Research Report

Plasma-CVD SiN$_x$ /Plasma-polymerized CN$_x$:H Multi-layer Passivation Films for Organic Light Emitting Diodes

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プラズマCVD-SiN$_x$ /プラズマ重合CN$_x$:H積層保護膜の有機EL素子への応用

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Abstract

Organic light emitting diodes (OLEDs) with thin-film passivation are expected to provide a means of producing next-generation flat-panel wide-area displays that are thin, lightweight, and flexible. Thick silicon nitride (SiN$_x$) films fabricated by a plasma-CVD method are already recognized as being a practical passivation film for OLEDs, but these are not suitable for automotive applications as cracks are generated in the films as a result of the thermal stress that is caused by the high temperatures that can arise in automobiles. To overcome this problem, we have developed plasma-CVD SiN$_x$ / plasma-polymerized hydrogenated carbon nitride (CN$_x$:H) multi-layer films that increase the longevity of passivated OLEDs in automotive applications. The films exhibit a high barrier performance against moisture even at high temperatures, because the thermal stress in the films is released by the soft CN$_x$:H layers and no cracks are produced. Indeed, OLEDs with a multi-layer passivation film lasted over 1000 hours in driving tests at 85 °C (initial luminance = 400 cd/m^2), while OLEDs with the thick SiN$_x$ passivation film soon failed and no longer emitted light.

Keywords: OLED, Thin-film passivation, Silicon nitride/Carbon nitride multi-layer film, Automobile, Thermal stress

要　旨

薄膜封止有機EL素子は薄型・軽量・大面積かつフレキシビリティを有した次世代フラットパネルディスプレイとして期待されている。代表的な封止膜としてプラズマCVD法で作製した窒化シリコン厚膜がよく知られているが，高温の車内環境下で使用した場合，熱応力により封止膜にクラックが発生して有機EL素子が破壊してしまうために，車載用途として使用することは困難である。そこで我々は車載環境に置いても十分な耐久性を有した新たな封止膜としてプラズマCVD-SiN$_x$／プラズマ重合CN$_x$: H多層積層封止膜の開発を行った。この封止膜はSiN$_x$膜の間に挟まれた柔らかいCN$_x$: H膜が応力緩和層として働くために熱応力によるダメージを受けず，高温環境下でも十分な封止性を保つことができる。実際，85℃の環境下で初期輝度400cd/m^{2}で駆動試験を行った結果，SiN$_x$厚膜封止有機EL素子はすぐに破壊されて光らなくなったのに対して，積層膜封止有機EL素子では1000時間以上発光し続けた。

キーワード　有機EL素子，薄膜封止，窒化シリコン／窒化炭素多層積層膜，車載，熱応力

1. Introduction

Light-emitting diodes based on organic materials are highly attractive candidates for flat-panel displays and the backlights of liquid crystal displays. Nowadays, thanks to developments in materials, device structures, and process techniques, organic light emitting diodes (OLEDs) with a luminous efficiency in excess of 70 lm/W[1, 2] and a lifetime larger than 10,000 hours[3] have been demonstrated, and red, green, and blue light emitting devices are already available.

OLED displays with thin-film passivation[4] are expected to find applications in next-generation wide-area flat-panel displays that are thin, lightweight, and flexible.[5, 6] Inorganic thin-films created by a chemical vapor deposition (CVD) method, with a thickness of a few micrometers, have been regarded as being well suited to this application because they offer a high barrier performance and good coverage. Indeed, silicon nitride (SiN_x) films fabricated by a plasma-CVD method[4] have already been shown to be well suited to OLED passivation. In automotive applications, however, the passivation films are required to show high reliability despite severe conditions including high temperatures and humidities. Unfortunately, under such conditions, the thick SiN_x films often crack or peel as a result of thermal stress, because they are hard and fragile. If thin SiN_x films are fabricated, their resistance to thermal stress can be improved, but their barrier and coverage performance degrades such that dark spots and dark areas appear. To achieve both qualities, researchers have assumed that a multi-layer structure consisting of hard inorganic films and soft organic films would be effective.[5]

In this paper, we describe how we used plasma-polymerized films for the soft organic films to develop plasma-CVD SiN_x /plasma-polymerized hydrogenated amorphous carbon nitride (CN_x :H) multi-layer passivation films specifically for automotive OLED displays. These films are expected to exhibit good stress relaxation qualities, given the soft CN_x :H layer inserted between the thin SiN_x layers. The deterioration in the barrier and coverage performance resulting from the thinner SiN_x layers is handled by adopting a multi-layer structure. Thus, this passivation is expected to offer an excellent barrier to moisture, high stress relaxation, and good coverage, thus making it ideal for automobile OLED passivation.

2. Preparation

2. 1 CN_x : H films

The CN_x : H films were fabricated by a plasma-polymerized deposition method using methane (CH_4) and nitrogen (N_2) gas. We used CN_x : H in preference to C:H because it is possible to reduce the intrinsic stress and improve the adhesion to the SiN_x layer by controlling the N_2 gas ratio. **Figure 1** shows the N_2 gas ratio dependence of the intrinsic stress in the CN_x : H films. The intrinsic stress was found to be a minimum at an N_2 gas ratio of 0.5, and this value was very small when compared with that for the C:H film (at an N_2 gas ratio of 0). We deposited the SiN_x film as the first layer because the CN_x : H film formed a granular structure on an Al electrode but not on the SiN_x /Al, as shown in **Fig. 2**. A granular structure, on which a deposited SiN_x film would probably form pinholes, is not appropriate for multi-layer passivation.

2. 1 OLEDs and passivation

An OLED was prepared by a vacuum evaporation system (TOKKI CM369), with a multi-layer passivation film grown in-situ using a plasma CVD multi-chamber system (SAMCO PD-3802L). The passivated OLED was fabricated without being exposed to the air by transporting the samples

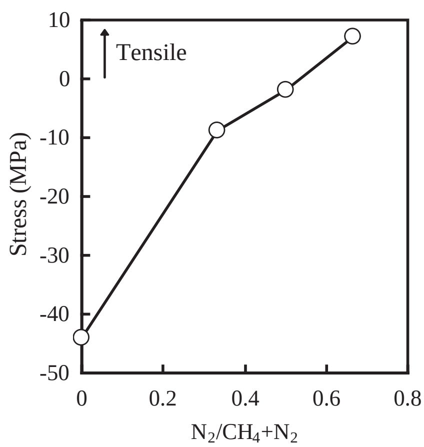


Fig. 1 N_2 gas ratio dependence of the intrinsic stress of CN_x : H films.

between the apparatus in a box purged with N_2 gas.

A typical OLED, as considered in this study, consists of Al/LiF/tris(8-hydroxyquinoline) aluminum (Alq_3)/N,N'-dimethylquinacridone (Me-Qd)-doped Alq_3/triphenylamine tetramer (TPTE) /phthalocyanine (H_2Pc)-doped copper phthalocyanine (CuPc)/indium tin oxide (ITO) with an emitting area of 3× 3 mm. The thickness of each of these layers was 100 nm, 0.5 nm, 40 nm, 20 nm, 50 nm, 10 nm, and 150 nm, respectively. H_2Pc-doped CuPc[7] and TPTE[8] were used because of their stability at high temperatures. An ITO- and SiO_2-coated soda-lime glass plate was used as the substrate. The ITO surface was polished to prevent the formation of pinholes. Before we deposited the organic materials, the substrate was irradiated with UV light in an oxygen atmosphere, after which it was immediately placed in the preparation chamber of the vacuum evaporation system. In the preparation chamber, the substrate was then exposed to Ar/O_2 plasma to remove any surface contamination.

The structure of the multi-layer passivation film was CN_x : H / SiN_x / CN_x : H / SiN_x /OLED, and the thickness of the CN_x : H layer was 500 nm, while that of the SiN_x layer was 200nm. The growth conditions for the SiN_x and CN_x : H films are given in **Table 1**. The intrinsic stress in both films was low enough to allow them to be fabricated on the soft organic films without cracking. For comparison, we prepared an OLED that was passivated by an SiN_x film of the same thickness as the multi-layer film (1.4 μm) and a can lid encapsulated OLED with BaO as its absorbent.

3. Results and discussion

3. 1 Structural analysis

Figure 3 shows a cross-sectional scanning electron

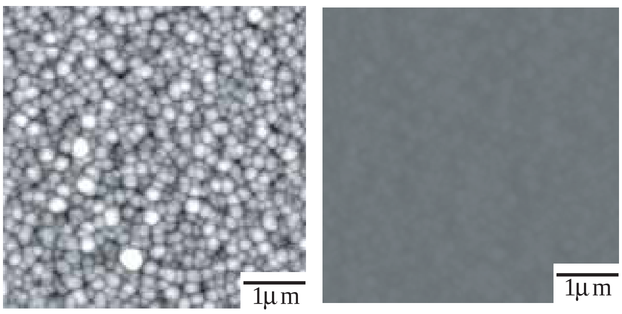
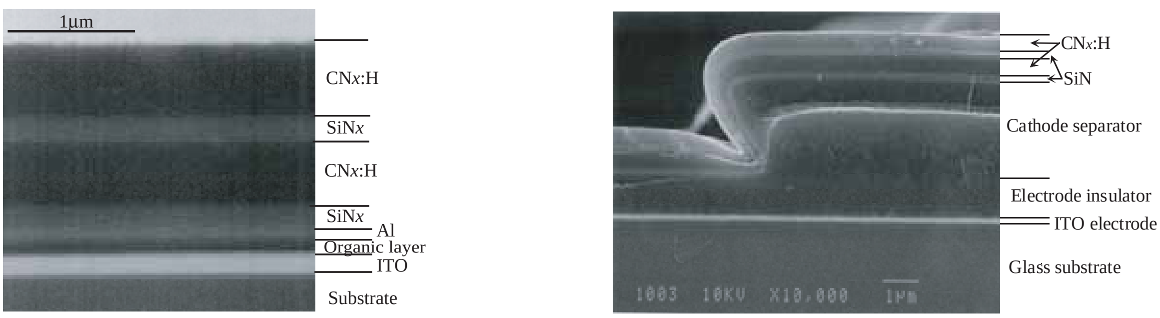


Fig. 2 AFM images of CN_x :H films on an Al film and a SiN_x / Al film.

Table 1 Growth conditions of SiN_x and CN_x :H.

Item	SiN_x	CN_x :H
Gas	$SiH_4/NH_3/N_2$	CH_4/N_2
Flow (sccm)	30 / 30 / 500	10 / 10
Pressure (Pa)	53	50
RF power density (W/cm^2)	0.03	0.16
Substrate temperature (^{o}C)	100	23
Thickness (nm)	200	500
Film stress (MPa)	20-30	< 5



(a) (b)

Fig. 3 Cross sectional SEM images of the multi-layer passivation on the OLED (a) and to the cathode separator (b).

microscope (SEM) image of the multi-layer passivation of the OLED (a). It also shows a cross-sectional SEM image of the multi-layer passivation on the cathode separator (b), which is required by a passive-matrix display, in order to observe the coverage performance. The samples were formed using a focused ion beam (FIB) technique. The passivation film on the OLED was fabricated using a continuous process with each layer being grown in order. No defects were observed in the OLED or the multi-layer passivation. All of the interfaces were smooth enough to prevent the generation of pinholes. The passivation film was also fabricated continuously on the cathode separator and each layer was grown in order, even on the sidewall. The coverage ratio was about 0.5, which can be attributed to the CN_x :H films. No cracks can be observed at the corners of the cathode separator, where the stress is usually concentrated. This fact indicates that multi-layer passivation is very effective at relaxing stress.

3. 2 Lifetime of OLEDs with multi-layer film passivation

Figure 4 illustrates the driving test performed on an OLED with multi-layer passivation at 85°C in the air. The results for the SiN_x -passivated OLED and the can lid encapsulated OLED are also shown. The initial luminance was 400 cd/m^2 at 85°C and the current was held at the initial value throughout the testing. The characteristics exhibited by the multi-layer passivated OLED were similar to the can lid encapsulated OLED. **Figure 5** shows charge-coupled device (CCD) images of the light-emitting area of the multi-layer passivated OLED both before and after the 1000-hour driving test. Some dark spots were observed before the test, but they didn't increase or expand, even after the test. This result indicates that the multi-layer passivation maintained its excellent moisture barrier property and caused no damage to the OLED, even at high temperatures.

In the case of the an OLED with the SiN_x passivation, however, dark spots and dark areas appeared and increased at the edges of the emitting area due to cracks forming in the SiN_x film, with the OLED ultimately being shortened. Given that these dark spots and dark areas did not appear when the OLED was driven at room temperature, and that the thick SiN_x film was so fragile that it easily cracked under stress, we can assume that this failure was caused by thermal stress. Indeed, the stress changed by about 80 MPa between room temperature and 85 °C, as calculated from the coefficients of linear thermal expansion of the SiN_x film (3.9×10^{-6}/ °C), as measured using the Si wafer-bending method with a laser-deflection system, and that of the soda-lime glass substrate (8.5×10^{-6}/ °C). In addition, because the stress in the hard SiN_x film fabricated on the soft organic film tends to concentrate and increase at defects or edges, the value of the thermal stress

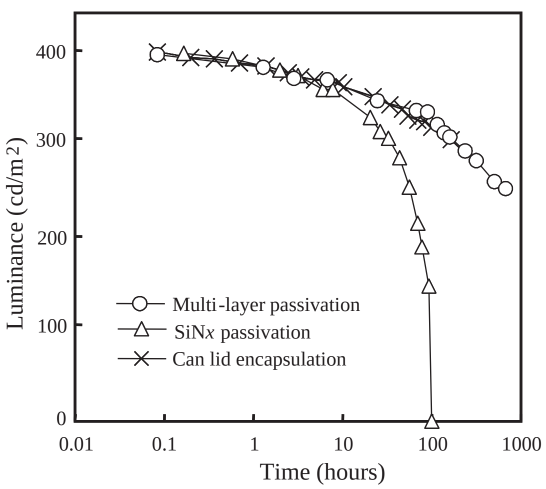


Fig. 4 Driving test of the OLEDs at 85 °C. Initial luminance was 400 cd/m^2 and the driving current was kept at initial value.

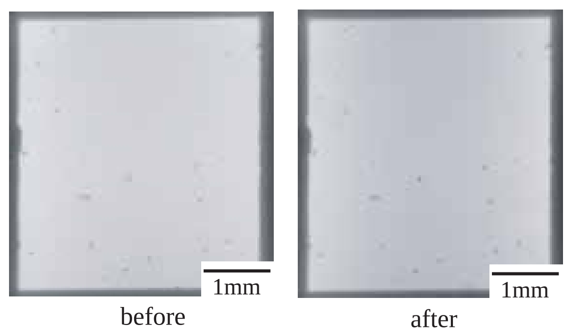


Fig. 5 CCD images of a light emitting area of the multi-layer passivated OLED before and after the driving test for 1000 hours at 85 °C.

between room temperature and 85 °C is considered large enough to form cracks in the SiN_x film.

These results indicate that multi-layer passivation is much more resistant to thermal stress than the SiN_x passivation. We assume that the high durability of the multi-layer passivation derives from the CN_x:H layer acting as a stress relaxation layer. Indeed, the stress relaxation ability of the CN_x : H layer is quite high because the CN_x : H film is polymer-like, which was supported by the results of the analysis by the CNH coder, in that the composition of the CN_x : H film thus formed was $C_{0.35}N_{0.08}H_{0.52}$, and the Young's modulus of the CN_x : H film was less than 5 GPa, which is extremely small compared with the SiN_x film (240 GPa).

4. Conclusion

We have developed plasma-CVD SiN_x /plasma-polymerized CN_x : H multi-layer passivation films for automotive OLED displays. For the multi-layer film, we adopted a CN_x : H /SiN_x /CN_x : H /SiN_x /OLED structure, so as to reduce the intrinsic stress and produce smooth individual layers. By using this multi-layer passivation, we successfully produced a passivated OLED with the same high-temperature longevity as the can lid encapsulated OLED. We believe that the excellent characteristics of the multi-layer passivation derives from the thermal stress relaxation ability of the CN_x : H layer. Thus, we expect to see the practical application of multi-layer passivation to automotive OLEDs.

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