Plasma polymer passivated organic light emitting diodes

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Abstract

Plasma polymerized para-xylene (PPpX) thin films deposited by plasma enhanced chemical vapor deposition (PECVD) were used to passivate the organic light emitting diodes (OLEDs). For OLEDs, indium tin oxide (ITO), N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD), tris-(8-hydroxyquinoline) aluminum (Alq$_3$) and aluminum (Al) were used as the anode, the hole transport layer (HTL), the emitting layer (EML) and the cathode, respectively. The OLED device with the PPpX passivation film (passivated device) showed similar electrical and optical characteristics to those of the OLED device without the PPpX passivation film (control device), indicating that the PECVD process did not degrade the performance of the OLEDs notably. The lifetime of the passivated device was two times longer than that of the control device. Passivation of OLEDs with PPpX films also suppressed the growth of dark spots. The density and size of dark spots of the passivated device were much smaller than those of the control device.

1.   Introduction

Since efficient organic light emitting diodes (OLEDs) were introduced by Tang and VanSlyke in 1987, OLEDs have been studied extensively due to their advantages such as active emission, low cost, red-green-blue output color, high brightness, wide viewing angle, low operating voltage and ease of fabrication [1–4]. The relatively short lifetime of OLEDs, however, is still a major obstacle for their commercial applications. There are two main factors that cause the degradation of OLEDs. One is the crystallization of organic materials by joule heating during operation and the other is the oxidation of these materials by interaction with water and/or oxygen in the atmosphere [5-7]. To increase the lifetime of OLEDs by preventing degradation of OLEDs, prevention of water and/or oxygen from diffusing into the organic material layers and then interacting with organic materials, i.e., passivation of OLEDs, is attempted. For thin film passivations, Funaki et al. used silicon nitride layers, and Kwon et al. used multilayers of high density polyethylene and aluminum lithium alloy [8-9].

Recently, many works on the applications of plasma polymers in electronic devices have been reported [10–12]. The properties of plasma polymer thin films are considered to be different from those of conventional chemically synthesized polymer films [13]. Due to the highly cross linked network structure of plasma polymers, plasma polymer thin films are pinhole free, mechanically and chemically stable, and strongly adherent to underlying layers. Therefore, plasma polymer thin films are expected to prevent water and/or oxygen diffusion into OLEDs and to be an effective passivation layer for OLED passivation [14]. In this work, we report OLED passivation using thin films of a plasma polymer. The plasma polymer used in this work was deposited by plasma enhanced chemical vapor deposition (PECVD) using para-xylene as the precursor, and was referred to as plasma polymerized para-xylene (PPpX).

2.   Experiments

Figures 1(a) and 1(b) show the device structures of an OLED without the PPpX passivation layer (control device) and an OLED with the PPpX passivation layer (passivated device). Indium tin oxide (ITO) coated glass was used as the substrate. Before loading into the deposition chamber, ITO coated glass was

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boiled in a mixture of NH$_4$OH, H$_2$O$_2$ and distilled water for 1 h and then ultrasonically cleaned with distilled water for 20 min. N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4-4'diamine (TPD) and tris-(8-hydroxyquinoline) aluminum (Alq$_3$) were used as the hole transport layer (HTL) and the emitting layer (EML), respectively. TPD (32 nm) / Alq$_3$ (48nm) was deposited on ITO by thermal evaporation at 10^{-6} torr.
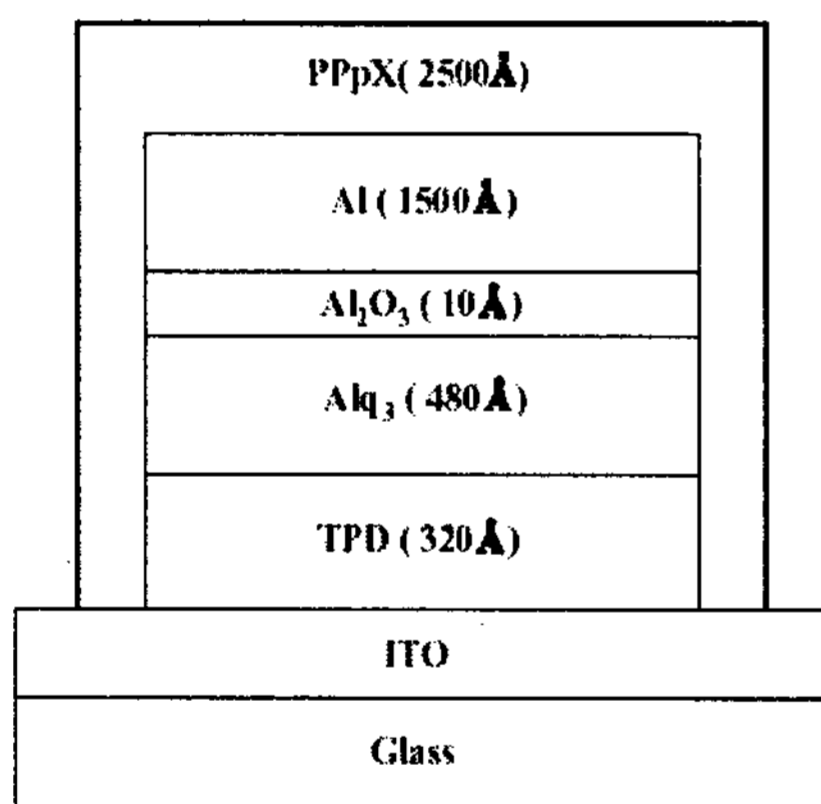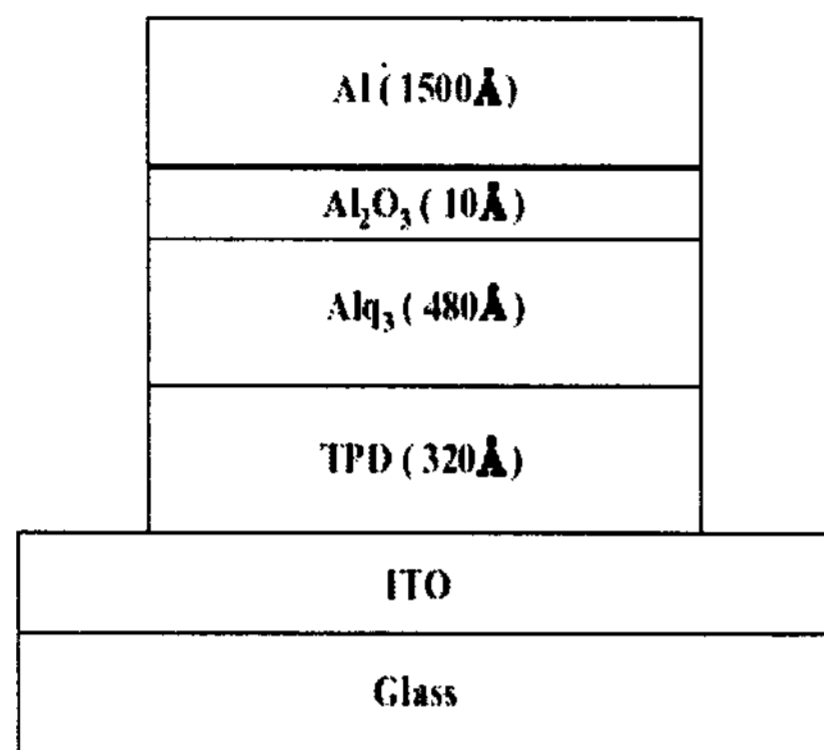

(a)

(b)

Figure. 1. Schematic diagrams of an OLED without the PPpX passivation layer (a) and an OLED with the PPpX passivation layer (b).

The deposition rates for the organic layers were 0.6–1.2 Å/s. In previous works, it was reported that the insertion of an Al$_2$O$_3$ thin film with a suitable thickness between the EML and the cathode was effective in improving the performance of OLEDs such as brightness and external quantum efficiency, and in our work, a 1 nm thick Al$_2$O$_3$ layer was inserted between the EML and the Al cathode [2].

Thermal evaporation deposition of a 150 nm thick Al cathode layer was performed at a pressure of 7 × 10^{-6} torr and a deposition rate of 5–10 Å/s. Some of the as-prepared OLED devices were moved to the PECVD chamber for deposition of the PPpX passivation layer. Details of the PECVD system used in this work are described elsewhere [10]. PPpX passivation films were deposited at a plasma power of 30 W at a deposition pressure of 1 torr for 20 min. The thickness of the PPpX film was 250 nm. For electrical measurements, a Keithley 2400 electrometer was used as a voltage source and current measurement device. The luminescence characteristics of the OLEDs were determined by measuring the photocurrent induced by the light emission from the OLEDs using a Keithley 485 picoammeter.

3.   Results and discussion

Figures 2(a), 2(b) and 2(c) show the current–voltage (I–V) characteristics, brightness-voltage (B-V) characteristics and external quantum efficiencies, respectively, of the control OLED device and the passivated OLED device. The passivated device showed similar I–V and B-V characteristics and external quantum efficiency 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. In our experiment, even for a longer PECVD deposition time, no notable difference in performance between the passivated device and the control device was observed.

Figure 3 shows the degradation characteristics of the control device and the passivated device. During the OLED degradation experiments, a current density of 15 mA/cm^2 was applied to both of the devices, yielding an initial brightness of ~400 cd/m^2 for the control device and the passivated device. The time duration required for the brightness of the OLED device to become half the initial value was referred to as the lifetime of the OLED device. The lifetime of the control device was 1,034 s while that of the passivated device was 2,250 s, which is two times longer than that of the control device. The lifetimes of the control and passivated OLED devices in this work were short compared to the OLED lifetimes reported elsewhere [9], presumably because a high current of 15 mA/cm^2 was passed through the OLEDs, and during the device fabrication process, organic
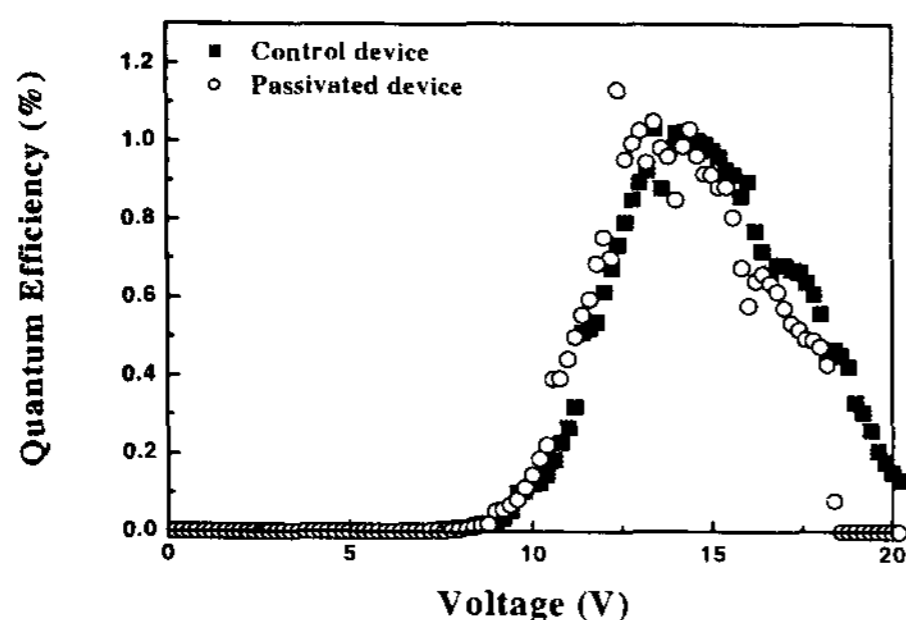
materials were exposed to room air, as will be described later.
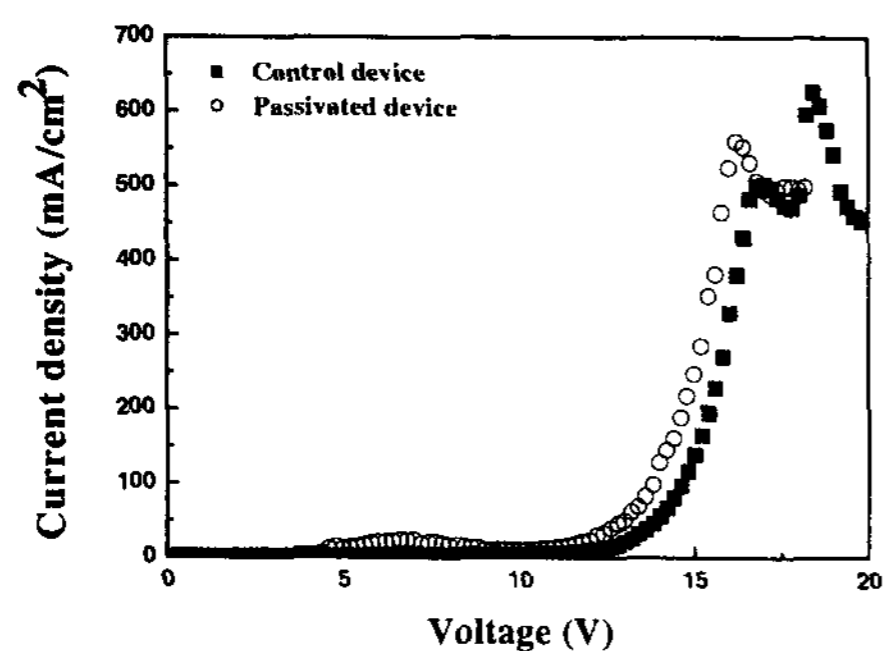
(a)
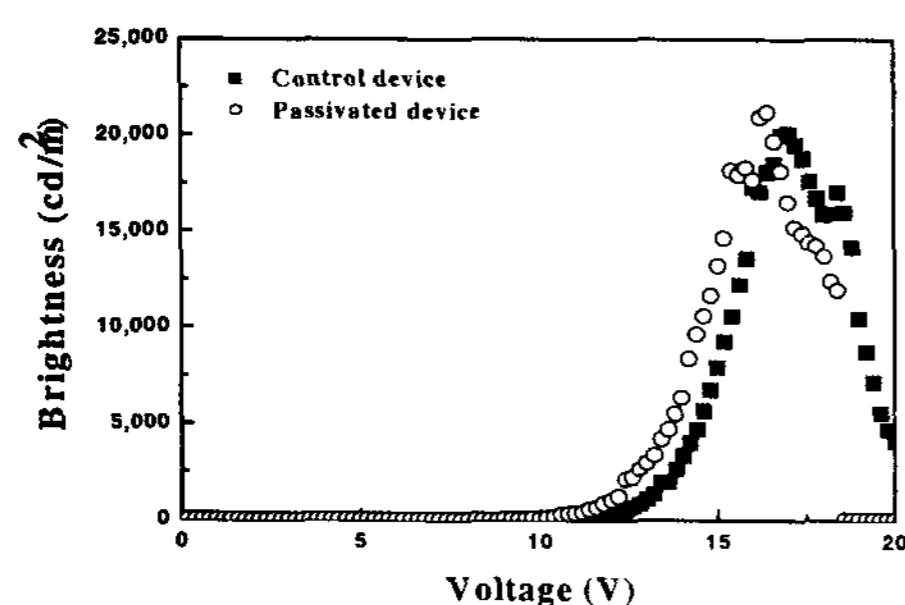
(b)

(c)

Figure 2. Current density versus applied voltage (a) and brightness versus applied voltage (b) characteristics and external quantum efficiency (c) for both the control device and the passivated device.

The lifetime of the passsvated device was longer than that of the control device, which indicates that the PPpX film was, to some extent, effective in passivating the OLEDs.
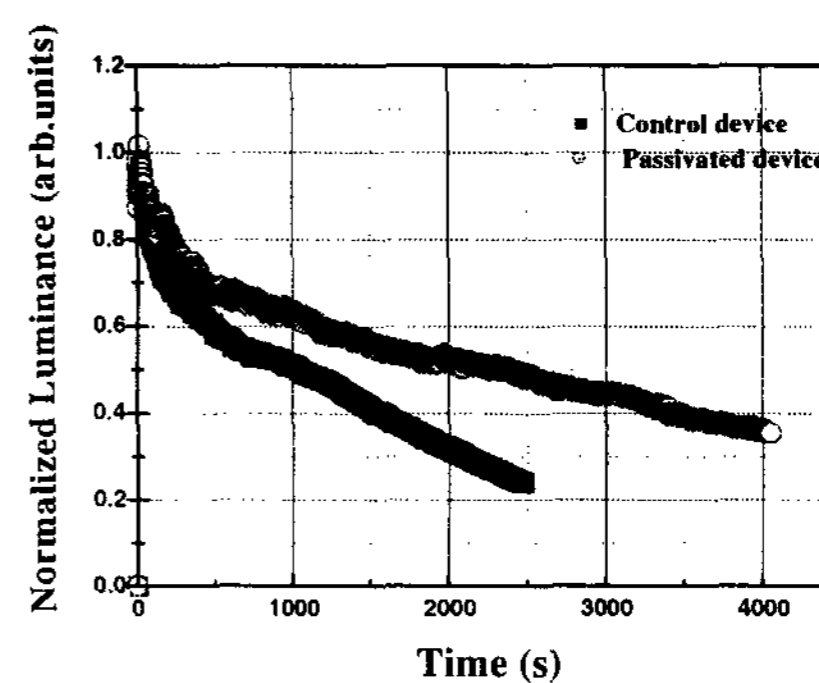

Figure 3. Degradation characteristics of the control device and the passivated device.

It is considered that the aforementioned properties of plasma polymers helped the PPpX film prevent the penetration of water and/or oxygen into the OLED devices and thus the PPpX passivated device showed longer lifetime than the control device. However, the enhancement of lifetime by PPpX passivation in our work is not as pronounced as that reported previously [9]. One reason for this is that our PPpX films may not completely prevent water and/or oxygen diffusion. Another possible reason can be speculated as follows. In our experiments, the organic layers were exposed to room air before deposition of the Al cathode layer, which was inevitable for alignment of the shadow mask for Al deposition. The ITO/TPD/Alq$_3$/Al$_2$O$_3$/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 prevented water and/or oxygen from diffusing into the OLEDs, there is a certain amount of water and/or oxygen inside the OLED devices, resulting in some degradation of the OLED devices.

Passivation of OLEDs with PPpX films also suppressed the growth of dark spots. Figures 4(a) and 4(b) show the optical microscopy images of the control OLED device and the passivated OLED device, respectively. As the device operation time increased from 550 to 1000 to 1500 s, the size of dark spots of the passivated device did not change notably, while the size of dark spots of the control device increased markedly. At all times, the density and size of dark spots of the passivated device were much smaller than those of the control device.
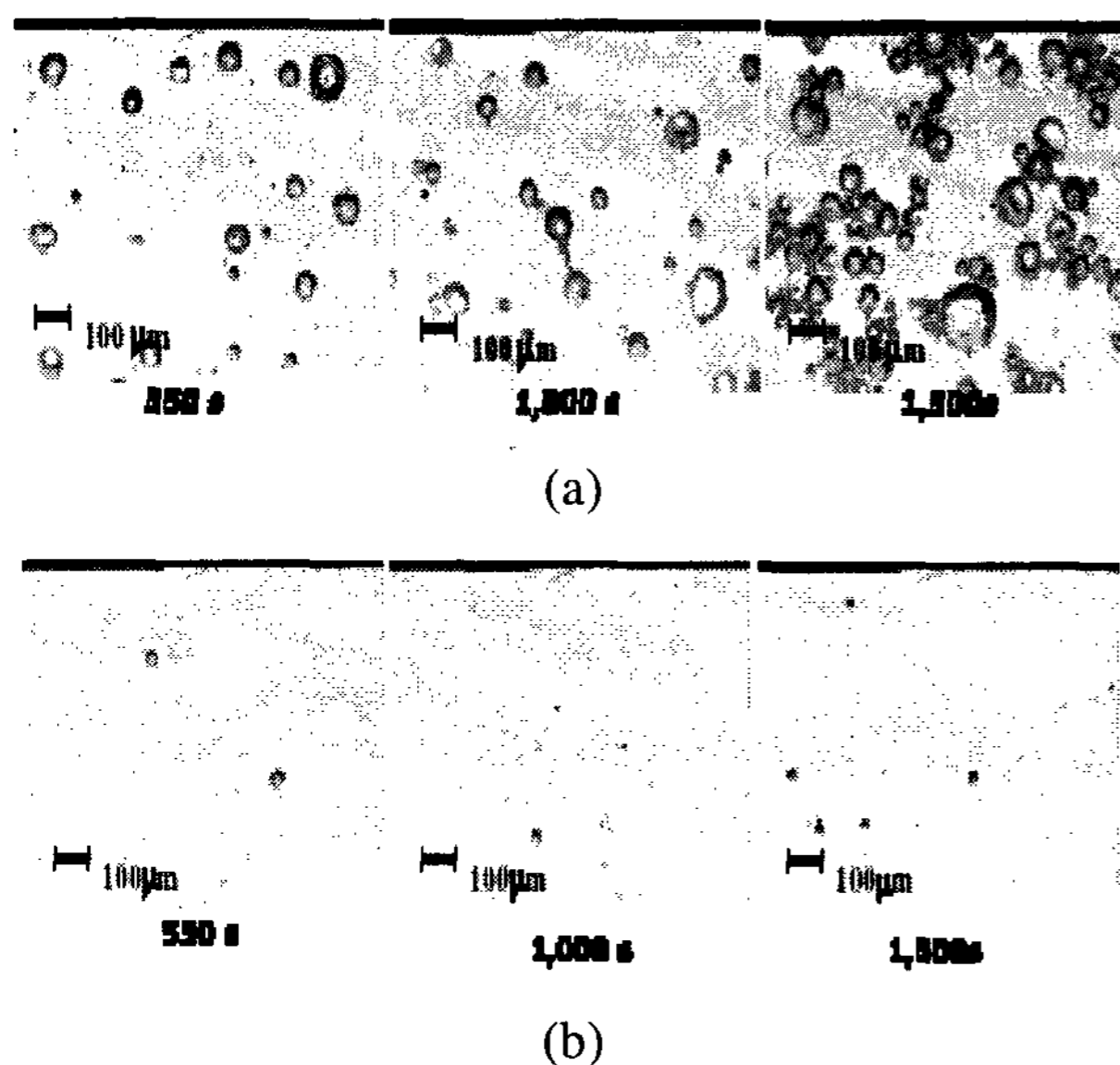
(a)

(b)

Figure 4. Optical microscopy images of the control OLED device (a) and the passivated OLED device (b).

4. Conclusion

In the summary, PPpX thin films were used to passivate OLED devices. The PPpX passivated device showed similar I–V and B-V characteristics and external quantum efficiency to those of the control device, indicating that the PECVD process for the deposition of the PPpX films did not degrade the performance of the OLEDs notably. The lifetime of the passivated device was two times longer than that of the control device, indicating that the PPpX film was, to some extent, effective in passivating the OLEDs. Passivation of OLEDs with PPpX films was also effective in suppressing growth of dark spots. Further optimization of plasma polymer film deposition and avoidance of exposure of the organic layers to room air before passivation film deposition are needed in order to improve the OLED lifetime by plasma polymer film passivation.

5. References

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