trap-free space charge-limited current (SCLC) was observed in the Alq_3-based electron-only devices once the device was fabricated only under UHV condition [7]. In this study, we did not observe such an obvious difference in the *J*-*V* characteristics of the devices fabricated under different pressures. The major reason for this discrepancy is probably due to the difference in the device structure. For the electron-only devices, the *J*-*V* characteristics are mainly governed by the electron transport in the Alq_3 layer. On the other hand, the *J*-*V* characteristics of double-carrier injection devices are probably determined by a combination of three processes such as injection, transport and recombination of carriers, both electrons and holes.

Operation stability of devices

Figure 2 demonstrates changes of luminance and voltage as a function of operation time. All devices were driven at a constant dc current of 250 mA cm^{-2}. At this current density, all devices initially showed the same initial voltage (V_0) of 11.5 V and similar initial luminance (L_0) of ≈ 10000 cd m^{-2}, as shown in Fig.1. Contrary to the similarity in the initial characteristics, a remarkable difference was observed in the durability of the devices. The half-life of the devices, which is defined as the time to reach half the initial luminance, strongly depends on the process pressure: 1.2 h (device A), 24.2 h (device B) and 31 h (device C). Based on the result of the residual gas analysis listed in Table 1, we conclude that the durability of the devices is governed by the amount of water rather than the pressure itself.

A number of molecules striking the substrate surface in unit area and time can be estimated by [9].

$$J = P / (2\pi kMT)^{1/2} \tag{1}$$

where P is the partial pressure of gas, k is the Boltzmann constant, M is the molar mass of the gas, and T is temperature. In the case of device A, the process pressure of 3.2×10^{-7} Torr is attributed to the vapor pressure of residual water. In this situation, the number of water molecules incident to the substrate is calculated to be 2.38×10^{14} s^{-1} cm^{-2}. On the other hand, Alq_3 was evaporated at 0.1 nm s^{-1}, which corresponds to 1.7×10^{13} s^{-1} cm^{-2}, where we use the density and molar mass of Alq_3 as 1.3 g cm^{-3} and 459.44 g mol^{-1} [10]. This means that the number of water molecules strike to the substrate exceeded that of the Alq_3 molecules by more than ten times in device A. The numbers of water molecules are much smaller in devices B and C, since the vapor pressure of water was lower than that in device A by more than one to two orders of magnitude. Thus, we conclude that the difference observed in the device durability can be ascribed to the incorporation of water in the Alq_3 layer.

Previous works have reported that humidity induces crystallization of Alq_3 layers [11]. This phenomenon causes the formation of dark spots in Alq_3-based OLEDs. However, no dark spots were observed in device A after the lifetime measurement. It has also been proposed that the Alq_3 molecule decomposes by the chemical reaction with water [6]. The fact that there were no obvious differences in the device kept at 80 °C for 30 h suggests that Alq_3 degrades by an electrochemical reaction during the operation of the devices. Fluorescence quenchers or non-radiative recombination centers may be formed by the electrochemical reaction of Alq_3 with water.

As shown in Fig. 2(b), the operation voltage increases with progression of the time after the initial voltage drop from 11.5 to 11.0 V, probably due to Joule heating. An increase in the voltage indicates that the decomposition product of Alq_3 act as electron traps as well.

The other possibility of the device degradation might be due to an oxidation of Al electrode. The Al electrode might react with residual water during thermal deposition. If this is the case, the initial device characteristics should depend on the amount of water during Al deposition. As it has been clearly demonstrated in the section 2.1, we have not observed significant differences in the initial characteristics of the devices fabricated under different process pressure.

4. Conclusions

We have shown enhanced stability of the Alq_3-based OLEDs fabricated under ultra-high vacuum conditions. The durability of the devices strongly depends on the process pressure. The analysis of the residual gas components indicates that the durability of the devices is governed by the amount of water. The decrease in luminance and the increase in voltage are pronounced in the devices fabricated under the presence of water. This suggests that Alq_3 molecule decomposes by an electrochemical reaction with water while the devices are under operation. Fluorescence quenchers and electron traps may be formed by the electrochemical reaction of Alq_3 with water.

Acknowledgements

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Figure captions

Fig. 1. Initial characteristics of devices fabricated under different process pressures: (a) current density vs voltage; (b) luminance vs current density for devices A (square), B (circle) and C (triangle).

Fig. 2. Stability of devices fabricated under different process pressures: (a) normalized luminance (L/L_0) and (b) voltage as a function of operation time. Devices were driven at a constant dc current density of 250 mA cm^{-2}. Initial luminances (L_0) for devices A (square), B (circle) and C (triangle) were 9220, 9810, and 10630 cd m^{-2}, respectively. The initial luminance was measured at 10 s after applying the dc current density. The initial voltage of all devices was 11.05 V.

Table 1

Base and process pressures and analyses of residual gas components during device fabrication.

Device	Pressure (Torr)		Ion current (A)			
	Base	Process	H_2O^+ ($m/z = 18$)	N_2^+ or CO^+ ($m/z = 28$)	O_2^+ ($m/z = 32$)	CO_2^+ ($m/z = 44$)
A	5.0×10^{-7}	3.2×10^{-7}	3.8×10^{-8}	2.0×10^{-9}	4.0×10^{-10}	5.5×10^{-10}
B	4.0×10^{-8}	4.8×10^{-8}	2.7×10^{-9}	1.6×10^{-9}	3.3×10^{-10}	4.1×10^{-10}
C	2.0×10^{-9}	1.6×10^{-8}	5.9×10^{-10}	1.0×10^{-9}	6.9×10^{-11}	2.2×10^{-10}

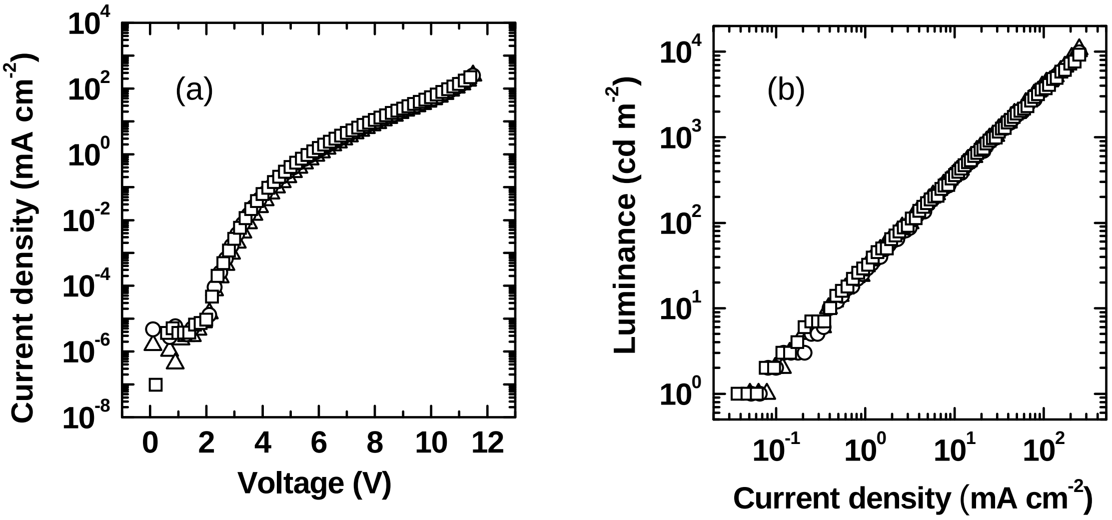

Figure 1 Ikeda et al.

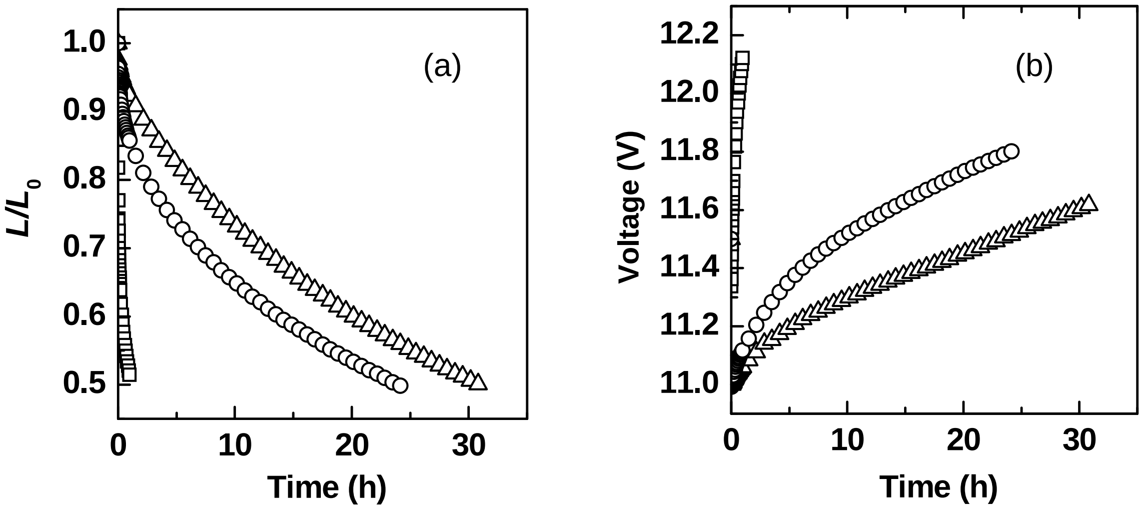

Figure 2 Ikeda et al