Passivation of organic light emitting diodes with a-SiN_x thin films grown by catalyzer enhanced chemical vapor deposition

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Abstract

The characteristics of a SiN_x passivation layer grown by a specially designed catalyzer enhanced chemical vapor deposition (CECVD) system and electrical and optical properties of OLEDs passivated with the SiN_x layer are described. Despite the low substrate temperature, the single SiN_x passivation layer, grown on the PC substrate, exhibited a low water vapor transmission rate of $2\sim6\times10^{-2}$ g/m^2/day and a high transmittance of 87 %. In addition, current-voltage-luminescence results of an OLED passivated with a 150 nm-thick SiN_x film compared to nonpassivated sample were identical indicating that the performance of an OLED is not critically affected by radiation from tungsten catalyzer during the SiN_x deposition.

1. Introduction

OLEDs have recently entered the display market as sub- and main window displays for cellular phones and MP3 due to their extremely thin thickness, high peak brightness, high dark room contrast, low power consumption, low cost, superviewing ability, and fast response time. However, organic materials used in OLEDs degrade rapidly when they are exposed to ambient air due to severe chemical reactions with oxygen and moisture in the air.[1] Thus the long-term stability of OLEDs is still limited. Although lid type encapsulation such as SUS and glass lid is typically used in OLEDs, it comes with its own set of problems such as the penetration of oxygen and moisture through epoxy resin, an increase in thickness, a complicated process, and difficulty of application to flexible OLEDs. To achieve further advances in the production of OLEDs and flexible displays, it will be necessary to develop high quality thin film passivation with a low water vapor transmission rate (WVTR), excellent reliability, long-term stability, and a high degree of transparency. In particular, a low temperature thin film deposition process would be desirable because high process temperatures are incompatible with the OLEDs and flexible display fabrication process. Furthermore plasma free process for thin film passivation would be desirable because the effect of the exposure OLEDs to plasma is harmful to organic materials in OLEDs. However, most reported thin film passivation techniques are plasma based process such as plasma enhanced chemical vapor deposition (PECVD), inductively coupled chemical vapor deposition (ICV-CVD), plasma enhanced atomic layer deposition (PEALD), and RF sputtering.[2-4]

In this work, we report on a plasma-free thin film passivation process for OLEDs and flexible OLEDs using a CECVD system. The increased lifetime of the OLED passivated by the SiN_x layer indicates that CECVD is a promising plasma-free passivation technique that can be used in place of the conventional plasma based-CVD technologies.

2. Experimental

Using the CECVD system, a SiN_x passivation layer was deposited on the bare glass, bare Si and the test cell at substrate temperature of 50℃. A mixture of SiH_4, NH_3 and H_2 was used for the deposition of the SiN_x passivation layer. To optimize the SiN_x growth condition, H_2 flow rate, NH_3 flow rate, working pressure and distance of catalyzer-substrate were varied. The temperature of tungsten catalyzer was kept at 1800℃ constantly during the SiN_x deposition. In addition, the substrate temperature was also maintained constantly at 50℃ by a movable electrostatic chuck system and cooling system. Figure

1 shows schematic deposition mechanism of SiN_x passivation layer in the CECVD system.

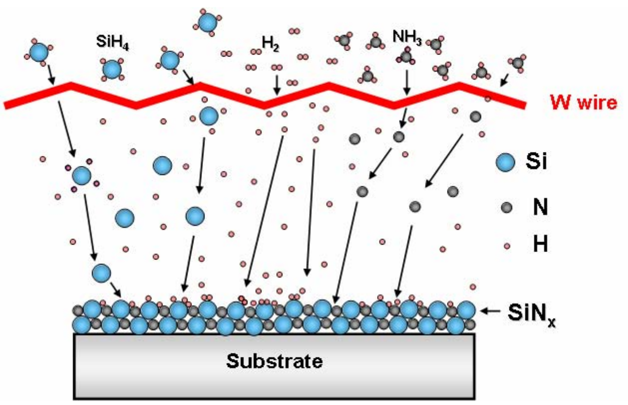

Fig. 1. Deposition mechanism of SiN_x film in CECVD

Ellipsometry and profilometer were used to measure the refractive index and thickness of SiN_x films. Optical transmittance through the SiN_x films was measures in the wavelength range from 220 to 800nm. The WVTR of the SiN_x films grown on polycarbonate (PC) substrate (10 cm × 10 cm) were determined at 38±2℃, 100% R. H. by MOCON for 72 hours. To investigate the thermal damage effect of high temperature tungsten catalyzer on electrical and optical properties, a 150nm-thick SiN_x passivation layer was deposited on the test sample with a structure of Al/LiF/BAlq/CBP+6% Ir(ppy)$_3$/NPB/ITO. After deposition of OLEDs were measured by using a Photo Research PR-650 spectrophotometer driven by a programmable dc source. Driven at 2 mA/cm^2, we measure device lifetime of OLED passivated with the SiN_x film at initial luminance of 500 cd/m^2.

3. Results and discussion

Figure 2 shows the deposition rate and refractive index of the SiN_x films on glass as a function of catalyzer-substrate distance at constant $SiH_4/NH_3/H_2$ ratio (32/480/1500 sccm), working pressure of 150 mTorr and catalyzer temperature of 1800 °C. It was shown that the deposition rate was monotonically decreased with increase of catalyzer-substrate distance. At distance of 100 mm, the maximum deposition rate of 45 nm/min was obtained. However, the IR value of the SiN_x films was kept constant regardless of catalyzer-substrate distance. This indicates that the stoichometry of CECVD grown SiN_x film is not influenced by catalyzer-substrate distance.

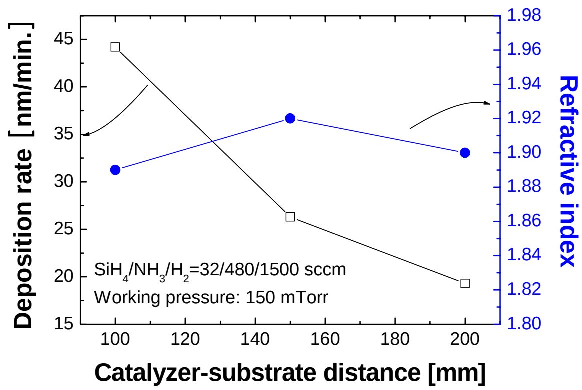

Fig. 2. Deposition rate and refractive index of the SiN_x films grown by CECVD as a function of catalyzer-substrate distance.

Figure 3 shows the deposition rate and refractive index as a function of H_2 flow rate at constant SiH_4/NH_3 flow rate, working pressure, and catalyzer-substrate distance.

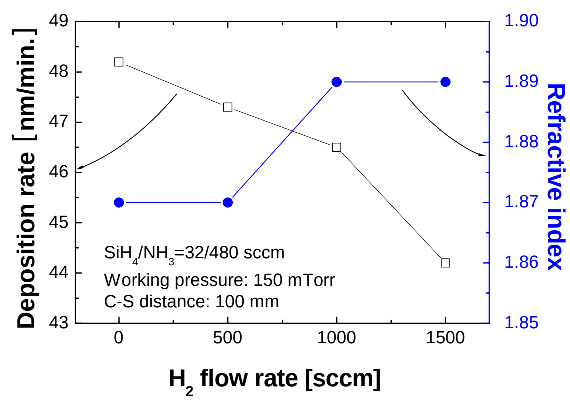

Fig. 3. Deposition rate and refractive index of the SiN_x films grown by CECVD as a function of H_2 flow rate.

It was shown that the deposition rate of the SiN_x film decreased with increasing H_2 flow rate. However, refractive index increased slightly with increasing of H_2 flow rate. Mohan et al have recently suggested that H atoms produced by the catalytic decomposition of H_2 plays an important role to dissociate the NH_3 .[5] However, the decrease of deposition rate in CECVD with increasing H_2 flow rate indicates that the effect of H_2 addition is less efficient when the NH_3 flow rate is high .[6]

The comparison of water vapor transmission rate (WVTR) of SiN_x film grown by ICP-CVD, PECVD and CECVD respectively is shown in Figure. 4. To measure WVTR of the SiN_x films grown by ICP-CVD, PECVD, and CECVD respectively, 150 nm thick SiN_x thin film were grown by different growing methods on PC substrate (100 × 100 mm) at optimized condition. The WVTR of SiN_x film grown by CECVD is much lower than those of SiN_x film grown by PECVD and ICP-CVD. The low WVTR value (0.02~0.06 g/day-m^2) of CECVD grown SiN_x film indicates that high density film is formed by chemical annealing effect and selective etching by hydrogen atoms during CECVD process.

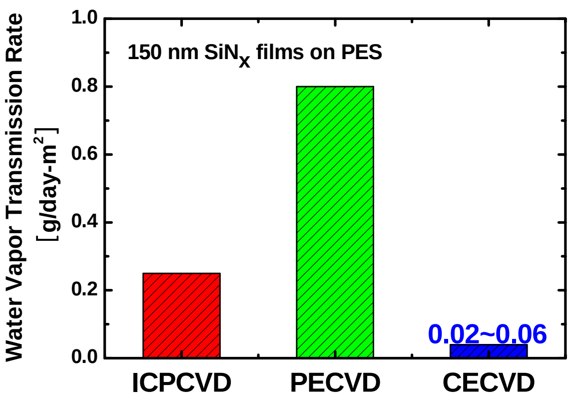

Fig. 4. Comparison of WVTR of the 100nm thick SiN_x film

To investigate thermal damage resulting from the tungsten catalyzer with a temperature of 1800 ^oC on the electrical and optical properties of the OLEDs, a 150 nm-thick SiN_x passivation layer was deposited over the Al cathode layer of a test sample. Figure 5 (a) shows J-V-L characteristics of the OLED passivated with a SiN_x layer prepared by CECVD and the reference OLED (Nonpassivated sample). The J-V-L curve of the OLED passivated with a SiN_x film shows an identical turn on voltage and forward bias behavior to that of the reference OLED. These J-V-L characteristics of OLEDs passivated with a SiN_x film indicates that the electrical and optical characteristics of the OLED are not critically affected by exposure to the high temperature tungsten catalyzer during the SiN_x deposition. Figure 5(b) shows a comparison of the luminance and power efficiency of the OLED passivated with SiN_x and the reference OLED. As expected from J-V-L results for the OLED, the identical luminance and power efficiency of the OLED passivated with the SiN_x layer to the reference OLED also indicates the potential of CECVD as a thermal damage free passivation technique.

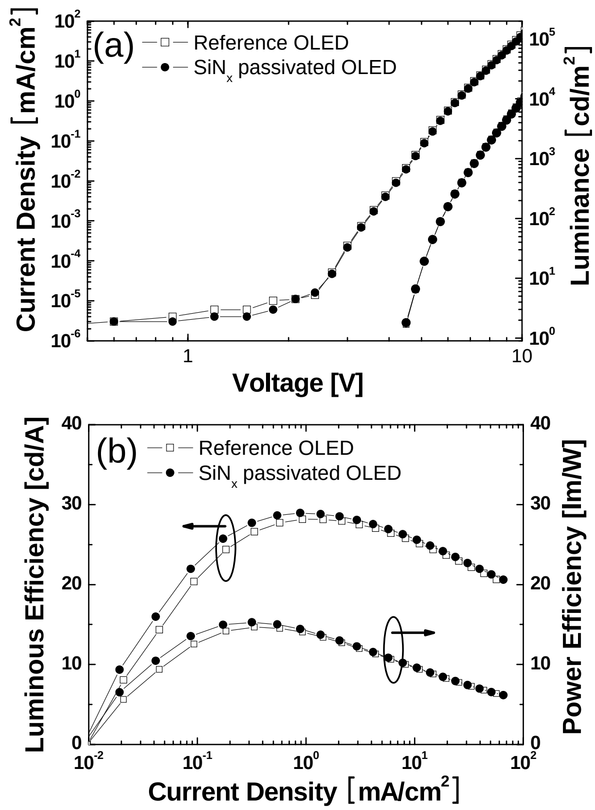

Fig. 5. (a) J-V-L characteristics and (b) efficiency of OLED passivated with 150nm-thick SiN_x film and nonpassivated OLED

Figure 6 exhibit the picture of OLED with CECVD grown SiN_x passivation layer. It was shown that OLED with SiN_x passivation layer is very thin due to removal of encapsulation glass. The picture shows that the thickness of OLED with thin film passivation layer fairly same to thickness of substrate glass (~0.7 mm).

Figure 7 shows the lifetime and operating voltage for an OLED passivated with a 150 nm-thick SiN_x film and a reference OLED. The operating lifetime of both the SiN_x passivated OLED and the reference OLED was measured at a dc-current drive of 2 mA/cm^2 with am initial luminance of 500 cd/m^2 at room temperature. The lifetime of the reference sample with an initial luminance of 500 cd/m^2 was approximately 53.5 h. The abrupt decrease in the luminance of the reference OLED is related to severe degradation of organic layers by direct intrusion of moisture and oxygen through the cathode layer.

However, the lifetime of the OLED passivated with a 150 nm-thick SiN_x film is longer than that of the reference sample. The lifetime of the passivated OLED is approximately 120 h.

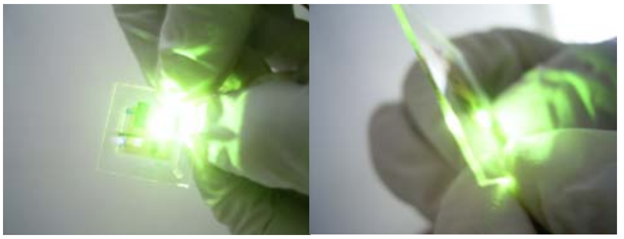

Fig. 6. Picture of OLED with CECVD grown SiN_x passivation layer

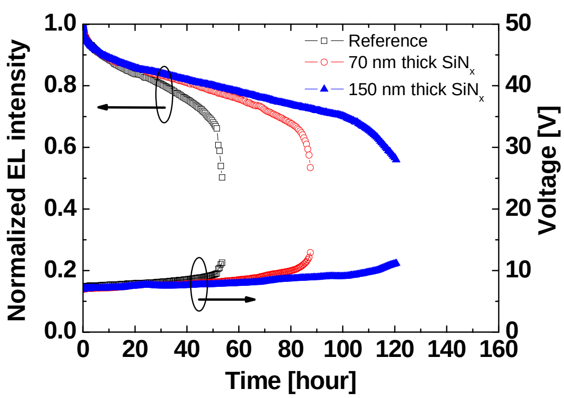

Fig. 7. Normalized luminance and voltage curve vs. operating time of OLED

In addition, the operating voltage of both OLEDs is gradually increased with an increase in operating time. It is noteworthy that the lifetime of the OLED could be prolonged by using a densely-grown single SiN_x film unlike other reported thin film passivation procedures, which use a thick or multilayer film. The prolonged lifetime of the OLED verifies that the SiN_x film grown by CECVD was very a good passivation layer, although a direct comparison of the lifetime with previously reported OLEDs with different types of thin film passivation layers is difficult because the lifetime of an OLED is significantly dependent on the type of organic materials, structure of the OLED and the quality of the OLEDs. Therefore, the identical J-V-L data and prolonged lifetime of the OLED passivated with SiN_x film grown by CECVD suggests that the CECVD technique is a promising plasma-free passivation technique that can be sued in place of conventional PECVD and ICPCVD.[6]

4. Summary

The passivation properties of SiN_x films grown by CECVD for use in OLEDs were investigated. Using a CECVD equipped with a tungsten catalyzer and BEC system, a high quality SiN_x film was deposited on PC substrates and a test cell at a substrate temperature of 50 ^{o}C. Even at a low substrate temperature, the 150 nm-thick SiN_x film grown on OLEDs showed superior barrier and optical properties. Due to local substrate heating by hydrogen recombination during SiN_x film deposition, a high density SiN_x film was produced without any additional substrate heating. These findings indicate that CECVD is a promising plasma free and low temperature thin film passivation technique for OLEDs and flexible OLEDs

5. References

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