

Characteristics of plasma polymerized para-xylene films as a passivation layer of organic light emitting diodes

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Abstract

For the longevity of OLEDs, passivation of OLEDs is an important process step since organic materials used in OLEDs are very vulnerable to moisture. In this work, the passivation effect of the plasma polymerized para-xylene (PPpX) layers was studied. The PPpX layers deposited by PECVD were formed on top of the cathode with various plasma powers of 50 - 90 W. Passivation effect of PPpX was significantly dependent upon the deposition plasma power of the PPpX film. The lifetime of OLEDs with the 70 W deposited PPpX passivation layer was about 5 times longer than that of the control device.

Key Words : organic light emitting diodes (OLEDs), passivation, plasma polymerized para-xylene, lifetime, permeability

Since demonstration of the double layer device was reported by Tang and Vanslyke in 1987 [1], the research on organic light emitting diodes (OLEDs) has been proceeded actively. OLEDs have been attracting a great deal of attention as flat panel displays in the next generation, which is due to their superior advantages such as low operating voltage, wide viewing angle, and ease of fabrication [2 - 4]. The brightness and the color tunability of OLEDs approached commercialization, but the short lifetime of OLEDs is still a major obstacle. The organic materials used in OLEDs are very vulnerable to moisture and oxygen in ambient, so that the passivation process is very important for the increased

lifetime of OLEDs [5 - 7]. The conventional passivation method used a sealing canister or glass with UV-cured epoxy. Such a passivation method can increase the weight and the thickness of OLEDs, and also this process is unsuitable for top emission OLEDs and flexible OLEDs. Recently, passivation of OLEDs by thin films has attracted a growing attention, because the thin film passivation can overcome many of the disadvantages of the conventional passivation method. Yamasita *et al.* used a multi-layer of poly-2-chloro-p-xylylene (PCPX) (0.6 μm) and poly-p-xylylene (PPx) (0.6 μm) as a passivation film [8]. Recently, Vitex System Inc. also introduced the BarixTM passivation

film that utilizes a decoupling layer of polyacrylate between multiple layers of barrier material such as Al_2O_3 [9].

An application of plasma polymer films to improve lifetime of OLEDs has been reported by Kho *et al* [10]. The plasma polymer films can be deposited by plasma enhanced chemical vapor deposition (PECVD) [11]. In PECVD of plasma polymers, precursors are transported into the deposition chamber, are activated and/or decomposed into reactive species by plasma and then condense on the substrate, forming thin films of polymers. Because of the highly cross-linked network structure, plasma polymer films are dense and chemically stable [12,13]. The plasma polymer film has a great adhesion to underlying layers, and it can be deposited at room temperature. Aforementioned properties of the plasma polymer films indicate

that plasma polymers deposited by PECVD can be an effective passivation layer for OLEDs [14].

In this work, we report on the characteristics of the plasma polymer film as a passivation layer of OLEDs. The plasma polymer film was deposited by PECVD using para-xylene as the precursor, and was referred to as plasma polymerized para-xylene (PPpX). In our experiment, the effect of deposition plasma power on the characteristics of the PPpX passivation layer was notable, and the variation of PPpX property with change of deposition plasma power was chiefly studied.

Figures 1 (a) show the device structures of OLEDs with the PPpX layer (passivated device) and figures 1 (b) show the chemical structure of para-xylene, tris-(8-hydroxyquinoline) aluminum (Alq_3), and N, N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD), respectively. OLEDs

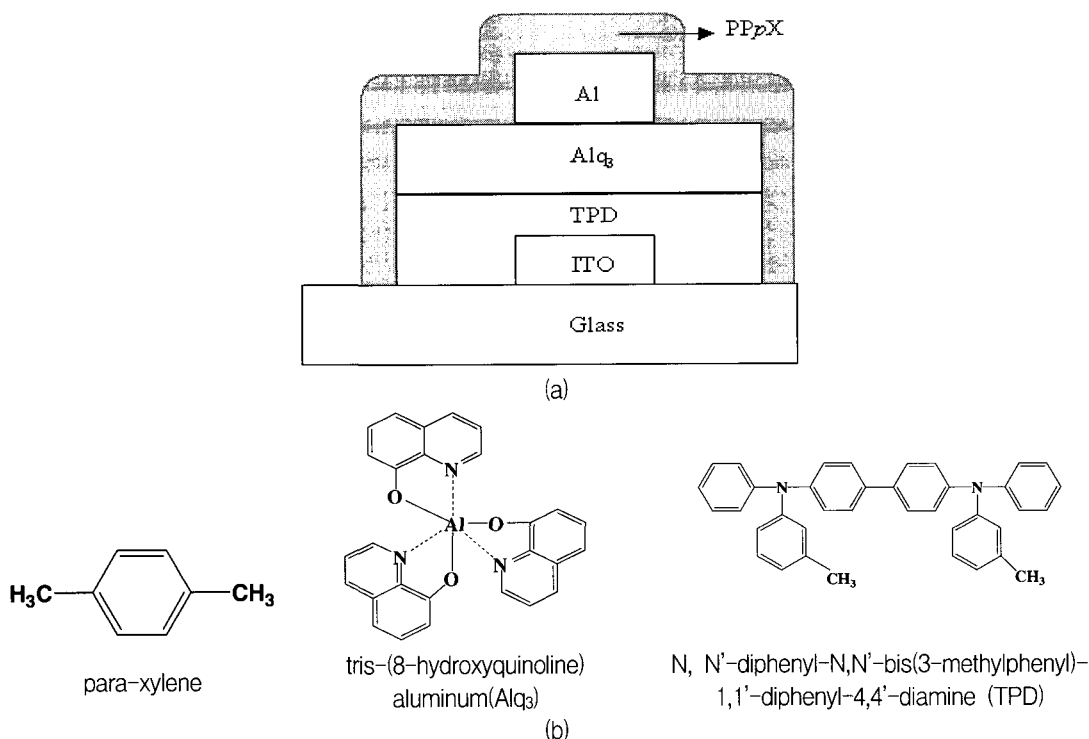


Figure 1. Schematic diagrams of the OLEDs with the PPpX passivation layer (a) and chemical structures of para-xylene, tris-(8-hydroxyquinoline) aluminum (Alq_3), and N, N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD) (b).

without and with the PpX layer was referred to as control device and passivated device. In our experiments, indium-tin-oxide (ITO) coated glass was used as the substrate for OLEDs. Before being loaded into the deposition chamber, the ITO coated substrates were cleaned in ultrasonic bath with acetone, methanol, and deionized water, respectively, and then dried with nitrogen blowing. TPD and Alq₃ were used as the hole transport layer (HTL) and the emitting layer (EML), respectively. The thickness of TPD and Alq₃ were 32 and 48 nm, respectively. The top cathode was prepared by sequential deposition of a thin (1 nm) LiF layer and a thick (120 nm) Al over-layer by thermal evaporation. Some of the as-prepared OLED devices were moved into the PECVD chamber for deposition of the PpX passivation layer. The para-xylene used as a precursor was contained in a bubbler and carried into the deposition chamber by Ar carrier gas. Deposition plasma power of PpX was varied in the range of 50–90 W, under the deposition pressure of 0.2 torr at room temperature. The thickness of the PpX films was fixed at 280 nm. OLEDs were operated in air at room temperature for all the experiments. For electrical measurements, a Keithley 2400 electrometer was used as a voltage source and current measurement equipment. The brightness characteristics of OLEDs were investigated by measuring the photocurrent induced by the light emission from the OLEDs using a Keithley 485 picoammeter.

Figure 2 shows the deposition rate of the PpX layer as a function of the deposition plasma power. As the plasma power was increased from 50 W to 90 W, the deposition rate decreased substantially, from 16.1 nm/min to 5.3 nm/min. In PECVD of plasma polymers, charged film-forming species can be incident onto the growing surface of the film with high kinetic energies obtained from the electric field. Depending on the depo-

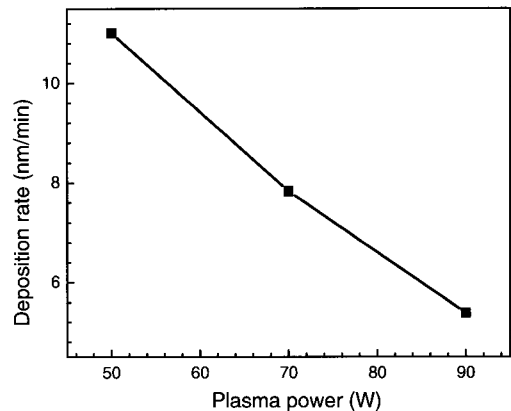


Figure 2. Deposition rate of the PpX film as a function of the plasma power.

sition condition, these incident species can be incorporated into the films or can sputter out parts of the growing films or both. In case of Fig. 2, it is thought that, the deposition rate decreased with increasing plasma power due to increase of sputtering of the growing film surface by energetic charged species, as was shown in ref. [15]. Similar behavior of deposition rate versus plasma power was observed for the PECVD deposition of metal-nitride using the same experimental setup used in this work [16]. With respect to the density of the plasma polymers, it is expected that the density of the plasma polymer increased as the deposition plasma power increases, because the previous report showed that the refractive index, which is related to the density of a film, of the plasma polymer increased as the deposition plasma power increases [16].

Figures 3(a) and 3(b) show characteristics of the current density–voltage (J–V) and luminance–voltage (L–V) of the control device and the passivated devices. The control device was referred to as OLED(0), and OLEDs whose PpX passivation layer was deposited with plasma power of 50, 70, and 90 W were referred to as OLED(50), OLED(70), and OLED(90), respectively. The passivated devices showed similar J–V and L–V

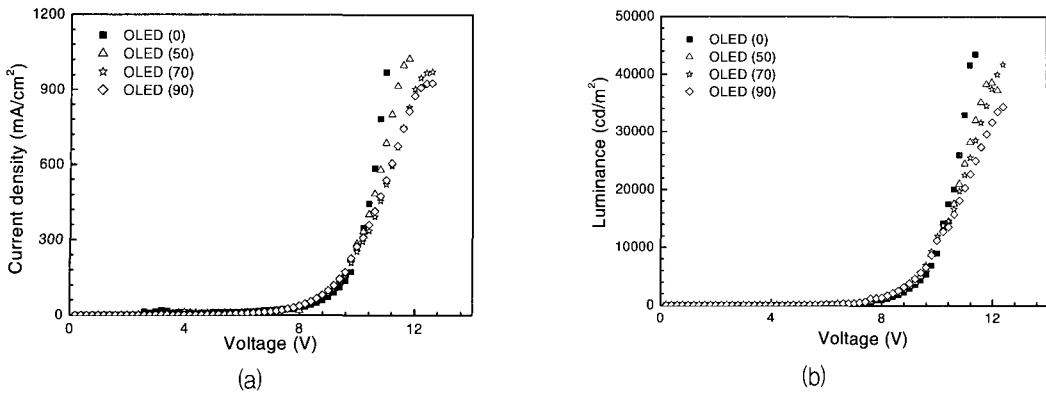


Figure 3. Current density versus applied voltage (a) and brightness versus applied voltage (b) for OLEDs without and with the PPpX passivation layer.

characteristics to those of the control device, indicating that during the deposition of the PPpX passivation films, the PECVD process, which involves radicals, ions, electrons, and energetic radiations, did not damage the OLEDs notably.

Performance of our OLEDs shown in Figure 3, however, is inferior to those reported elsewhere [5,6]. The inferior performance of our OLEDs can be considered due to several reasons including the followings. In our experiments, the organic layers were exposed to room air before deposition of the LiF/Al cathode layers, which was inevitable for alignment of the shadow mask for LiF/Al deposition. The ITO/TPD/Alq₃/LiF/Al structures were also exposed to room air when they were loaded into the PECVD deposition chamber. Due to the exposure of the organic layers to room air before the deposition of the PPpX passivation layer, even though the PPpX film reduced water vapor penetration into the OLEDs, there is a certain amount of water vapor inside the OLED devices, resulting in some degradation of the OLED devices. Figure 4 shows the time decay characteristics of the OLEDs with 280-nm passivating PPpX films deposited with various plasma powers. During OLED lifetime experiments, a current density of $\sim 0.2 \text{ mA/cm}^2$ was applied to OLEDs, yielding an initial brightness of 300

cd/m^2 . The time duration required for the brightness of OLEDs to become half the initial value was referred to as the lifetime of OLEDs. The lifetime of OLED(0) was 3.28 h, while the passivated devices OLED(50), OLED(70), and OLED (90) were 5.40, 17.41, and 9.54 h, respectively. Lifetime of the passivated devices increased with the increase of the plasma power up to about 70 W. The lifetime of OLED(70) was about ~ 5 times longer than that of OLED(0). OLED(90), however, showed a shorter lifetime than OLED (70). It is suggested that the degradation of OLEDs is chiefly due to two factors, intrinsic and extrinsic [17]. The intrinsic factor

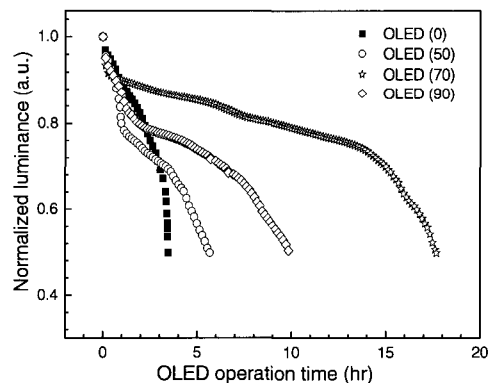


Figure 4. Time decay characteristics of the OLEDs with 280-nm passivating PPpX films deposited with various plasma powers.

involves factors such as defects and/or traps in the device, and degrades the OLED device in the early stage of the operation. On the other hand, the extrinsic factor is related to factors such the device fabrication atmosphere and/or water vapor penetration, and reduce the performance of the OLEDs in the later stage of the OLED operation. In Figure 4, OLED(50) and OLED(90) showed a faster degradation than OLED(0) in the very early stage of operation probably due to the intrinsic factor. However, in the later stage, OLED(0) degraded much faster than OLED(50) and OLED(90) due to the extrinsic factor such as high permeation of water vapor.

Figure 5 shows the optical images observed from outside of the glass substrate as a function of the PPpX deposition power. As the plasma power increased to 70 W, density of bubbles decreased. Further increase of plasma power to 90 W increased the bubble density. Previous works [5,18] suggested that bubbles, increase of which reduces the lifetime of OLEDs, are formed chiefly by hydrogen evolution from water vapor penetrated into the OLED devices through an electrochemical reaction during OLED operation. The data shown in Figure 5 are consistent with the data in Figure 4, in that an OLED with a longer lifetime shows a lower bubble density.

Figures 6 (a) and 6 (b) show the surface morphologies and root mean square (RMS) roughness values of the PPpX films deposited on glass substrates measured by atomic force microscopy (AFM). As the deposition power increased to 70 W, surface morphology improves and RMS roughness decreases. At 90 W, however, surface morphology becomes worse and RMS roughness gets bigger than at 70 W. It is thought that improvement of surface morphology and roughness reduced the penetration of water vapor into the interior of the OLED devices, decreasing bubble density and thus increasing OLED lifetimes. With good surfaces, the passi-

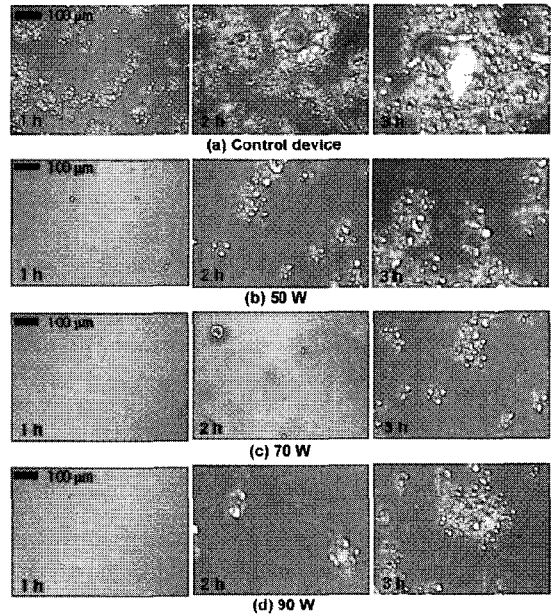


Figure 5. Optical image of the OLED with various operation time as a function of the PPpX deposition power. The PPpX layers were not deposited (a), were deposited at 50 W (b), at 70 W (c), and at 90 W (d).

vation layer has a reduced density of defects such as pinholes and pores, which can be paths of water vapor penetration. Reduction of bubble formation and increase of OLED lifetime by improving the surface morphology of the cathode layer were also reported in Ref. 16, in which no passivation layer was employed and the Al cathode layer acted as a blocker of water vapor.

In conclusions, the PPpX passivation layer deposited by PECVD with a suitable deposition condition increased the lifetime of OLEDs. The PPpX layers were formed on top of the OLEDs, and performance of the passivated devices was not inferior to the control device, indicating that the PECVD process for the deposition of PPpX layer did not degrade the OLEDs. As the PPpX deposition power is increased to 70 W, the passivation effect increased. Lifetime of the OLED with the PPpX passivation layer deposited at 70 W

was ~ 5 times longer than that of OLED without the PpX layer. Further increase of plasma power to 90 W yielded worse surface morphology and roughness, resulting in reduced passivation effect.

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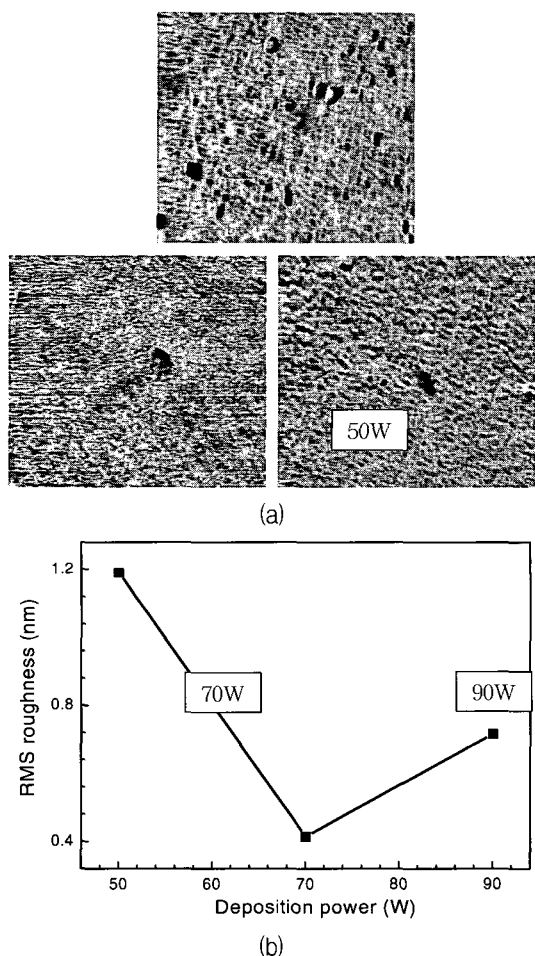


Figure 6. Surface morphologies (a) and RMS roughnesses (b) of the deposited PpX films with various plasma powers.

References

- [1] C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- [2] C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys. Lett.* **65**, 3610 (1989).
- [3] C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.* **56**, 799 (1990).
- [4] Y. Ohmori, A. Fujii, M. Uchida, C. Morishima, and K. Yoshino, *Appl. Phys. Lett.* **62**, 3250 (1993).
- [5] M. Schaer, F. Nuesch, D. Berner, W. Leo, and L. Zuppiroli, *Adv. Funct. Mater.* **11**, 116 (2001).
- [6] A. B. Chwang, M. A. Rothman, S. A. Mao, R. H. Hewitt, M. S. Weaver, J. A. Silvernail, K. Rajan, M. Hack, J. J. Brown, X. Chu, L. Moro, T. Krajewski, and N. Rutherford, *Appl. Phys. Lett.* **83**, 413 (2003).
- [7] Y. Kijima, N. Asai, and S. I. Tamura, *Jpn. J. Appl. Phys.* **38**, 5274 (1999).
- [8] K. Yamashita, T. Mori, and T. Mizutani, *J. Phys. D: Appl. Phys.* **34**, 740 (2001).
- [9] P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. K. Shi, M. Hall, E. Mast, C. Bonham, W. Bennett, and M. B. Sullivan, *Displays* **22**, 65 (2001).
- [10] S. Kho, D. Cho and D. Jung, *Jpn. J. Appl. Phys.* **41**, L1336 (2002).
- [11] D. Jung, H. Pang, J. H. Park, and Y. Son, *Jpn. J. Appl. Phys.* **38**, L84 (1999).
- [12] S. Cho, Z. Park, J. Kim, and J. Boo, *Surf. Coat. Tech.* **174**, 1111 (2003).
- [13] M. Yoshida, T. Tanaka, S. Watanabe, M. Shinohara, J. Lee, and T. Takagi, *Surf. Coat. Tech.* **174**, 1033 (2003).
- [14] L. F. Quattropani, P. Groening, D. Ramseyer, and L. Schlapbach, *Surf. Coat. Tech.* **125**, 377 (2000).
- [15] H. Yasuda, *Plasma polymerization*, (Academic press, 1985) pp. 179.
- [16] Y. C. Quan, J. Joo, and D. Jung, *Jpn. J. Appl. Phys.* **38**, 1356 (1999).
- [17] W. Reiss, *Organic Electroluminescent Materials and Devices*, (1997) Chap. 2.
- [18] S. M. Jeong, W. H. Koo, S. H. Choi, S. J. Jo, H. K. Baik, S. J. Lee, and K. M. Song, *Thin Solid Films* **475**, 227 (2005).