# Top emission inverted organic light emitting diodes with $N_2$ plasma treated Al bottom cathodes

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## Abstract

*Effects of $N_2$ plasma treatment of the Al bottom cathode on the characteristics of top emission inverted organic light emitting diodes (TEIOLEDs) were studied. TEIOLEDs were fabricated by depositing an Al bottom cathode, a tris-(8-hydroxyquinoline) aluminum ($Alq_3$) emitting layer, an N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-diphenyl -4,4′diamine (TPD) hole transport layer, and an indium tin oxide (ITO) top anode sequentially. The Al bottom cathode layer was subjected to $N_2$ plasma treatment before deposition of the $Alq_3$ layer. X-ray photoelectron spectroscopy suggested that the existence of and the amount of $AlN_x$ between the $Alq_3$ emitting layer and the Al bottom cathode significantly affect the characteristics of TEIOLEDs. The maximum external quantum efficiency of the TEIOLED with an Al bottom cathode subjected to $N_2$ plasma treatment for 30 s was about twice as high as that of the TEIOLED with an untreated Al bottom cathode.*

## 1. Introduction

Since Tang and VanSlyke reported efficient thin film organic light emitting diodes (OLEDs), there has been significant improvement in the performance and stability of OLEDs [1]. Due to their advantages of high luminous efficiency at all three primary colors at low voltage, low power consumption, large viewing angle, ease of fabrication and low cost, OLEDs are considered as the potential candidate for the next generation flat panel display [1-3]. Top emission OLEDs (TEOLEDs) will be very useful because TEOLEDs can emit light through the top electrode, and in the presence of thin film transistor arrays lying under the OLEDs, as is the case of active matrix displays [4-10], high portion of the emitted light can be utilized.

In this work, we report that, in the fabrication process of the TEIOLEDs, a proper $N_2$ plasma treatment of the Al bottom cathode before the deposition of the organic layers significantly improved characteristics of TEIOLEDs. $N_2$ plasma treatment is thought to generate a very thin aluminum nitride layer between the cathode and the organic emitting layer, and this thin insulating aluminum nitride layer is considered to enhance the electron injection from the cathode.

## 2. Experiments

Figure 1 shows the structure of TEIOLED used in this work. Aluminum (Al), tris-(8-hydroxyquinoline) aluminum ($Alq_3$), N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) and ITO were used as a bottom cathode, an emitting layer (EML), and a hole transporting layer (HTL), and top anode, respectively. The thicknesses of Al, $Alq_3$, TPD and ITO were 150, 48, 32 and 100 nm, respectively.

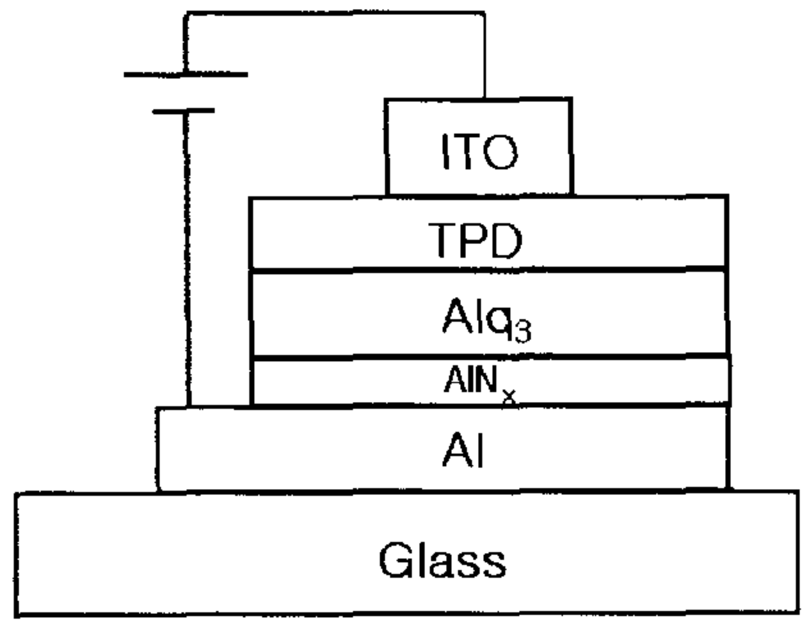

**Figure 1. Structure of theTEIOLED.**

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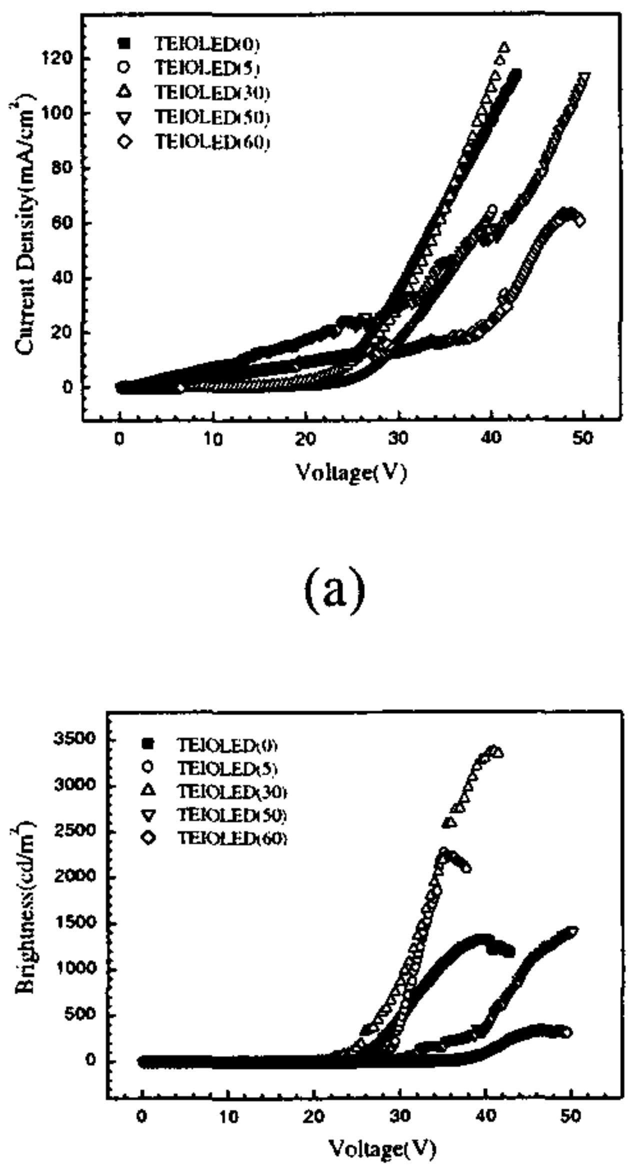
Deposition rates for the Al cathode layer and the organic layers were 5.0-8.0Å/s and 1.0-1.3Å/s, respectively. For the fabrication of TEIOLEDs with an $N_2$ plasma treated Al bottom cathode, after the Al bottom cathode layer was deposited on a glass substrate by the thermal evaporation method, the Al/glass sample was taken out of the evaporation chamber and moved into a plasma treatment chamber, where the surface of the Al layer was exposed to $N_2$ plasma. Details of the plasma treatment system are described in ref.11. The plasma gas used was 99.999 % pure nitrogen, and the pressure of $N_2$ plasma was 0.2 torr. $N_2$ plasma treatment time was varied in the range of 0-60 s. After deposition of the organic layers on the Al cathode layer or the plasma-treated Al cathode layer, the sample was immediately transferred to a sputter deposition chamber for ITO deposition. The ITO electrode was formed on top of the organic layers by r.f. sputtering of ITO. The ITO target, housed in a magnetron sputtering gun, was 10 % $SnO_2$ and 90 % $In_2O_3$ by weight with 99.99 % purity. The sputtering gas was 99.999 % pure argon (Ar). The base pressure of the sputtering system was $5\times10^{-6}$ torr, and the pressure during the sputtering process was $6\times10^{-3}$ torr, with the Ar flow regulated by a mass flow controller at 100 sccm. The r.f. sputtering power was 30 W, resulting in a deposition rate of 0.8 Å/s. The sheet resistance of a 100 nm thick as-deposited ITO film was 200 Ω/ , which was sufficiently small for making top anodes. The TEIOLEDs were operated in air for all the experiments. A Keithley 2400 electrometer was used for current density-voltage characteristics as a voltage source and current measurement equipment. Brightness of the TEIOLEDs was investigated by measuring the photocurrent induced by light emission from the TEIOLEDs using a Keithley 485 picoammeter. In order to study the chemical change of the Al surface by $N_2$ plasma treatment, we performed X-ray photoelectron spectroscopy (XPS). XPS was recorded on a VG Microtech ESCA 2000 using Mg Kα source (13.5 kV). The base pressure of the XPS chamber was maintained in the $10^{-9}$ torr range during the experiments.

## 3. Results and discussion

Figures 2(a) and 2(b) the show the change of current density versus applied voltage (J-V) and brightness versus applied voltage (B-V) characteristics, respectively, of the TEIOLEDs with the variation of $N_2$ plasma treatment time in the range of 0-60 s, for a fixed $N_2$ plasma power at 30 W.



(a)

(b)

**Figure 2. Change of (a) J-V and (b) B-V characteristics of the TEIOLEDs with the variation of the $N_2$ plasma treatment time.**

TEIOLEDs whose Al bottom cathode was plasma treated with $N_2$ plasma power for 0, 5, 30, 50, and 60 s were referred to as TEIOLED(0), TEIOLED(5), TEIOLED(30), TEIOLED(50) and TEIOLED(60), respectively. In regard to J-V characteristics, there was not much improvement in the performances of TEIOLEDs with the $N_2$ plasma treated Al bottom cathode. In regard to B-V characteristics, however, TEIOLED(5) and TEIOLED(30) showed better performance than TEIOLED(0). TEIOLED(30) showed a higher maximum brightness than TEIOLED(5). Further increase of $N_2$ plasma treatment time to 50 s and 60 s reduced the performance of the TEIOLEDs, and TEIOLED(50) and TEIOLED(60) showed electroluminescent properties inferior to that of TEIOLED(0). Figure 3 shows external quantum efficiencies of the TEIOLEDs. TEIOLED(0), TEIOLED(5), TEIOLED(30), TEIOLED(50), and TEIOLED(60) showed maximum external quantum efficiencies of 0.18 %, 0.32 %, 0.41 %, 0.16 %, and 0.07 % at 35 V, 34 V, 34 V, 46 V, and 43 V, respectively.

TEIOLED(30) showed a much higher quantum efficiency than the other TEIOLEDs.

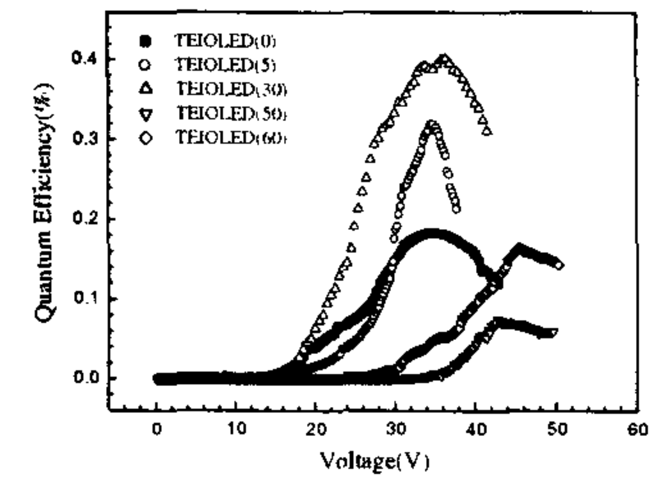


**Figure 3. Change of external quantum efficiency of the TEIOLEDs with the variation of the $N_2$ plasma treatment time.**

The maximum external quantum efficiency of TEIOLED(30) was about 2 times as high as that of TEIOLED(0). Comparison of our TEIOLEDs with a bottom emission OLED (BEOLED) fabricated in our laboratory revealed that TEIOLED(0) showed a performance inferior to that of the BEOLED, which did not contain an insulating layer between the Al cathode and the $Alq_3$ EML and can be referred to as BEOLED(0). BEOLED(0) started to show observable light emission at ~ 5 V and showed a maximum external quantum efficiency of 0.6 % whereas TEIOLED(0) started to show observable light emission at ~15 V and showed a maximum quantum efficiency of 0.18 %. The inferior performance of TEIOLED(0) is considered to be due to several reasons including the following. First, the ITO anode for TEIOLED cannot be annealed at high temperatures after deposition and the resistance of the ITO anode cannot be reduced to a point low enough for the low voltage operation of the TEIOLEDs [12]. Second, during the deposition of the top ITO anode by sputtering with a plasma power of 30 W, the underlying layers, especially the TPD layer, could be damaged by the plasma [13].

Some reports have found that insertion of a thin insulating layer such as $Al_2O_3$ between $Alq_3$ and the cathode can increase the injection of electrons from the cathode to $Alq_3$ and thus improve the quantum efficiency [13,14]. One possible mechanism for such an enhancement based on the tunneling theory was suggested. An $Al_2O_3$ layer is an insulator with a large band gap. The presence of the $Al_2O_3$ layer allows for a large voltage drop across it and thus moves the Fermi level of Al closer to the point where it is aligned with the lowest unoccupied molecular orbital (LUMO) of $Alq_3$. This results in more electrons being injected from the cathode into the LUMO of the organic $Alq_3$ layer, leading to an increase in electroluminescence [13,14]. An optimum amount of aluminum oxide is needed to improve the performance of the OLEDs. Too small of an amount of aluminum oxide may not increase the alignment between the metallic Al Fermi level and the LUMO of the $Alq_3$, and in the case of too high of an amount of aluminum oxide, the tunneling barrier is too thick for efficient tunneling.

Since the existence of and the amount of a thin insulating layer between the emitting layer and the metallic cathode affect the performance of the OLED, we investigated the chemical structures of the surface of the Al cathode layer that was subjected to $N_2$ plasma treatment for various plasma treatment times by XPS.

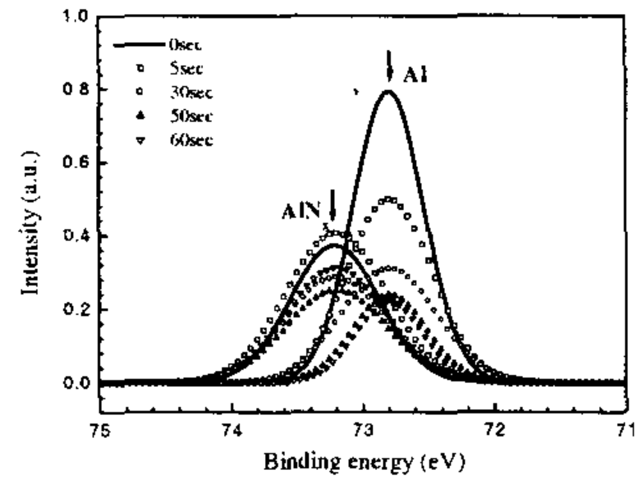


**Figure 4. Al 2p XPS spectra of the surface of the $N_2$ plasma treated Al bottom cathode layer.**

Figure 4 shows the deconvoluted Al 2p XPS spectra of the Al layer subjected to $N_2$ plasma treatment for various periods of time. Peaks related to metallic aluminum (Al) and the aluminum nitride ($AlN_x$) could be assigned [15,16]. As the $N_2$ plasma treatment time increased, $I(AlN_x)/I(Al)$ increased, where $I(AlN_x)$ and I(Al) refer to the areas of the $AlN_x$ peak and the Al peak, respectively.

From the data shown in Figs. 3 and 4 explanations in refs. 13 and 14, the following suggestions can be made. The existence of and the amount of $AlN_x$, which is considered to be formed by the reaction of Al and reactive nitrogen species in the $N_2$ plasma, significantly affect the performance of the TEIOLEDs. Since the increase of the $N_2$ plasma treatment time increased the amount of $AlN_x$, TEIOLED(5) and TEIOLED(30) are thought to have a thin insulating $AlN_x$ layer between the $Alq_3$ layer and the Al bottom cathode. This thin $AlN_x$ layer increased the electrons injection from cathode to $Alq_3$, and TEIOLED(5) and TEIOLED(30) showed higher electroluminescences than TEIOLED(0). For treatment times of 50 s and 60 s, the amount of $AlN_x$ is considered to be too much to increase the electron injection. In our experiment, it is thought that the $N_2$ plasma treatment time of 30 s yielded the most suitable amount of $AlN_x$, and TEIOLED(30) showed the highest quantum efficiency.

## 4. Conclusion

In conclusion, we have studied the effects of the $N_2$ plasma treatment of the Al bottom cathode layer on the characteristics of TEIOLEDs. TEIOLEDs were fabricated by depositing an Al bottom cathode, an $Alq_3$ emitting layer, a TPD hole transport layer, and an ITO top anode sequentially. The characteristics of the TEIOLEDs were affected significantly by $N_2$ plasma treatment time. XPS results suggested that the formation of $AlN_x$ between the $Alq_3$ emitting layer and the Al bottom cathode significantly affects the characteristics of TEIOLEDs. In our case, the optimum $N_2$ plasma treatment time was 30 s. The external quantum efficiency of the TEIOLED with an Al bottom cathode subjected to $N_2$ plasma treatment for 30 s was about twice as high as that of the TEIOLED with an untreated Al bottom cathode.

## 5. References

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