<<Research Paper>> Journal of the Korean Vacuum Society Vol.15 No.1, January 2006, pp.64~72

Degradation Mechanisms of Organic Light-emitting Devices with a Glass Cap

Yong Suk Yang*, Hye Yong Chu, Jeong-Ik Lee, Sang-He Ko Park,
Chi Sun Hwang, Sung Mook Chung, Lee-Mi Do, and Gi Heon Kim

Electronics and Telecommunications Research Institute, Daejeon 305-350

(Received December 9, 2005)

We demonstrated organic light-emitting devices (OLEDs) based on the organic thin-film materials such as tris-(8-hydroxyquinoline) aluminum (Alq_3). The structure of OLEDs was vacuum deposited upon transparent and thin glass substrates pre-coated with a transparent, conducting indium tin oxide thin film. The luminance characteristics, current, capacitance, and dispersion factor for degraded OLEDs, which were made by various bias currents (0.5 mA $\leq I_{Bias} \leq$ 9 mA), are studied. The current dependences of lifetime were divided at approximately 2 mA, and they represented nearly linear behaviors but had different slopes in a logarithmic plot of lifetime versus bias current. With lighting OLEDs, the anomaly of capacitance, as shown in the C-V curve, occurred because of two factors, polarization in the bulk of organic materials and the interface between the metal and organic layers. In decayed OLEDs that had lower bias currents of less than 2 mA, it was found that the degradation of luminance was related to both the decrease of polarization and to the lowering of the injection barrier.

Keywords : OLED, Lifetime, Capacitance, Energy barrier height

Ⅰ. Introduction

Organic light emitting devices(OLEDs) have drawn particular attention due to their potential use in various lighting applications, including lighting purposes. [1-5] But, Tang and VanSlyke have reported a fatal shortcoming in these devices: OLEDs that use well-known EL materials such as tris-(8-hydroxyquinoline) aluminum (Alq_3) have shown a decrease of up to 50 % of their initial EL intensities after 100 h. [1] Moreover, Hamada *et al.* have found that operating OLEDs in air resulted in a 99 % loss of EL intensity in as little as 150 min. [6] This very short device lifetime is a very serious problem that must be overcome for OLEDs to be used to their full potential in conditions where moisture and oxygen are present. [7,8] In addition, the lifetime of OLEDs can also be negatively affected by other factors, such as the OLEDs structure, substrate treatment (especially for substrate- coated ITO), doping in the hole transport layer or emission layer, and so on.[9]

This paper reports on the fabrication and lifetime properties of OLEDs encapsulated by a glass cap. This encapsulation method has been

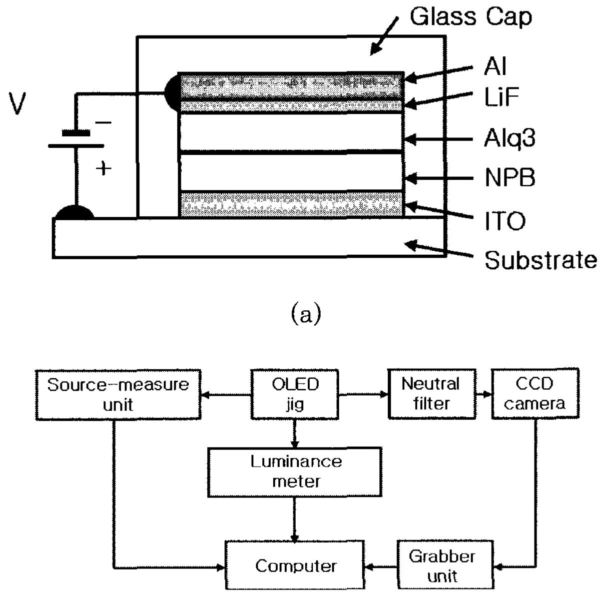
---

* [E-Mail] jullios@etri.re.kr

conventionally used for the passivation of OLEDs based on glass substrates and is composed of a glass can containing desiccants.[10] The glass cap blocks the entrance against air effectively but it cannot prevent the progress of internal degradation of OLEDs by a high DC current. The decay of luminance and the change of capacitance for encapsulated OLEDs were investigated in terms of their lifetime and electrical properties, respectively.

II. Experimental

Small molecular OLEDs were fabricated by a vacuum deposition technique and their configuration was as follows: indium-tin oxide (ITO, 150 nm) /N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB, 50 nm)/ tris(8-hydroxyquinoline) and aluminium (Alq_3, 60 nm)/LiF (1 nm)/Al (100 nm) on a glass substrate. The OLED structure is presented in Fig. 1 (a). ITO-coated glass substrates with a surface resistance of 10 ~ 20 Ω sq^{-1} were cleaned in ultrasonic baths of acetone and methanol. The NPB and Alq_3 were the hole transporting layer and the emitting layer, respectively. The cathode was the bi-layer of LiF and aluminum. The layers of NPB and Alq_3 as well as the metallic cathode were all deposited by thermal evaporation (below 10^{-3} Pa). The area of the test pixel was approximately 4 mm^2. The devices were encapsulated by a conventional method using a glass cap and desiccants. The process of the glass encapsulation was carried out under a nitrogen glove box. In order to evaluate the effect of the glass encapsulation, OLEDs without encapsulation and with the glass cap were prepared and the degradations of their emission efficiency and luminescence were examined. The electrical, capacitance, and lifetime properties were measured at room temperature by a source-measure unit (Keithlrey 238), an impedance analyzer (HP4195), and photometers (Minolter LS-100 and CS-1000), respectively. Emission images of the OLEDs were taken throughout the lifetime measurement by a black-and-white CCD camera, as described in Fig. 1(b). All the temperature-dependent data were obtained by a low temperature system using a cryostat chamber and a temperature controller (Lake Share 340).



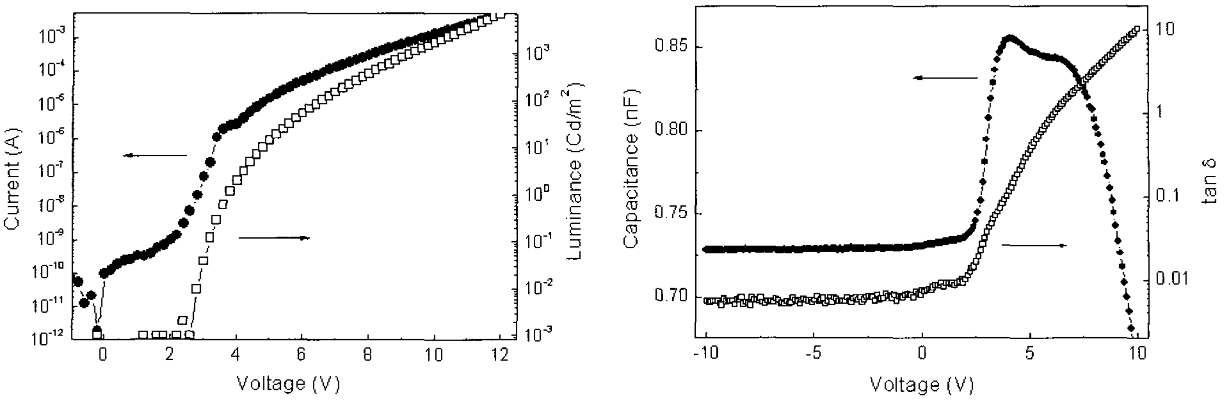
(a)

(b)

Fig. 1. (a) The OLED structure studied, and (b) the block diagram of electric and luminance measurement system.

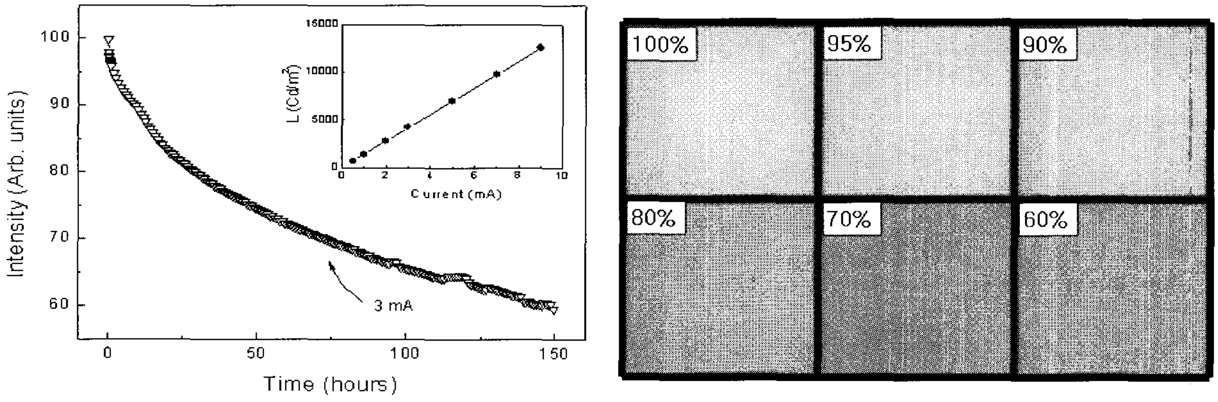
III. Results and Discussion

Figure 2(a) shows the typical current - voltage - luminance (*I-V-L*) curves of. OLEDs. The onset bias was approximately 3.8 V, corresponding to an average electric field of approximately 0.35 MV/cm. The peak external quantum efficiency was approximately 2 % at



(a) (b)

Fig. 2. (a) Typical current-voltage-luminance (*I*–*V*–*L*) curves, and (b) *C*–*V* and tan δ–*V* characteristics of OLEDs. The inset of Fig. 2(a) is the luminance-current (*L*–*I*) characteristics of fabricated OLEDs.



(a) (b)

Fig. 3. (a) Decay curves of normalized luminance for a constant bias current of 3 mA, and (b) luminance images observed by a black-and-white CCD camera.

11.4 V, and a brightness of 7.1 × 10^3 cd/m^2 was measured at 12 V. Figufre 2(b) represents the capacitance-voltage (*C*–*V*) and dispersion factor - voltage (*tan δ*–*V*) characteristics of the OLEDs. The *C*–*V* measurements were performed for the diode structure of OLEDs by applying a small AC amplitude of 10 mV and a frequency of 10 kHz. The sweep rate was 1.5 V/s. The area of the capacitor and the total thickness of organic layers are 4 mm^2 and 110 nm, respectively. A diode behavior was observed featuring a steep increase in *tan δ* in the forward direction. This indicates the efficient charge-carrier injection and transport above a certain voltage called a turn-on voltage. Above the turn-on voltage, anomalies of capacitance occurred; these might be related to the formation and alignment of dipole moments in the bulk of organic materials and the interface between the metal and organic layers. [11]

Figure 3(a) shows the typical decay curve of normalized luminance for 4 mm^{2-}encapsulated OLEDs on a glass substrate. The devices were tested at room temperature and ambient pressure under the condition of DC bias currents. The magnitude of the bias current was 3 mA. Initial luminance of the device was approximately 4.2 × 10^3 cd/m^2, as shown in the inset of Fig. 3(a). The operational lifetime was measured at 5-minute intervals from the initial luminance to a degradation of 60 %. Figure 3(b) illustrates the black-and-white CCD images of encapsulated OLEDs operating at 3 mA. In the range of high luminance above 120 cd/m^2, a CCD image was observed through an optically neutral filter. The photographs of 0, 5, 10, 20, 30, and 40 %-decayed OLEDs under the constant currents represented the gradual decrease of luminance. In the decayed images, the deviation of brightness was less than 5 %, and no dark spots or edge shrinkages appeared.

Figure 4(a) shows the decay curves of normalized luminance for 4 mm^2-encapsulated OLEDs on a glass substrate. The magnitude of the DC bias current was between 0.5 mA and 9 mA. Initial luminances for all devices were between 6.8 × 10^2 cd/m^2 and 1.25 × 10^4 cd/m^2, as shown in the inset of Fig. 3(a). The operational lifetime was measured at 5-minute intervals from the initial luminance to a degradation of 60 %. As the bias current became larger, the lifetime at x % ($x < 100$) of the starting value became shorter and shorter. This result indicates that the lifetime of OLEDs might depend on not only the influences of moisture and oxygen but also on the magnitude of the bias currents. For comparison, the lifetimes of devices with and without glass cap encapsulation were investigated under the same bias current of 0.5 mA. The devices without encapsulation had a very short lifetime of approximately 75 h and their images exhibited many dark spots after the lifetime measurement at atmosphere. Figure 4(b) describes the logarithmic plot of lifetime versus bias current for the encapsulated OLEDs, and was obtained from the data of luminance decay shown in Fig. 4(a). The 60 %, 70 %, 80 %, and 90 % points of the initial luminance were introduced into this figure. The current dependence of lifetime was changed to approximately 2 mA. Specifically, the current dependence of lifetime in the lower bias current region of less than 2 mA ($I_{Bias} \leq 2$ mA) represented a nearly linear behavior; that is, $log(t) \propto n\ log(i)$, where t is the lifetime, n the proportional factor, and i the bias current. The analogous tendency was also observed in the region higher than 2 mA ($I_{Bias} > 2$ mA). The factors n were approximately −1.35 and −2.5 in the regions of $I_{Bias} \leq 2$ mA and $I_{Bias} > 2$ mA, respectively. The lifetimes measured in $I_{Bias} \leq 2$ mA were smaller than

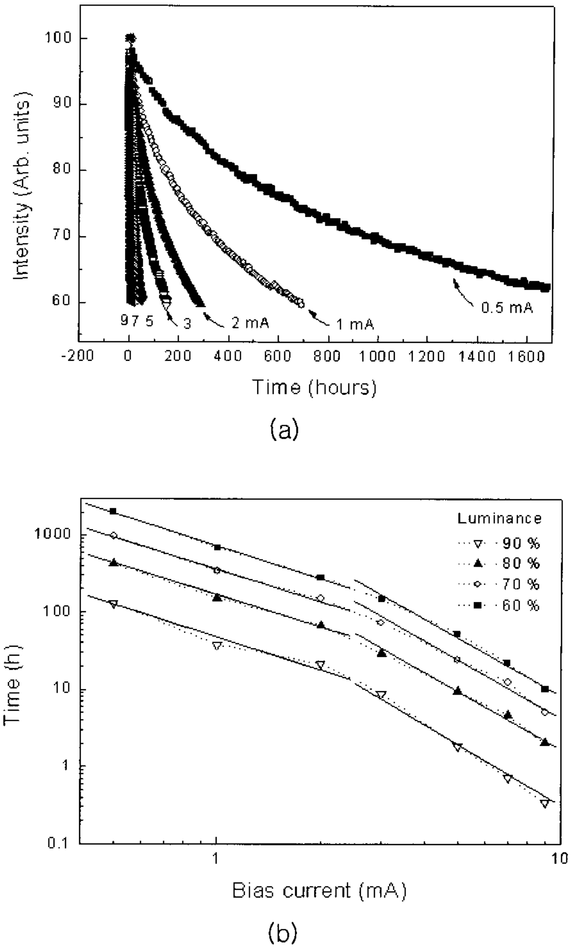


Fig. 4. (a) Decay curves of normalized luminance for the different bias currents and (b) logarithmic plot of lifetime versus bias current in encapsulated OLEDs.

the values extrapolated from the linear fitting of data in $I_{Bias} > 2$ mA.

Figures 5(a) to (h) illustrate the black-and-white CCD images of encapsulated OLEDs operating at 1, 3, 5, and 7 mA, respectively. The photographs of 40 %-decayed OLEDs under the constant currents are given in Figs. 5(b), (d), (f), and (h), respectively. In these images (Figs. 5(b), (d), (f), and (h)), the deviation of brightness was less than 5 %, and no dark spots or edge shrinkages appeared. It at first seemed possible that encapsulation with the glass cap effectively protected the devices from moisture and oxygen and would prolong the lifetime of the device. However, the lifetime of the OLEDs is also greatly affected by the bias current, so the lifetime at I_{Bias} of 7 mA was approximately 30 times shorter than at I_{Bias} of 1 mA.

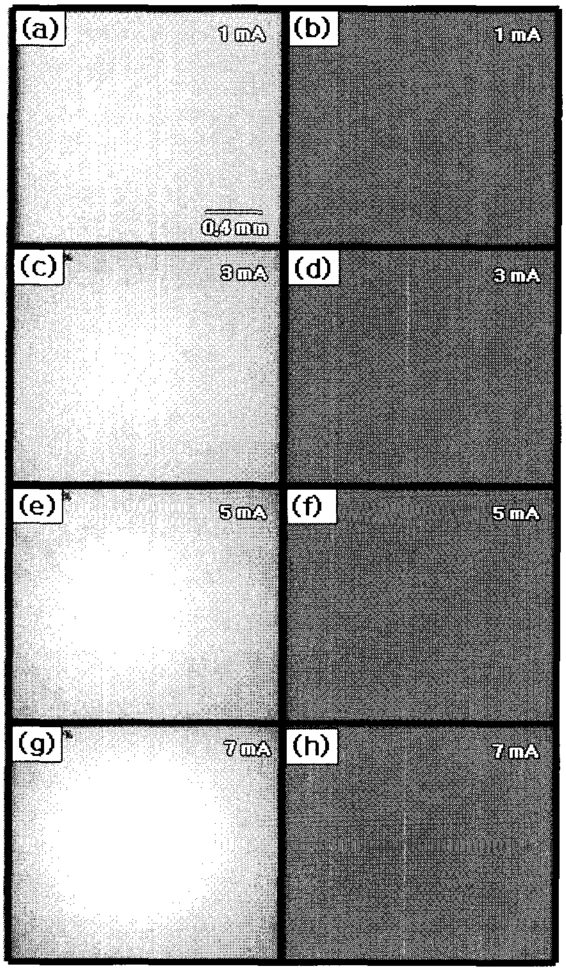


Fig. 5. Luminance images observed by a black-and-white CCD camera. (a), (c), (e), and (g) are the initial images of OLEDs operating at 1, 3, 5, and 7 mA, respectively. (b), (d), (f), and (h) are the images of 40 %-decayed OLEDs under the constant currents of 1, 3, 5, and 7 mA, respectively.

The *C*−*V* and *tan* δ−*V* characteristics for the different luminance decays between 0 % and 50 % are described in Figs. 6(a) and (b), respectively. The bias current was 1 mA. Figure 6(c) shows the voltage dependence of the accumulated charge (ΔQ) for the different luminance decays. The ΔQ is obtained by integrating the anomaly of capacitance as

$$\Delta Q = \int_0^V (C(V) - C_o)\, dV \quad ,$$

where $C(V)$ is the capacitance at a voltage V and C_o is the capacitance at V = 0 V. The charge density in the initial state was calculated to be approximately 10^{11} cm^{-2}, which was less than the surface charge densities ($10^{12} \sim 10^{13}$ cm^{-2}) between Alq$_3$ and metals reported by Lee *et al.*[12] With decreasing luminance, the threshold voltage shifted toward a higher voltage and the maximum of ΔQ decreased from 0.62 nC to 0.09 nC.

To study the characteristics of the injection barrier for initial and 50 %-decayed OLEDs, the temperature dependence of static currents was investigated in the region of low temperatures. With an external voltage of 15 V, the static current was measured at a constant temperature. Figure 7(a) depicts a plot of $log(I)$ versus V measured at various low temperatures for initial OLEDs. Figures 7(b) and (c) presents the I−V curves for degraded OLEDs under the bias currents of 1 mA and 7 mA, respectively.

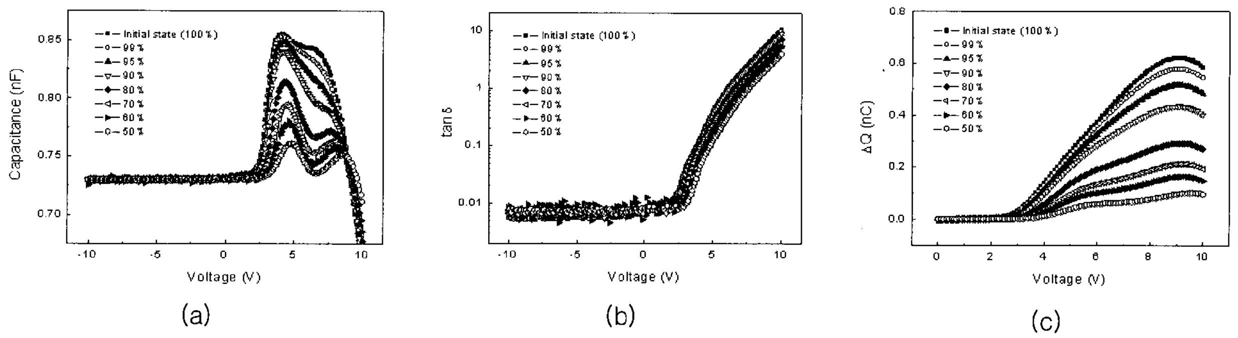


Fig. 6. (a) $C-V$, (b) tan $\delta-V$, and (c) ΔQ-V characteristics for the different luminance decays of encapsulated OLEDs. The bias current was 1 mA.

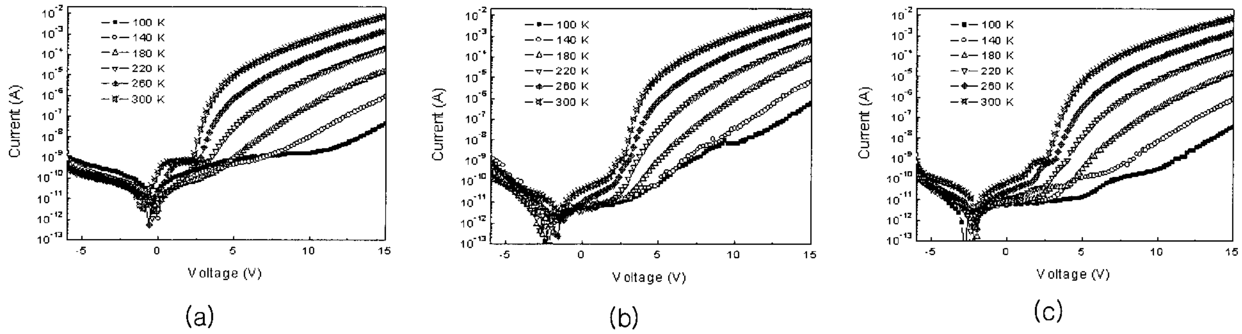


Fig. 7. (a) $I-V$ characteristics of initial OLEDs measured at various low temperatures. Temperature- dependent $I-V$ curves of 50 %-decayed OLEDs under the constant currents of (b) 1 mA and (c) 7 mA.

Figure 8(a) shows a plot of J/T^2 versus $1000/T$, where J is the current density and T is the temperature. Two distinguishable tendencies of the static current in leaning were evident in the range of 100 K to 330 K. The height of the injection barrier, commonly called a Schottky barrier, in the diode structure of the OLEDs was calculated by using the field-enhanced Schottky emission model.[13-15] As given in Fig. 8(b), the barrier heights at higher and lower temperatures in the initial state of OLEDs were 0.228 eV ($T >$ 167 K) and 0.092 eV ($T <$ 167 K), respectively. The presence of a barrier to electron injection in the Alq3/cathode interface at room temperature has been studied by Barth *et al.* [15] and Hung *et al.* [16] The height in $T >$ 167 K agreed with the reported values (0.2 ~ 0.3 eV). [15, 16] As the bias current decreased in the region of $I_{Bias} \leq$ 2 mA, the barrier heights were reduced to 0.181 eV and 0.075 eV at T >

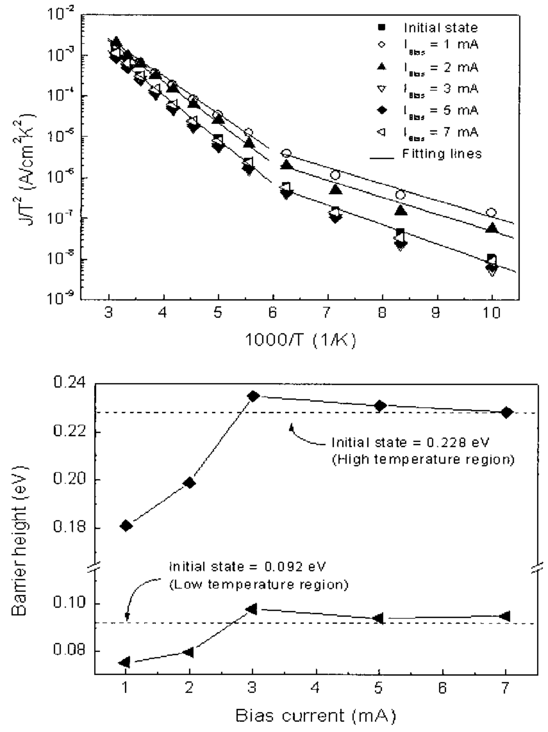


Fig. 8. (a) Temperature-dependent current curves and (b) barrier heights for the initial and 50 %-decayed OLEDs. The level of bias currents was from 1 mA to 7 mA.

167 K and T 〈 167 K, respectively. The lowering of the barrier height caused reduced polarization in the interface between the metal and organic layers. It might also have affected the internal field and the recombination zone of electrons and holes, thus generating weak EL and, moreover, accelerating the decay of luminance. This result coincided with other findings, such as the *C−V* curves and spectrum data for the different bias currents. Finally, we found that the state of the degraded OLEDs in the condition of $I_{Bias} \leq 2$ mA, contrary to $I_{Bias} > 2$ mA, affected the decrease of polarization, the blue shift of spectrum (or the change of recombination zone), and the lowering of barrier height.

Ⅳ. Summary

We fabricated the encapsulated OLEDs on a glass substrate and studied their electric characteristics by using, *I−V−L*, *C−V*, and *tan δ−V* measurements. The operational lifetime of OLEDs was measured from the initial luminance to a 50 % degradation at a constant current. The luminance decreased after the lifetime measurement in accordance with the magnitude of the bias currents. Above the turn-on voltage, the anomaly of capacitance in a *C−V* curve was observed by the formation of polarization in bulk and in the organic/metal interface. Phenomena such as the diminution of polarization, the shift of spectrum, and the lowering of barrier height were discovered in the degraded OLEDs under the bias currents of $I_{Bias} \leq 2$ mA.

Acknowledgements

This work has supported financially by the Korean Ministry of Information and Communication.

References

[1] C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).

[2] K. Nagayama, T. Yahagi, H. Nakada, T. Tohma, T. Watanabe, K. Yoshida, and S. Miyaguchi, Jpn. J. Appl. Phys. **36**, L1555 (1997).

[3] G. Parthasarathy, P. E. Burrows, V. Khalfin, G. G. Kozlov, and S. R. Forrest, Appl. Phys. Lett. **72**, 2138 (1998).

[4] C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J. M. Shaw, Science **283**, 822 (1999).

[5] Y. S. Yang, S. H. Kim, J. Lee, H. Y. Chu, L. Do, H. Lee, J. Oh, and T. Zyung, Appl. Phys. Lett. **80**, 1595 (2002).

[6] Y. Hamada, C. Adachi, T. Tsutsui, and S. Saito, Jpn. J. Appl. Phys. **31**, 1812 (1992).

[7] H. Aziz, Z. D. Popovic, C. P. Tripp, N. Hu, A. Hor, and G. Xu, Appl. Phys. Lett. **72**, 2642 (1998).

[8] K. K. Lin, S. J. Chua, and S. F. Lim, J. Appl. Phys. **90**, 976 (2001).

[9] H. Aziz, Z. D. Popovic, N. Hu, A. Hor, and G. Xu, Science **283**, 1900 (1999).

[10] P. E. Burrows, V. Bulovic, S. R. Forrest, L. S. Sapochak, D. M. McCarty, and M. E. Thompson, Appl. Phys. Lett. **65**, 2922 (1994).

[11] G. G. Malliaras, Y. Shen, D. H. Dunlap, H. Murata, and Z. H. Kafafi, Appl. Phys. Lett. **79**, 2582 (2001).

[12] S. T. Lee, X. Y. Hou, M. G. Mason, and C. W. Tang, Appl. Phys. Lett. **72**, 1593 (1998).

[13] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1969), pp. 492−501.

[14] Y. S. Yang, S. J. Lee, S. H. Kim, B. G. Chae, and M. S. Jang, J. Appl. Phys. **84**,

5005 (1998).

[15] S. Barth, U. Wolf, H. Bässler, P. Müller, H. Riel, H. Vestweber, P. F. Seidler, and W. Rieβ, Phys. Rev. B **60**, 8791 (1999).

[16] L. S. Hung, L. S. Liao, C. S. Lee, and S. T. Lee, J. Appl. Phys. **86**, 4607 (1999).

≪연구논문≫ 한국진공학회지 제15권 1호, 2006년 1월, pp.64~72

유리 덮개로 보호된 OLED 소자의 발광특성 저하 연구

양용석* · 추혜용 · 이정익 · 박상희 · 황치선 · 정승묵 · 도이미 · 김기현

한국전자통신연구원, 대전 305-350

(2005년 12월 9일 받음)

우리는 tris-(8-hydroxyquinoline) aluminum (Alq3)와 같은 단분자 유기물 박막을 사용하여 유기물 발광 소자(OLEDs)를 제작하였다. OLEDs는 ITO가 증착된 유기 기판 위에서 제조되었고, 수명 측정 이후의 OLEDs에 대한 발광, 축전 용량, 유전 손실 특성 등을 측정하였다. 여기서, 수명 측정을 위하여 사용한 인가 전류는 0.5 mA 에서 9 mA 까지였고, 수명의 인가 전류 의존성은 약 2 mA 부근에서 다르게 관찰되었다. C-V 특성 곡선에서 나타난 축전 용량의 봉우리들은 유기물 내의 분극과 유기물과 금속의 경계에서 나타난 분극의 영향으로 추측된다. 그리고, 2 mA 보다 낮은 전류 하에서 수명 측정 후 발광특성이 저하된 OLEDs에서는 소자 내의 분극 크기의 감소와 전하 유입 장벽의 낮아짐이 같이 관찰되었다.

주제어 : 유기 발광소자, 수명, 축전용량, 에너지 장벽 높이

* [전자우편] jullios@etri.re.kr