Analysis of Transient Degradation Behaviors of Organic Light-Emitting Diodes under Electrical Stress

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Abstract: Despite the wide application of organic light-emitting diodes (OLEDs), the performance of OLED devices is sometimes limited by their reliabilities. In this paper, we report the transient degradation behaviors of fluorescent blue OLEDs, where both the current and luminance initially increase under electrical stress within a short stress time. We analyze the degradation mechanism in terms of the carrier recombination and transport. From the comprehensive analyses of electrical and optical characteristics, it is suggested that the electron transport is responsible for the initial transient behavior of the device.

Keywords: organic light-emitting diodes; degradation; transient; charge recombination and transport

1. Introduction

Since the development of multi-layer organic light-emitting diodes (OLEDs) in 1987 [1], the device performance has been improved tremendously over the past decades. Owing to the merits of organic materials and improvements of their efficiencies, the application of OLEDs is widespread and anticipated to be expanded even further [2,3]. Despite the advantages compared with inorganic counterparts, however, the utilization of OLEDs is sometimes limited by their reliabilities. Especially, OLEDs are vulnerable to environments such as water vapor and oxygen [4]. Hence, remedies to enhance the storage lifetime shortened by the external factors have been pursued intensely and a significant progress has been made [5]. With the strict standards, the encapsulation of OLEDs has now become quite reliable for harsh environments. Thus, the degradation during the device operation requires more attention to improve the device reliability further.

In general, the monitoring of luminance reduction is used to evaluate how fast the device degrades [6]. The degradation curve is empirically fitted with a stretched exponential decay function [7]. The device lifetime, which is defined, for example, as the elapsed time when the luminance is decreased to the half of its initial value, follows the power law depending on the aging current [6]. This method can be applied universally as there is no assumption involved for the test. However, physical foundation on the properties of the luminance decay is not considered sufficient. Moreover, the dominant cause of the device degradation cannot be determined from this empirical evaluation.

The chemical analyses to clarify the OLED degradations have also been used popularly [8,9]. These methods examine the chemical products after the acceleration test. By investigating the chemical products inside the device, one can guess a chemical reaction involved during the device operation. However, these analyses require destructive probing after which the device does not function any longer. Also, they take additional time...
as the OLED devices contain many different kinds of chemicals from the deposition of multi-layer structures.

Taken together, the methods described above can give a clue why the device has degraded. However, characterization and understanding of the performance degradation from the device point of view is necessary and beneficial in industry. The device analyses and modeling based on the physical mechanisms can give more insights into how the device degrades than the conventional chemical reaction or decomposition suggests. For this purpose, introducing quantitative factors from the electrical and optical properties of OLEDs [10,11] is essential in evaluating how the device degradation progresses. From the analyses, the direction for further enhancing the device performance can also be determined, which leads to save resources and time.

In this paper, we analyze the transient behavior of the OLED device characteristics under electrical stress, where both the current and luminance at a given voltage initially increase before the degradation occurs. The quantitative factors are used to characterize how the device behaves under electrical stress and a model that can explain this observation is presented.

2. Sample and Experiments

In order to examine the degradation of OLEDs, samples having blue fluorescent emissive layers (EMLs) were prepared on a glass substrate and encapsulated to get rid of any effect of water vapor and oxygen on the device degradation. The emission wavelength and the size of the sample were ~450 nm and 2 x 2 mm², respectively. See Figure 1 for a schematic representation of the device. Indium tin oxide (ITO) and Al are used as an anode and a cathode, respectively, while α-NPD and Alq₃ layers are inserted as a hole transport layer (HTL) and an electron transport layer (ETL). The LiF layer is intended as an electron injection layer (EIL).

Figure 1. Schematic device structure of the OLED devices under study.

In order to investigate the device degradation, constant current-density stresses were applied for 168 h. The driving conditions were set to be 2.5 x J₀D and 15 x J₀D, respectively, where J₀D was the normal device operation current density. As the devices were operated, luminance-current-voltage (L-I-V) characteristics were measured. The data were collected in shorter steps during the first 24 h of stress to investigate the initial variation in detail. After that, the data were collected in steps of 24 h. A Keithley 2602B sourcemeter was used for characterizing the electrical properties and applying the constant current density stresses. The luminance of the samples was detected by a Si photodiode (Hamamatsu S2201).

3. Results and Discussion

In Figure 2, the current density-voltage (J-V) curves of devices under electrical stress are shown. For the stress level of 2.5 x J₀D, the device characteristics seem to be almost
unchanged during 168 h. On the other hand, the current variation under high current stress ($15 \times J_D$) increases at a fixed voltage, which shows the typical device degradation. More variation under higher stress level can also be found in the $L$-$J$ curve depicted in Figure 3. However, simple $L$-$J$-$V$ curves alone are not sufficient for analyzing the degradation phenomena in detail.

In Figure 4, the current density at the operating voltage ($V_D$) for each experiment is selected and plotted as a function of operation time. Commonly, the variation in current density can be divided roughly into two regions. In case of the stress test at $2.5 \times J_D$ (Figure 4a), the overall trend shows that the current density at $V_D$ increases up to 96 h after an initial decrease in the current density at $V_D$ (region 1). After 96 h, the device degradation of decreasing current density with the operation time is observed (region 2). The similar tendency is observed for the stress test at $15 \times J_D$ (Figure 4b). Due to the higher stress condition, the device begins to degrade earlier (after 48 h) than the case shown in Figure 4a. Although the intervals collecting the device degradation data are different for each experiment, the overall trends are clear. Furthermore, the reliability tests for 168 h seem to be sufficient for observing the degradation behaviors shown in Figure 4.

To investigate the electrical properties further, the ideality factors, $n_{\text{ideal}}$, defined as

$$n_{\text{ideal}} = \frac{q}{k_B T} \left( \frac{\partial \ln J}{\partial V} \right)^{-1}$$

are plotted as a function of operation time in Figure 5. Here, $q$ is the elementary charge, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. As seen in Figure 2, one can deduce that the overall shapes of $J$-$V$ curves during the device operation are quite similar since $n_{\text{ideal}}$ is related to the slope of $\ln J$ vs. $V$ curve.
Figure 4. Current densities at $V_D$ as a function of operation time for the constant current stresses at (a) $2.5 \times J_D$ and (b) $15 \times J_D$.

Figure 5. Variations of $n_{\text{ideal}}$ at $J_D$ for the constant current stresses at (a) $2.5 \times J_D$ and (b) $15 \times J_D$.

Furthermore, the value and tendency of $n_{\text{ideal}}$ give clues about dominant carrier recombination and transport mechanisms [12,13]. At low current density ($<10^{-3}$ mA/cm$^2$), it is seen that $n_{\text{ideal}}$ is ~2, which indicates that the Shockley-Read-Hall (SRH) recombination inside the emissive layer (EML) is dominant in the device [13]. In general, it is known that the mobility for the hole transport is much higher than that for the electron transport in organic semiconductors [14]. Thus, the dominant recombination mechanism would be the SRH recombination by the electron capture in this region. As the current increases, $n_{\text{ideal}}$ is seen to increase due to the additional voltage drop caused by the series resistance in the layers outside the EML. From $n_{\text{ideal}}$ in the driving current region (indicated by a dotted line marked by $J_D$), the device resistance in Figure 5a seems almost constant under electrical stress, as indicated by overlapping curves. However, $n_{\text{ideal}}$ at $J_D$ for the higher current stress shown in Figure 5a is slightly increased due to the effect of rapid device degradation.

For further analysis, the change in luminance at $J_D$ as a function of operation time is shown in Figure 6. In region 1, for the case of $2.5 \times J_D$ device operation, which is depicted in Figure 6a, the overall luminance increases whereas the applied voltage decreases with respect to the operation time. After 96 h, the luminance is almost saturated. This trend in device degradation is more pronounced under higher electrical stress (Figure 6b). The device efficiency is investigated next to identify why the luminance of the sample varies under electrical stress.
Figure 6. Luminance at $J_D$ as a function of operation time for the constant current stresses at (a) $2.5 \times J_D$ and (b) $15 \times J_D$.

The external quantum efficiencies (EQE, $\eta_{EQE}$) of the degrading devices under electrical stress are shown in Figure 7. It is noted in Figure 7 that there is little change in shape except the minute changes at very low current densities ($\approx 10^{-2}$ mA/cm$^2$), which reflects the initial current variation before 24 h in Figure 4. For the case of the stress test at $2.5 \times J_D$ (Figure 7a), the EQE is almost the same during device operation up to 168 h, which shows the same tendencies as the current and luminance variation.

Figure 7. Device EQEs under constant current stresses at (a) $2.5 \times J_D$ and (b) $15 \times J_D$.

In order to investigate further, the EQE curves are shown in Figure 8 after normalizing with respect to respective peaks. The reason why the normalized EQEs show this trend can be explained by considering the factors constituting the EQE. It is known that the EQE can be divided into the internal quantum efficiency (IQE, $\eta_{IQE}$) and the outcoupling efficiency ($\eta_{out}$) [15]:

$$\eta_{EQE} = \eta_{IQE}\eta_{out} \quad (2)$$

Figure 8. Variation of the normalized $\eta_{EQE}$ as a function of current density for the constant current stresses at (a) $2.5 \times J_D$ and (b) $15 \times J_D$. 
η_{IQE} is defined as the ratio of the number of generated photons per unit time inside the EML to the number of injected electrons per unit time. η_{out} indicates a fraction of photons escaping from the EML to free space. In general, η_{out} can be predominantly affected by the device structure. Many researchers have attempted to increase η_{out} by modifying the layer structure with such things as the layer grating, the microlens array, and the inserted scattering particles [16]. Since the device structure was not changed during the operation in this case, the variation of the efficiency curve is not attributable to η_{out}.

The analysis above implies that the variation of the efficiency curve should be caused by the change in η_{IQE}. The IQE of an OLED device can be expressed as the product of three factors [15]:

$$\eta_{IQE} = \eta_{S/T} \eta_{q}$$

(3)

where γ is the charge-carrier balancing factor, η_{S/T} is the spin singlet/triplet factor, and η_{q} is the effective radiative efficiency. First of all, η_{S/T} is determined by how the EML layer forms excitons. In our experiments, η_{S/T} can be regarded as constant as the fluorescent light-emission process for our device is not changed [17]. Furthermore, the shape of the efficiency curve is the result of the competition between the radiative and nonradiative recombinations, which is related to η_{eff}. As we can see in Figure 8, the shape does not change during the operation after the initial 24 h, indicating that η_{eff} has not been hampered under the electrical stress. In other words, the effect of electrical stress is outside the EML, i.e., in cladding layers. Therefore, it is thought that the change in cladding layers has caused the variation in γ, relating to the observed transient behavior.

As deduced from the analysis of the efficiency curves, one can ask what triggers this phenomenon. While each chemical should be stable enough to have a minimal impact on the device performance, it has been reported that the reaction between LiF/Al and Alq_{3} is possible during deposition [18], as supported by the electron energy-loss spectroscopy. As a result of the reaction, the dissociated Li ions can migrate into the EML as the device is operated. Then the states of the migrated Li ions can be formed in the vicinity of the LiF/Al:Alq_{3} interface. In this case, the migrated Li ions can play an important role in the observed transient behavior as shown in Figure 9. For the EML, it can act as defects, which degrades the device’s lifetime. However, the reason why both the current density at V_{D} and the luminance at J_{D} increase (region 1) by the migration of Li ions should be deduced from the nature of organic semiconductors.

Figure 9. Schematic diagram of Li ion migration in the device, leading to the enhancement of electron
injection (LUMO: lowest unoccupied molecular orbital, HOMO: highest occupied molecular orbital, ETL: electron transport layer, HTL: hole transport layer).

The bonding strength between organic molecules is dominated by the weak dipole interaction, also known as the van der Waals interaction [17]. Thus, the carrier transport based on the band theory may not be applicable because the band formation in organic solids is weak. In a disordered system, the main charge transfer mechanism is the hopping process via quantum-mechanical tunneling [19]. The injected charges may hop by emitting or absorbing phonons. In this phonon-assisted hopping, the hopping transition rate, $W_{ij}$, from an initial state in a position $r_i$ with an energy $E_i$ to a final state in a position $r_j$ with an energy $E_j$ is given by the Miller–Abraham formulation [19]:

$$W_{ij} = \nu_0 \exp\left(-2\alpha |r_{ij}|\right) \exp\left(-\frac{E_j - E_i + |E_j - E_i|}{2k_B T}\right),$$

where $\nu_0$ is the hopping frequency, $\alpha$ is the inverse of the decay length, $|r_{ij}|$ is the distance between the states. The states induced by the migrated Li ions can lead to the interstate distance shortened, which would enhance the electron injection. Moreover, the work function of Li is ~2.3 eV, lower than the lowest unoccupied molecular orbital of Alq3 [20–22]. Due to this nature of the work function, electron hopping assisted by Li ions can be facilitated. Consequently, the $\gamma$ factor would increase owing to the enhanced electron transport as schematically described in Figure 9.

However, once Li ions migrate further into the EML, the effect of transport enhancement ceases to exist, thus reducing the current conduction as seen in region 2 in Figure 4. Although the migrated Li ions can assist the electron injection initially, excessive migration with further stress would eventually degrade the EML, thus detrimental to the device as illustrated in Figure 10.

![Figure 10. Schematic diagram of excessive Li ion migration in the device, quenching the exciton formation after 96 h of electrical stress.](image)

As shown in Figure 4, the operation time when the current and luminance increase initially are shortened under higher stress current. It indicates that the rate of Li migration
increases with the level of stress current. Although the effect of Li migration on the reliability of OLED may seem trivial, this effect is rather pronounced at the low-current operation. This investigation suggests that by optimizing the LiF layer or applying a more stable EIL, the lifetime of an OLED device could be extended further.

4. Conclusions

The transient behavior, where both the current at $V_D$ and the luminance at $I_D$ initially increase under a constant-current stress, has been observed for the blue fluorescent OLED device. Analyses of the quantitative factors such as the ideality factor and the quantum efficiency obtained from the $L-I-V$ characteristics of the device have suggested that the carrier transport/injection into the EML can be responsible for this phenomenon, rather than the change in recombination properties of the EML. The enhancement in electron transport has been pointed to play a role here, possibly caused by the migrated Li ions in the ETL. While the microscopic study is further required at the moment, the analyses presented in this work would be useful in industry for comprehensive utilization of the $L-I-V$ characteristics to deduce a physical model behind a degradation phenomenon.

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