Effects of nitrous oxide and nitrogen plasma treatment on the indium-tin-oxide anode of organic light-emitting diodes

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In this paper, the surface of the indium-tin-oxide (ITO) anode of an organic light-emitting diodes (OLED) device is processed by N_2O or N_2 gas in a plasma enhanced chemical vapor deposition (PECVD) instrument. Compared to the non-treated OLED device, the process through the N_2O plasma improves the characteristics of OLED device, while opposite effect will be achieved by using the N_2 plasma. Under the optimized experimental condition, the turn-on voltage of the N_2O plasma treated OLED (4.5 V) is lower than that of the OLED without plasma process (6V). In addition, the luminance of the OLED with its ITO anode surface treated by the N_2O plasma is improved to 8500 cd/m^2, and is higher than 6200 cd/m^2 of the untreated OLED.

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1. Introduction

In recent years, the organic light-emitting diodes (OLEDs) have attracted worldwide enthusiastic attention owing to their great potentials for full-color flat panel display devices [1-3]. Indium-tin-oxide (ITO) is widely used as transparent electrodes for OLEDs due to its high conductivity, high transparency and high work function [4]. ITO is also an effective anode contact for holes injection. It is well-known that the optoelectronic properties of the ITO film are sensitive to its surface conditions.

Therefore, many ITO surface treatments, such as wet treatment, UV ozone treatment [5-6], oxygen (O_2) plasma treatment [7], Cl2 plasma treatment [8], coating treatments with self-assembly monolayers [9] and carbon tetrafluoride (CF4) plasma treatment [10], have been employed to improve the device performances. Until now, the CF_4 plasma treatment is still one of the most effective methods. However, the CF_4 plasma treatment has several drawbacks. The CF_4 gas is not only expensive but also harmful to human body. At the same time, we notice that there are no reports about the effects of the nitrous oxide plasma treatment of ITO anode surface on the optoelectronic performance of OLED devices. In this paper, the effects of nitrous oxide (N_2O) and nitrogen (N_2) plasma treatments [11] of the ITO surface on the performances of OLED devices are analyzed. Our results indicates that OLED device performance can be improved through the ITO surface treatments by using N_2O plasma, but worse performance is obtained in the device treated by N_2.

2. Fabrication

In this work, an OLED device with a structure is designed, as shown in Fig. 1, and the fabrication process of the OLED device is described as follows.

The main methods for preparing ITO thin films are magnetron sputtering [12], thermal evaporation [13], electron beam evaporation [14], etc. In this paper ITO thin films on glass substrates were purchased from Kaivo (thickness of 150 nm and sheet resistance of 18-20Ω/square). Then the sample is in sequence cleaned by de-ionized water, acetone, detergent and isopropanol in an ultrasonic cleaner respectively for 10 min, and is blown dry with high-purity nitrogengas. Afterwards, the ITO surface of the sample is treated by N_2O gas in a plasma enhanced chemical vapor deposition (PECVD) instrument with a radio frequency (RF) power supply (13.56 MHz, Advanced Energy).

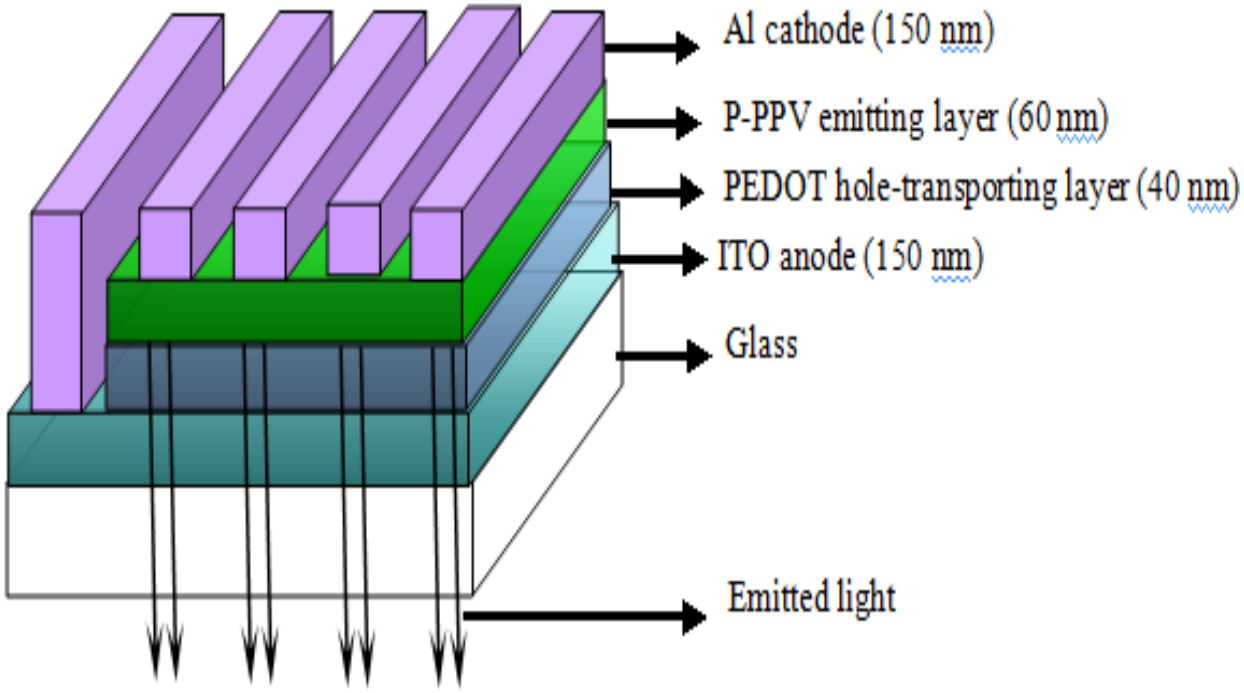

Fig. 1. The structure of the designed OLED device

The flow rate and pressure of N_2O (or N_2) gas for the plasma treatment are kept at 50 sccm and 30 Pa, respectively. The RF power and treatment time are varied at each experiment in order to find the optimum electrical condition of the OLED device. After the N_2O (or N_2) plasma treatment, a 40-nm-thick poly (3,4-ethylenedioxythiophene)-polystyrene sulphonic acid (PEDOT-PSS) layer (Clevios P VP. Al 4083 (H. C. Starck, Clevios GmbH, Leverkusen, Germany)) and a 60-nm-thick poly(2-(4-ethylexyl) phenyl-l, 4-phenylene vinylene)（P-PPV）layer are in sequence spin-coated on the ITO surface as the hole-transporting layer and the emitting layer of the OLED device, respectively. The molecular structure of P-PPV is shown in Fig. 2. At last, the Al cathode layer is deposited on the top of the P-PPV layer by conventional thermal evaporation in a vacuum chamber at a base pressure of 6×10^{-4} Pa and a deposition rate of 1 nm/s. The active area of the fabricated OLED device is 1.5 mm^2.

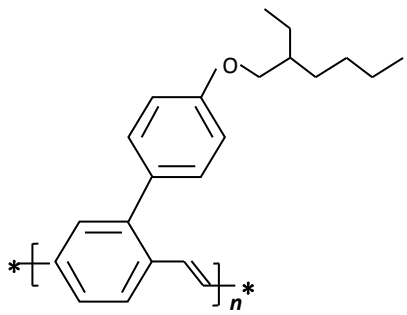

Fig. 2. The molecular structure of P-PPV

3. Results and discussion

Through a measurement system including a Keithley 2400 source, a calibrated silicon photodiode and Keithley 2000 picoammeter, the electrical and luminescence characteristics of the fabricated OLED devices are measured at room temperature in the open air. Figures 3 and 4 respectively show the dependences of current density and luminance on the voltage of the fabricated OLEDs after the plasma surface treatment on ITO surface by using N_2 and N_2O on the condition of 30 Pa of operating pressure, 50 sccm of gas flow rate, 50 W of PECVD power for 10 min. As shown in Figs. 3 and 4, the current density and luminance of OLEDs fabricated on N_2O-plasma-treated ITO surface increase more significantly at a lower voltage than those of OLEDs fabricated on untreated ITO surface. The turn-on voltage (defined as the voltage needed to deliver a luminance of 1 cd/m^2) of the OLEDs by the N_2O plasma surface treatment also decreases. But the luminance decreases and the turn-on voltage increases by the N_2 plasma surface treatment.

As shown in Fig. 4, the highest luminance of 8500 cd/m^2 is obtained at 9 V by the N_2O plasma treatment, 5125 cd/m^2 at 12.5 V by the N_2 plasma treatment, and 6200 cd/m^2 at 14 V for the untreated ITO, respectively. It can be also seen in Fig. 4 that the turn-on voltage of the OLED devices treated by the N_2O plasma is about 4.5 V and it is lower than that of the non-plasma-treated OLED devices (6.0V). However, the OLED devices treated by the N_2 plasma shows the highest turn-on voltage of 6.5 V.

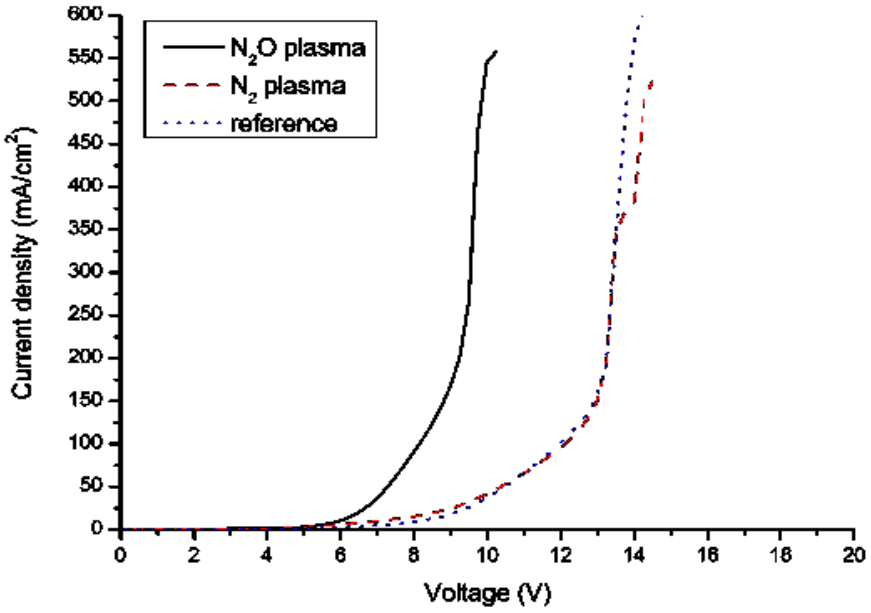

Fig. 3. The dependence of current densities on voltages of the OLEDs fabricated on the ITO glass surface pretreated by using N2 and N2O plasma treatment and a reference OLED untreated by the plasma treatment

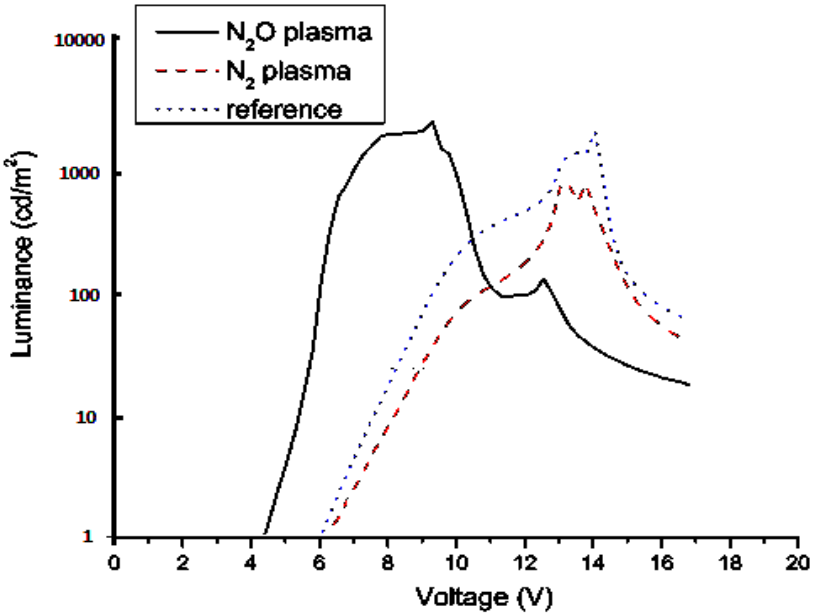

Fig. 4. The dependence of luminances on voltages of the OLEDs fabricated on the ITO glass surface pretreated by using N_2 and N_2O plasma treatment and a reference OLED untreated by the plasma treatment

Fig. 5 presents the dependence of luminance efficiency on the current of the OLED devices. Compared to that of the non-plasma-treated OLED devices (10 cd/A at 4.0 mA), the luminous efficiency of N_2O-plasma-treated OLED devices (22.5 cd/A at 4.0 mA) increases, while the luminance efficiency of N_2-plasma-treated OLED devices decreases (2.5 cd/A at 4.0 mA). We know that the increase of luminous efficiency at the same current of the device treated by the N_2O plasma reduces the joule heating of the device during the device operation, and therefore, the operation life of the device is believed to be increased.

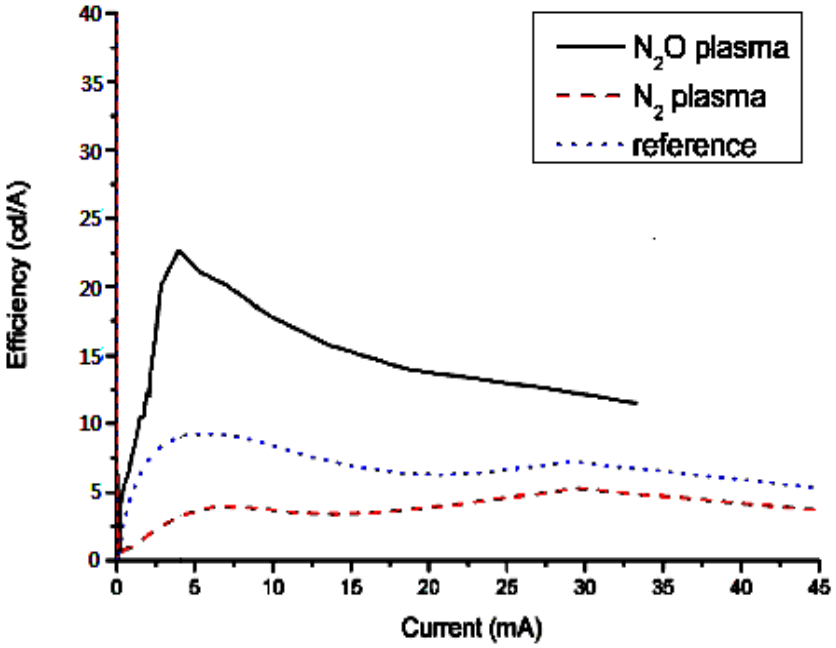

Fig. 5. Luminance efficiency–current characteristics of OLEDs fabricated on the ITO glass surface pretreated by using N_2 and N_2O plasma treatment and a reference OLED untreated

In the process of N2O/N2 gas plasma surface treatment. The donor concentration on the surface of the ITO film is reduced.The Sn-based neutral defect complexes and oxygen reduced by them could trap the electrons left behind. An electron depletion layer formed on the surface of the ITO film enhances hole injection [15]. As is known to us, the effects of O_2 plasma treatments are usually attributed to the enhancement of the ITO work function and the removal of carbon contaminants from the ITO surface [16]. Similar to the O_2 plasma treatment, N_2O plasma treatment also has the same function. Under the effect of the RF power, nitrous oxide will produce oxygen plasma, which will decrease ITO surface Sn:In ratio and increase ITO surface oxygen concentration. Besides, N_2O will be ionized into the O^{-2} and N^+ ions. The O^{-2} will cause the reduction of the oxygen vacancy in the ITO surface which is equivalent to the reduction of donor concentration in the ITO. N^+ will enter the lattice gap and act as an acceptor which can absorb the electrons, and it is equivalent to the increase of acceptor concentration in the ITO surface. From the formula $E_F = E_c + k_0 T \ln(\frac{N_D}{N_C})$, it is known that the decrease of the donor concentration and the increase of the acceptor concentration will lead to the reduction of the Fermi level of ITO. From the formula $E_w = E_0 - (E_F)$, the reduction of Fermi level will result in the increase of the work function of ITO. So the work function of ITO is increased after the N_2O treatment, and then the barrier height between ITO and P-PPV will be decreased. These can bring about an enhancement of charge-carriers injections through the interface, and therefore lead to a more balanced injection of electrons and holes. Finally, there is a great improvement of the device performances. For example, the turn-on voltage of the device is decreased. Nitrogen gas can not generate N_2O plasma under the condition of the RF power, and thus there is no performance enhanced in device treated by N_2 plasma.

In order to find the optimum experimental conditions, the experimental power and the time of N_2O plasma treatment are changed. Figures 6 and 7 show the current density-voltage and luminance-voltage characteristics of OLEDs devices untreated and treated by N_2O plasma treatment at different RF power (50 W, 100 W and 150 W) when the plasma treatment time, gas flow rate and system pressure are kept for 10 min, 50 sccm and 30 Pa respectively. As shown in Fig. 7, it is clear that holes injections become more effective if the ITO surface is treated by N_2O plasma, so that a decrease of drive voltage follows. Figure 7 presents the dependences of luminance on the voltages of the OLED devices treated by N_2O at different power. The OLED device treated by N_2O with the power of 50 W has the highest luminance of 8500 cd/m^2.

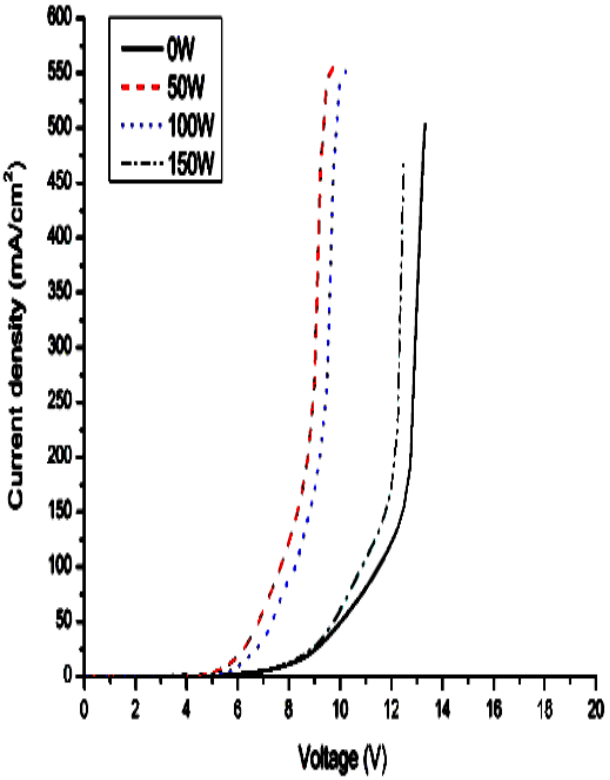

Fig. 6. Current density-Voltage characteristics of OLEDs untreated and treated by N_2O plasma treatment at 50 W, 100 W and 150 W, respectively

Fig. 8 shows the details of the turn-on voltages for the OLED devices in Fig. 7. In this figure, it can be seen that the lowest turn-on voltage is observed for the device whose ITO surface is treated by N_2O plasma at the power of 50W, while the OLED device whose ITO surface is treated at the power of 150W shows a raised turn-on voltage. Thus, in this work, the best treatment power for ITO surface treatment by N_2O plasma is 50 W.

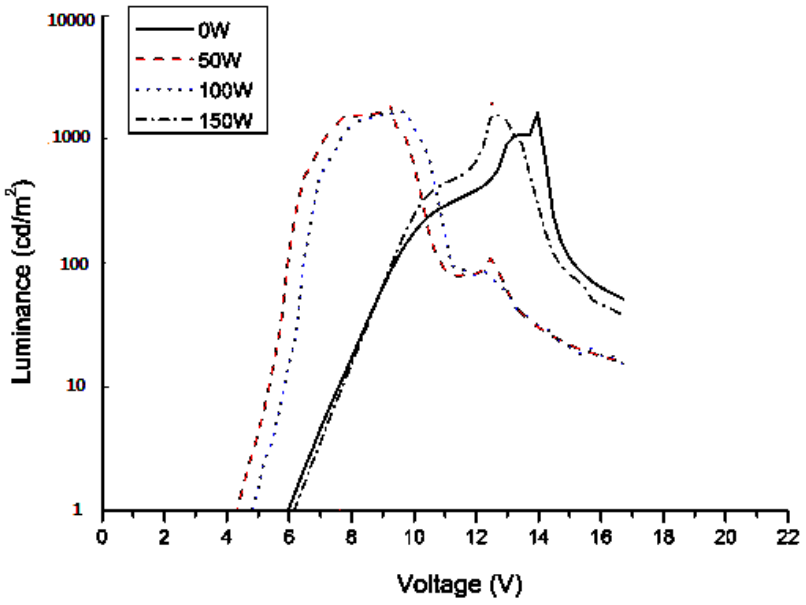

Fig. 7. Luminance-voltage characteristics of OLEDs untreated and treated by N2O plasma treatment at 50 W, 100 W and 150 W, respectively

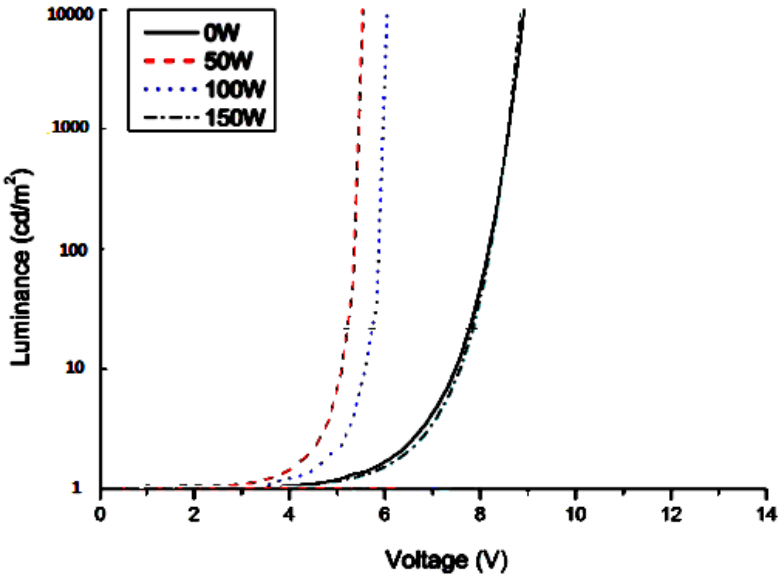

Fig. 8. Details of the turn-on voltages for the OLED devices in Fig. 7

Table 1 shows the turn-on voltage of OLEDs devices untreated and treated by N2O plasma treatment for different time when the plasma treatment power, gas flow rate and system pressure are kept for 50 W, 50 sccm and 30 Pa, respectively. The lowest turn-on voltage is observed for the device whose ITO surface is treated by N2O plasma for 10 min (3V). However, the effect seems to be weaken for the device treated for 20 min, because the surface degradation is generated by the irradiation of long time N2O plasma.

Table 1 Turn-on voltages of the OLED devices treated by N2O plasma for different exposure time

Exposure time (min)	0	5	10	20
Turn-on voltage (V)	5	4	3	3.5

4. Conclusion

In this work, the effects of ITO surface plasma treatment by PECVD using N2O and N2 on the device characteristics of the OLEDs were investigated. Compared with those ITO-untreated OLEDs, the ITO surface plasma treatment by using N2O significantly enhanced the holes injections from the anode and improved the OLED device performances, while the performances of the OLED device with ITO surface treated by N2 plasma was worsened. Meanwhile, experiments also revealed that the OLED device turn-on voltage changed with increasing the plasma power and the exposure time. Thus, when processing plasma treatment to ITO surface, there is an optimized condition in our experimental system for obtaining the best OLED device performance, i.e., exposure time of 10 min and plasma power of 50 W. The turn-on voltage of the OLED device decreased from 5V to 3 V after the ITO surface treatment by the N2O plasma, and its highest luminescence increased from 6200 to 8500 cd/m2.

Acknowledgments

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