Effects of interfacial stability between electron transporting layer and cathode on the degradation process of organic light-emitting diodes

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The authors have demonstrated that the increase of electron injection barrier height between tris(8-hydroxyquinoline)aluminum (Alq_3) and LiF/Al cathode is one of the most critical parameters to determine the reliability of organic light-emitting diode with the typical structure of indium tin oxide/N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl) benzidine/Alq_3/LiF/Al. The electrical properties of several devices (hole only, electron only, and integrated double-layered devices) have been measured in the function of operating time to analyze the bulk and interface property changes. Bulk properties of trap energy and mobility in an organic layer have been estimated by using trap-charge-limited currents and transient electroluminescence measurements. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2817939]

Organic electronic devices have attracted considerable attention in a wide variety of applications such as organic light-emitting diodes (OLEDs), organic thin film transistor, and organic photovoltaic devices because of their easier process to fabricate and lower cost for the real applications.[1,2] Tremendous efforts have been made to improve the performances and to analyze the physical and chemical mechanisms of the organic electronic devices. The luminous efficiency and operational reliability of OLEDs for a real application have been significantly improved for the last decade.[3,4] It is doubtless desirable to have an efficient material for better performance of OLEDs. A device fabrication process can also contribute to enhance the performance.[5,6] Various interface manipulations at an organic/electrode interface have been a helpful method for better performance of OLEDs because interface properties play an important role in charge injection and stability of devices.[7–9] Many efforts have been also made on the energy level alignments to reduce the charge injection barrier height at an organic/electrode interface.[10,11] Surface treatments of anode have been one of the most popular methods to obtain higher work function of indium tin oxide (ITO), resulting in more efficient hole injection and longer operational stability.[8] It is also highly desirable to develop a lower work function material for a cathode to have effective electron injection. At the same time, many efforts have been made to understand the degradation mechanism in terms of materials and device structures. An emitting material of tris(8-hydroxyquinoline)aluminum (Alq_3) can react with injected hole to form cationic Alq_3 which can be a fluorescence quencher in the typical double-layered OLEDs.[12,13] Cathode oxidation and electrochemical reactions at an organic/cathode interface for luminous degradation have been also reported.[14–16] Although many efforts to analyze the luminous efficiency and stability of OLEDs have been done, we still lack information to understand the operational degradation mechanism of OLEDs under the electrical aging process.

In this letter, we have demonstrated that bulk properties and hole transporting layer of N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl) benzidine (NPB) are not responsible for the operational degradation on the electrical aging but the electron injection barrier height from LiF/Al cathode to Alq_3 which is the most critical parameter to determine the stability. The electron injection energy barrier height is getting higher as the operating time elapses and induces the operational voltage increase.

In order to investigate the degradation process, various structures of devices were fabricated. The devices were fabricated on ITO coated glass with a sheet resistance of $15\Omega/\square$. All devices were encapsulated with BaO in a dry nitrogen glovebox to protect them from moisture in ambient atmosphere. For transient electroluminescence (EL) measurements, a pulse generator (HP8114A) and a photomultiplier tube (2 ns response time) were used to detect signal and the detected signals were stored in a digital storage oscilloscope.

Devices A and B were aged at a constant current density of 50 mA/cm^2 and the degradation of the devices accompanied with an increase of driving voltage, as shown in Fig. 1. Inserting a thin layer of buckminsterfullerene (C_{60}) between the ITO anode and NPB layer can significantly not only reduce the hole injection barrier[17] but also improve the stability of devices. These results can be ascribed to the surface-induced dipole of C_{60} and improved interfacial adhesion

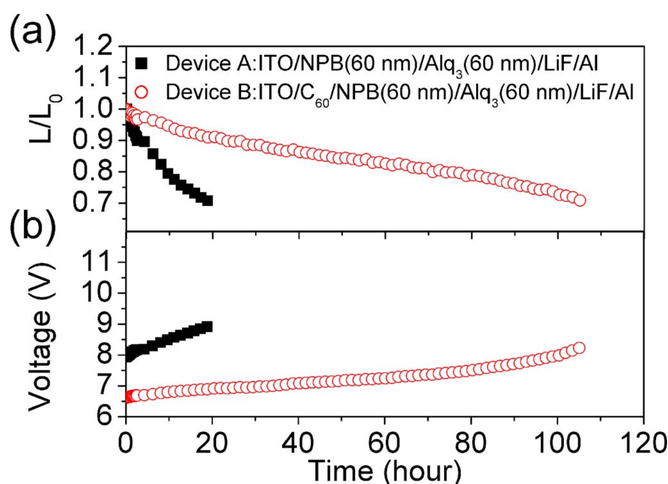

FIG. 1. (Color online) (a) Luminance decay and (b) voltage rise curves for the devices A and B at a constant current density of 50 mA/cm^2.

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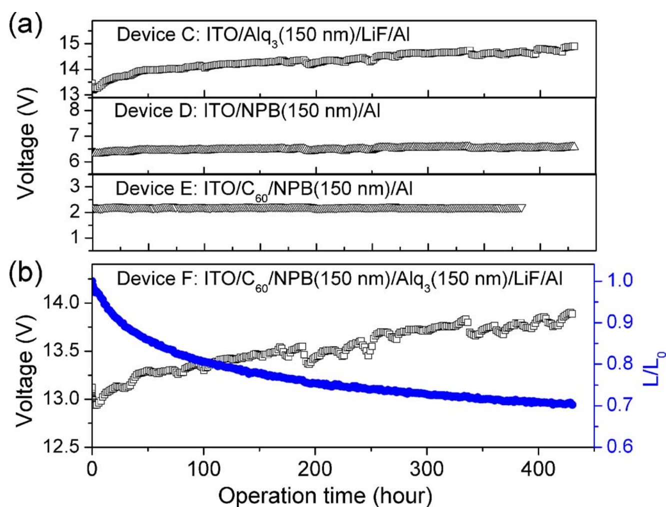

FIG. 2. (Color online) (a) Driving voltage versus operation time for the carrier only devices C, D, and E. (b) Driving voltage rise and luminance decay versus aging time for device F at a constant current density of $50\ mA/cm^2$.

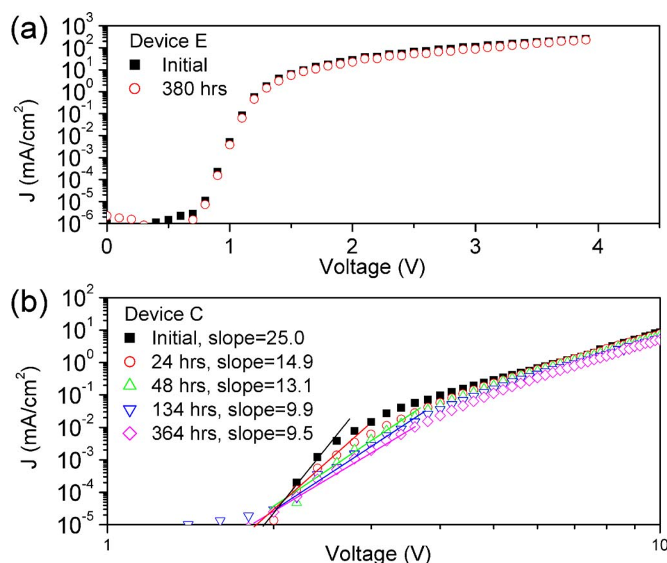

FIG. 3. (Color online) Comparison of *J-V* characteristics before and after electrical aging for (a) the hole only device E and (b) the electron only device C.

between organic materials and ITO substrates.[18] The operational voltage increase was observed in both devices with and without C_{60} layer. However, it is particularly noteworthy that both the initial voltage and the voltage increase of the device with C_{60} are much smaller than those without C_{60} layer. These results will be very helpful to improve the operational stability by lowering the resistance and electric fields of the devices at the same current density.

To distinguish the contribution for the increased voltage during the electrical aging, the typical carrier only devices with the structures of C: ITO/Alq_3(150 nm)/LiF(1 nm)/Al, D: ITO/NPB(150 nm)/Al, and E: ITO/C_{60}(2.5 nm)/NPB(150 nm)/Al were fabricated. Figure 2(a) shows the applied voltage versus electrical aging time at a constant current density of $50\ mA/cm^2$. The electron dominating device (device C) has much higher initial voltage and voltage increase after the electrical aging than those of hole dominating devices (devices D and E). Devices C and D have the initial voltages of 13.2 and 6.3 V and the voltage increases of 14.5 and 6.5 V, respectively after the electrical aging for 400 h. More importantly, device E shows much lower initial voltage of 2.2 V and the voltage increase after the electrical aging is almost negligible. This effect is ascribed to the lowered hole injection barrier height by surface-induced dipole by C_{60}.[17] This result strongly indicates that the magnitude of electric field on the device with the same current density is different. The magnitude of electric field across NPB in devices D and E are 0.42×10^6 and 0.15×10^6 V/cm, respectively. Lower operational voltage is usually more helpful to obtain longer operational stability in a typical double-layered structure in the current works. Figure 3(a) shows that the *J-V* characteristics of device E before and after the electrical aging for 380 h are almost identical. This result strongly suggests that the degradation process of device B cannot be ascribed to the hole transporting layer properties. It is very well known that the electron mobility of Alq_3 is ten to hundred times lower than that of NPB. Therefore, it can be easily understood that the device C has higher operational voltage of 13.3 V and the largest electric field of 0.89×10^6 V/cm across the organic layer of Alq_3. The significant increase in operational voltage has been also observed in device C after the electrical aging process.

To investigate the device performances, we fabricate device F having the integrated structure of devices C and E. Device F has the brightness of $336\ cd/m^2$ at $50\ mA/cm^2$. The voltage increase during the electrical aging is shown in Fig. 2(b). The initial voltage of 13.0 V is similar to that of device C. Alq_3 is mainly responsible for the total voltage of the integrated structure of device F. If the applied bias is distributed through NPB and Alq_3 in device F, the relative magnitude of electric field on Alq_3 is 6.5 times higher than that on NPB. The relatively strong electric field on Alq_3 implies that Alq_3 is more likely to be responsible for the degradation process. Thermal stability of NPB could be another critical issue for the degradation of OLEDs. Therefore, we carefully monitored optical microscopic images of the devices D, E, and F after the electrical aging. However, we could not observe any trace of crystallization of NPB. Moreover, as shown in Fig. 3(a), the *J-V* characteristics of device E after the electrical aging for 380 h are the same as before electrical aging. These results strongly suggest that the physical and electrical properties in the hole transporting layer of NPB have not been changed during the electrical aging process. As a supporting result, it is recently reported that the thermal stability of NPB can be improved by C_{60} to suppress the crystallization of NPB by annealing under high temperature of 120 °C.[18] Even though the high current density of driving current might induce the Joule heat on NPB layer, the crystallization by Joule heat during the electrical aging might be negligible in the current works.

Kondakov *et al.* reported that the accumulation of deep traps and luminescence quenchers is a general phenomenon associated with the operational degradation of OLEDs.[19,20] Popovic *et al.* reported that the increase of trapped charges is revealed by the increase in the operational driving voltage of the OLEDs.[13] Alq_3 cations near the organic interface of NPB/Alq_3 can act as nonradiative recombination centers that result in the decreased luminance efficiency.[12] To test the bulk properties and trap state effects of Alq_3, we have measured the electron trap state and mobility of Alq_3 by trap-charged-limited model[21] (TCLM) and transient EL techniques. From the temperature dependence of *J-V*

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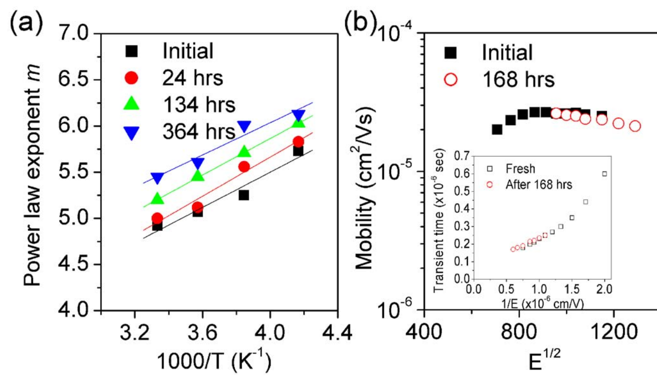

FIG. 4. (Color online) (a) Power law exponent value of m vs $1/T$ for the different electrical aging times in device C. The slope corresponds to the trap state in energy level. (b) Estimated electron mobility of Alq_3 in device B by transient electroluminescence measurements. The inset shows a plot of transient time vs $1/E$.

characteristics of device C, the power law exponent m versus $1/T$ shown in Fig. 4(a) was obtained. According to the TCLM, the slope of m versus $1/T$ corresponds to the trap state in energy level. We found that the trap state in energy of Alq_3 is identical to the value of 0.10 eV which is not related with the increased voltage with the operation time. To investigate the contribution of cationic form of Alq_3 to the electron mobility of Alq_3 the electron mobilities of Alq_3 in device B before and after the electrical aging were evaluated by transient EL measurements. The mobility of Alq_3 after the electrical aging for 168 h is almost the same as the initial value of 2×10^{-5} cm/V s, as shown in Fig. 4(b). This is quite interesting because we could not observe the mobility changes by the cationic form of Alq_3, which might exist in the device after the electrical aging. We assume that the cationic form of Alq_3 might exist only near by the interface of NPB/Alq_3 and its concentration might not be enough to affect the electron mobility of Alq_3.

The increases of m in the J-V characteristics of device C with the electrical aging are shown in Fig. 4(a). The power law of exponent m larger than two has been interpreted as the drift of charge carriers under the influence of traps or field dependent mobility models. As discussed above, the bulk properties of trap energy and mobility of Alq_3 have not been changed. We suggest that the increases of m were caused by the increases of barrier height between Alq_3 and LiF/Al. Figure 3(b) represents the double log J-V characteristics of device C at room temperature and it can be clearly observed that the slope in the Schottky thermionic emission region decreases from 25 to 10 after the electrical aging. The current density of Schottky thermionic emission is described by the following equation:

$$J = A^{*}T^{2}\exp\left[-\left(\phi_B + \sqrt{\frac{e^3F}{4\pi\varepsilon}}\right)\Big/(kT)\right], \qquad (1)$$

where A^* is the modified Richardson constant, ϕ_B is the injection barrier height, e is the electronic charge, F is the electric field, ε is the permittivity, k is Boltzmann's constant, and T is the temperature. A^* is the Richardson constant. The charge injection barrier height ϕ_B can be estimated from the relationship between $\ln J$ versus $F^{1/2}$. However, quantitative differences are concerning the Richardson constant A^* and the temperature dependence. Therefore, the J-V characteristics in Fig. 3(b) qualitatively reveal that the electron injection barrier between Alq_3 and LiF/Al has been increased after the electrical aging process. The increased injection barrier height not only causes the driving voltage increases but also results in the recombination zone shift with luminance degradation. The possible reason to cause the change of electron injection barrier height can be a diffusion of LiF molecule into organic layer of Alq_3 from the Al cathode. It is still in controversy whether the chemical bond of LiF in the electrical aging is broken or not.[22] However, if any form of LiF (or free Li atom) diffuses into organic layer of Alq_3 in the electrical aging, it will induce the variation of electron injection barrier height. Another possible explanation could be the oxidation of the organic/cathode interfacial region accelerated by a high electrical field of aging.

We have demonstrated that the increase of electron injection barrier height is one of the most critical parameters that are responsible for the degradation of OLEDs. The electrical and physical properties of hole transporting layer of NPB have not been changed before and after the electrical aging process. The bulk properties of electron trap state in energy and electron mobility of Alq_3 were also almost identical to the initial properties. Only the electron injection barrier height from LiF/Al to Alq_3 was changed during the electrical aging process. The degradation of the typical double-layered structure of OLEDs can be mainly ascribed to the electron injection barrier height increase.

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