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ScienceDirect
Thin Solid Films 516 (2008) 553 – 557
www.elsevier.com/locate/tsf

Cat-CVD SiN passivation films for OLEDs and packaging

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Available online 15 August 2007

Abstract

A Roll-to-roll type catalytic chemical vapor deposition (Cat-CVD) apparatus was developed for the application to flexible organic light-emitting diode (OLED) displays and packaging. Silicon nitride (SiN_x) films were prepared by this roll-to-roll type apparatus at temperatures below 60 °C. It was found that these SiN_x films are highly moisture resistant, and the water vapor transmission rate (WVTR) on plastic substrates could be lowered to 0.01 g/m^2 day. Roll-to-roll type Cat-CVD is one of the most promising methods for the preparation of barrier films for OLED displays and packaging.

Keywords: Cat-CVD; Passivation; Barrier film; Roll to roll; Silicon nitride; Organic light-emitting diode; Water vapor transmission rate; Ca corrosion test

1. Introduction

Plastic materials are widely used in various application fields, because they are cheap, light and flexible. However, the moisture resistance of plastic substrates is low. For example, the water vapor transmission rate (WVTR) of a 0.1 mm-thick polyethylene naphthalate (PEN) substrate is 2 g/m^2 day. WVTRs of 10^{-6} and 1 g/m^{2}day are required for organic light-emitting diode (OLED) displays and food packaging, respectively. Therefore, various types of moisture-resistant films on plastic substrates have been investigated.

Silicon nitride (SiN_x) prepared by catalytic chemical vapor deposition (Cat-CVD) is chemically stable, optically transparent and highly moisture-resistant [1]. In this method, source gas molecules are decomposed by catalytic cracking reactions on a heated catalyzer placed near the substrate [2]. So far, highly moisture-resistant SiN_x films on a Si substrate have been obtained at substrate temperatures between 20 and 100 °C using a mixture of SiH_4, NH_3 and H_2 as a source gas [3–5]. The stress of SiN_x on a Si substrate can be controlled from compressive to tensile by changing the deposition conditions and the stress is, in general, lower than 100 MPa [6]. The deposition rate was as high as 100 nm/min [7].

The above results were obtained using a batch type apparatus with a flat substrate holder. Roll-to-roll type processes are required for industrial applications. In this article, the properties of SiN_x films prepared by a roll-to-roll type Cat-CVD apparatus on plastic substrates were introduced.

2. Experimental details

A photograph of a roll-to-roll type Cat-CVD apparatus made by Ishikawa Seishakusho is shown in Fig. 1. A tungsten wire 0.5 mm in diameter was used as the catalyzer. This catalyzer was set at the bottom of the chamber at a distance 100 mm away from the cooling drum. A mixture of SiH_4, NH_3 and H_2 was introduced into the chamber though a showerhead at the bottom. To suppress heating of the plastic substrate by thermal radiation from the heated catalyzer, the plastic substrate was stretched by a force of 5 kgw to improve the contact between the substrate and the cooling drum.

SiN_x films were continuously deposited on the plastic substrate 0.1 mm in thickness and 300 mm in width. The deposition conditions are summarized in Table 1. The gas pressure, the deposition

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0040-6090/$ - see front matter
doi:10.1016/j.tsf.2007.06.220

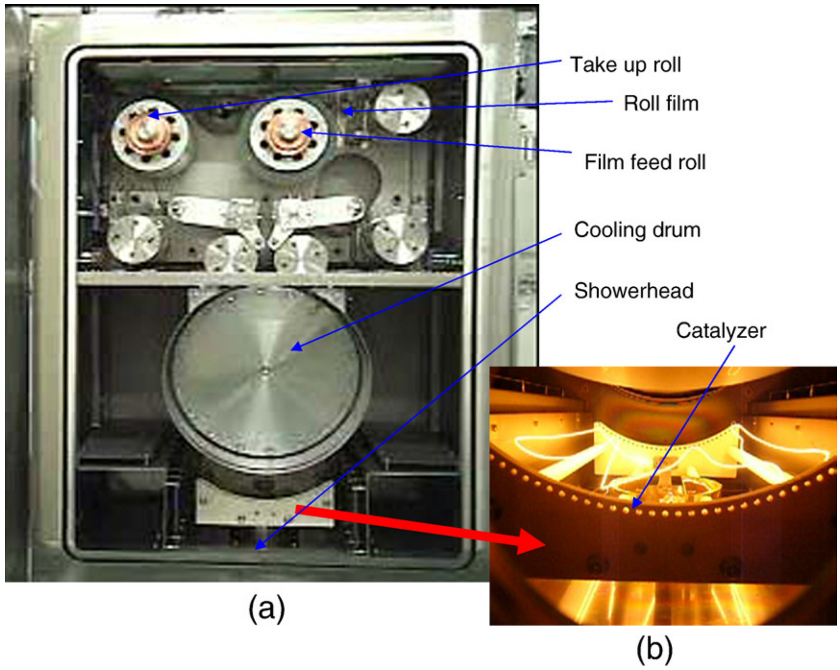

Fig. 1. Photograph of a roll-to-roll type Cat-CVD apparatus. Chamber inside (a) and catalyzer (b).

roll temperature and the substrate temperature were 30 Pa, −20 °C and 60 °C, respectively.

The Si-, N- and O-atom contents in SiN_x films were estimated by X-ray photoelectron spectroscopy (XPS). The optical transmittance of SiN_x films on the PEN substrate was measured from 300 to 800 nm using a spectrophotometer.

The WVTR of SiN_x films on PEN substrates was evaluated by the cup and MOCON methods. The diameters of the samples for the cup and MOCON methods were 40 and 80 mm, respectively. The MOCON method used only the sample with low WVTR because the detection limit for the cup and MOCON methods were 0.3 and 0.01 g/m^2day, respectively. The transmission mechanism of water vapor in SiN_x films was investigated using a Ca corrosion test. The cross section of the sample for the Ca corrosion test is illustrated in Fig. 2. A Ca film 500 nm in thickness was deposited by vacuum evaporation on a PEN substrate coated with a SiN_x film. A Cu film 80 nm in thickness was, then, continuously deposited on the Ca film. This sample was then pasted on a glass substrate using an adhesive agent. The color of the Ca film changes when exposed to the transmitted water vapor.

Finally, a PEN substrate with a SiN_x film was applied to an OLED device to check its reliability over time. The cross section of an OLED device is shown in Fig. 3. A PEN substrate with a SiN_x film was used as a cover film. The lifetime of the OLED covered with the PEN substrate was evaluated at 60 °C and 90%RH.

3. Results and discussion

3.1. Properties of SiN_x film prepared by roll to roll type Cat-CVD apparatus

The N/Si ratio and the O content of the SiN_x film prepared under condition A in Table 1 are shown in Fig. 4. In this case, the SiN_x film was continuously deposited on a PEN sheet 13 m in length, and the properties were measured at 2-m intervals. The film thickness was 40 nm and the deposition rate was 4 nm/m/min. The N/Si ratio was almost constant at about 1.2. The O content was higher at 1 m, but it levelled off. The WVTRs were lower than 0.3 g/m^2day which is the detection limit for the cup method.

The optical transmittances of a PEN substrate and a PEN substrate with a SiN_x film are shown in Fig. 5. The transmittances at 500 nm were 85% and 83%, respectively. The decrease in the transmittance should be due to the difference in the refractive indices of SiN_x ($n=1.9$) and PEN ($n=1.7$).

The N/Si ratio and the O content of SiN_x films prepared under condition B in Table 1 are shown in Fig. 6 as a function of SiH_4 flow rate. As the SiH_4 flow rate increases, the N/Si ratio decreases from 1.2 to 0.4 and the O content increases from 10 to 35%. It seems that N atoms are replaced by O atoms with air exposure.

The WVTR is shown in Fig. 7 as a function of SiH_4 flow rate. As the SiH_4 flow rate increases, the WVTR increases from ≈0.1 to 2 g/m^2day. The WVTR of SiN_x films must be related to the O content because the WVTR and O content showed similar dependence on SiH_4 flow rate as shown in Figs. 6 and 7. SiN_x films with O content over 30% may not have high moisture

Table 1
Deposition conditions for SiN_x films

Condition	A	B	C
SiH_4 flow rate (sccm)	4	4–8	10
NH_3 flow rate (sccm)	10	10	30
H_2 flow rate (sccm)	400	400	400
Catalyzer length (m)	2.3	2.3	3.2
Catalyzer temperature (°C)	1750	1750	1800
Feed rate (m/min)	0.1	0.1	0.3