Effect of Ambient Gas on the Early Stage of the OLED Degradation

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Abstract

We report on the effect of ambient gas on the OLED degradation. The operating voltage and quantum efficiency increases when the device is exposed to the atmospheric gas and then returns to the initial level of the device in vacuum when the atmospheric gas is evacuated. These changes in the OLED performance can be attributed to the ambient gas pressure.

1. Introduction

Short lifetime of organic light-emitting diodes (OLEDs) is one of significant problems for their practical applications. Degradation of OLED devices causes decrease in luminance and efficiency, higher operating voltage and eventual failure [1]. Various reasons of degradation which is related with oxygen and water vapor in atmosphere have been reported [2-4], but there is no established theory to explain it clearly. To keep from being exposed to air, OLED displays are encapsulated with a glass or stainless steel can in commercial products. On the other hand, device measurement is usually carried out in vacuum or glove box which is filled with rare gases. But vacuum condition is different from atmospheric condition even though there was no water vapor or oxygen in inert gas. In this work we have studied OLED degradation mechanism by investigating the effect of ambient gas on the current-voltage-luminance (I-V-L) characteristics of OLED. In particular, we compared the I-V-L characteristics of OLED measured in vacuum with those measured in nitrogen gas.

2. Experimental

In order to investigate the effect of various ambient gases, we fabricated all OLED devices with the same structure. The devices were constructed by sequential deposition of 4,4',4"-tris{N,(3-methylphenyl)-N-phenylamino}-triphenylamine (m-MTDATA) as a hole injection layer [5], N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α–NPD) for a hole transport layer, of tris(8-hydroxyquinoline) aluminum (Alq_3) layer as an emitting and electron transport layer, and LiF (0.5 nm)/aluminum (100 nm) cathode, without breaking vacuum, on the pre-patterned ITO glass substrate. The thickness of m-MTDATA, α–NPD, and Alq_3 were 15, 60, and 70 nm, respectively.

The device was mounted in an airtight chamber. The variation of voltage and luminance of the device upon continuous application of a constant current was measured with repeated cycles of infusing gas and pumping out every minute. This process was repeated on the same sample at different pressures of the gas and current densities.

3. Results and discussion

Fig. 1 shows the variation of voltage and luminance with repeated cycles of ambient air exposure and evacuation for the device under continuous bias of a constant current of 2 mA (100 mA/cm^2). The voltage and light intensity changes abruptly at the time of air injection, or vacuum pumping. When the ambient condition is changed from vacuum to air, the operation voltage increases instantly and then slowly increases with time. When evacuating the air, the operation voltage shows a slight overshoot and then decreases continuously to the voltage level of just before the air exposure. The luminance variation behavior is similar with the voltage variation.

It has been reported that the diffusion of moisture and oxygen caused chemical and physical changes of the cathode layer and resulted in the growth of dark spots when the device was exposed to air [6]. In addition, V.-E. Choong *et al*. [7] reported that the O_2 exposure reduced the photoluminescence (PL) quenching of Alq_3, which was caused by the gap states formed at the cathodic interface Alq_3. The oxidation of cathode metals recovers the PL of Alq_3 [7]. Therefore, one can attribute the luminance increase upon exposure to air, shown in Fig. 1, to the oxygen diffusion accompanied by formation of a thin oxide layer at the Alq_3/cathode interface. Then, the probability of exciton quenching at the Alq_3/cathode interface can be reduced, resulting in the increased quantum efficiency. The formation of a thin oxide layer at the Alq_3/cathode interface can also cause the operating voltage to increase.

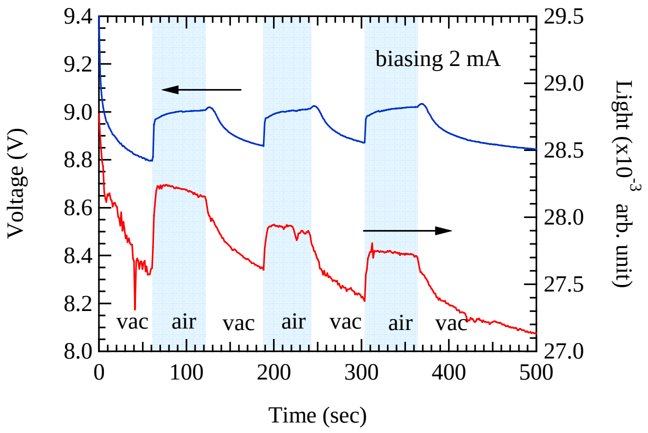

Fig. 1. Variation of voltage and light intensity with repeated cycles of air exposure and evacuation at room temperature.

However, reversible behavior of the voltage and luminance variation with repeated cycles of air exposure and evacuation, shown in Fig. 1, can not be fully understood with oxidation of the cathode layer since such oxidation process is irreversible. Thus, other mechanisms may govern such reversible variation of the OLED characteristics. In order to obtain the clue we carried out the same experiment using dry nitrogen gas rather than air. Fig. 2 shows the variation of voltage and luminance while alternating between vacuum and various pressures of dry nitrogen for the device under continuous bias of a constant current of 2 mA. The overall behavior of Fig. 2 is very similar with the case of air exposure and evacuation, shown in Fig. 1. The voltage and light intensity increase when infusing nitrogen gas and then decrease when evacuated. In addition, the light intensity increment becomes higher as the N_2 gas pressure increases from 0.05 MPa to 0.2 MPa. Furthermore, the luminance decay over time was slower under higher pressure. Therefore, we consider that change of pressure causes reversible variation of the voltage and luminance, irrespective of air or nitrogen.

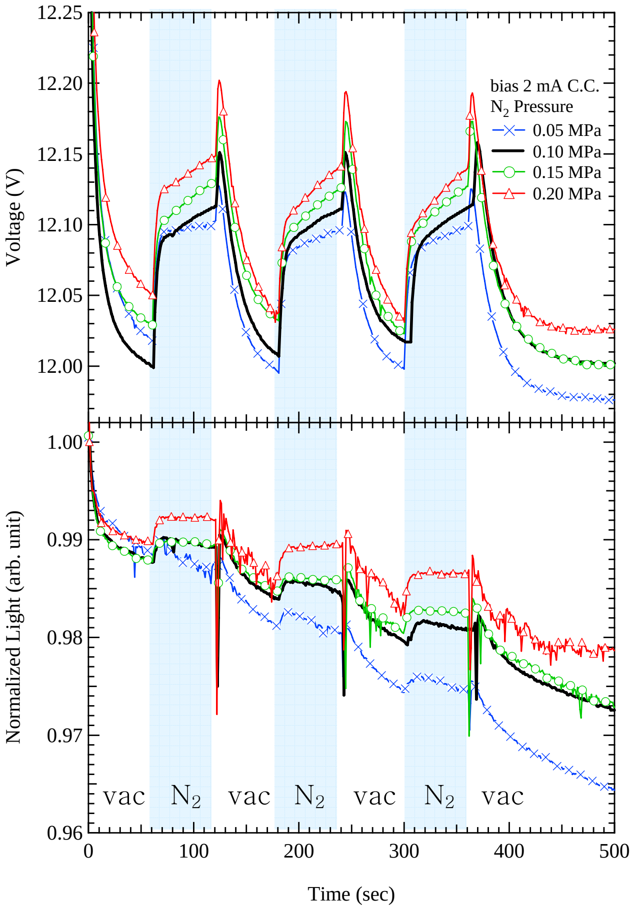

Fig. 2. Variation of voltage and light intensity (normalized at the initial level) while alternating between vacuum and various pressures of dry nitrogen gas.

Figs. 1 and 2 show that the voltage and luminance (or quantum efficiency) increase as the pressure increases. Since the charge transport in organic materials occurs mainly via a hopping process [8], the voltage increase with gas infusion implies that the hopping process may be hindered by the diffusion of gas molecules. We conjecture that diffusion of gas molecules may increase the intermolecular distance and thereby reduce the hopping rate of carriers between organic molecules. Then the increased quantum efficiency at high pressure can be explained by improved electron-hole balance due to the reduced hole mobility.

We found an interesting result while changing the biasing current at a fixed nitrogen pressure at 0.1 MPa. Fig. 3 shows the voltage variation with repeated cycles of nitrogen infusion and evacuation for the device at various bias currents. The voltage is normalized at the first nitrogen injection point (elapsed time of about 60 seconds). When the nitrogen gas of 0.1 MPa is infused, the operation voltage increases for the bias current above about 0.8 mA, but the voltage decreases for the bias current below about 0.7 mA. Therefore, the effect of pressure on the carrier transport appears quite complicated. Although the exact mechanism for the opposite behavior of the voltage variation with the current density is not clear, we consider that it may be related with the change from the hole-dominant current at low current density to the bipolar current flow at high current density in the α–NPD/Alq_3 device. In this respect, it is noted that the hole conduction dominates in a low current region due to the α–NPD/Alq_3 interface energy barrier as well as low mobility of Alq_3 while the electron transport through the Alq_3 layer limits the total current flow in a high current region [9, 10]. We suppose that changing point is between 0.7 mA and 0.8 mA, corresponding to current density of about 40 mA/cm^2. We plan to take more systematic study to clarify this phenomenon.

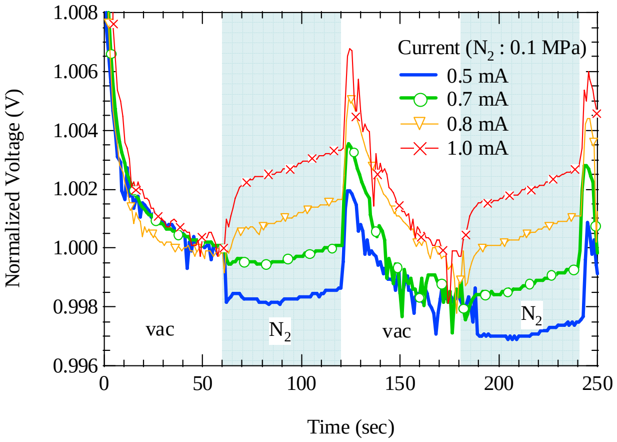

Fig. 3. Normalized voltage variation with changing the current. Nitrogen gas pressure was fixed at 0.1 MPa.

4. Summary

We measured the voltage and luminance variation with repeated cycles of gas infusion and evacuation for the devices biased at a continuous constant current. The device characteristics were changed with the gas pressure and current density. We attribute this effect to the change of the carrier transport under the pressure. Diffusion of gas molecules may increase the intermolecular distance and thereby reduce the hopping rate of carriers between organic molecules. In addition, it appears that the gas pressure may affect the transport of holes and electrons differently, which requires a further systematic study.

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6. References

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