Water and oxygen permeation of silicon nitride films prepared by plasma-enhanced chemical vapor deposition

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Abstract

Silicon nitride (SiNx) films deposited on flexible polyethersulfone (PES) substrates by plasma-enhanced chemical vapor deposition (PECVD) have been investigated for water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) barrier applications. Details of the NH3/SiH4 flow ratio and chamber pressure effects on the SiNx/PES properties in terms of chemical bonding, transmittance, refractive index, deposition rate, adhesion, roughness, OTR and WVTR were investigated. When the NH3/SiH4 flow ratio increased from 1.43 to 10, evident variations in refractive index and transmittance of the SiNx/PES samples were observed. Moreover, as the chamber pressure increases from 26.7 to 133.4 Pa, the deposition rate, adhesion and roughness increase while no evident variations in WVTR and OTR were observed. Under optimum conditions, the WVTR and OTR of 100-nm-thick SiNx barrier coating on PES at 150 °C decreased to a value of near 0.01 g/m2/day and 0.01 cm3/m2/day, respectively. This indicates that the SiN barrier on PES has high potential for flexible display applications.

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1. Introduction

Recently, high-temperature-resistant polymers like polyethersulfone (PES) are becoming increasingly important for many applications [1,2]. A major application area has appeared for this technology, namely polymer-based organic light-emitting diode (OLED) displays, which require perfect encapsulation against inward permeation of water and oxygen [3]. Both vapors can oxidize the metallic cathode, which reduces the electron injection in the OLED and thereby drastically decreases its performance. In order to reduce the rate of permeation of vapors through polymers, several barrier options have been proposed and utilized.
Although the water vapor transmission rate (WVTR) of PES (~50 g/m²/day; thickness: 200 μm) is higher than that of the PET (~16 g/m²/day; thickness: 188 μm), the PES substrate can withstand process temperatures of up to 180 °C, which is higher than that of PET (~120 °C). Since polymeric materials generally have low resistance to heat, barrier coatings must be conducted at a low temperature in order to avoid thermal damage to a polymeric substrate. Higher process temperatures provide more flexibility in device process design and better quality deposited films. In this study, we have investigated the characterization of silicon nitride (SiNₓ) films on flexible PES substrates by PECVD for transparent barrier applications. Silicon nitride possesses excellent physical and chemical properties, such as transparency from ultraviolet to infrared, good thermal stability, chemical inertness, and wear and corrosion resistance. Details of the deposition parameters (NH₃/SiH₄ flow ratio and chamber pressure) on the SiNₓ properties in terms of transmittance, refractive index, chemical bonding, deposition rate, adhesion, roughness will be described. Especially, the permeation properties, i.e. oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) of the SiNₓ/PES samples will be discussed.

2. Experimental details

Silicon nitride films were deposited on PES or Si (100) substrates by PECVD in a parallel plate, capacitively-coupled-plasma (13.56 MHz) reactor with an electrode spacing of 4 cm. A gas showerhead (150 cm in diameter) served as the powered electrode and was isolated electrically from the reactor by a ceramic spacer. On the grounded electrode, a ceramic heater capable of temperatures up to 400 °C was used to heat the substrate up to 10×10 cm². The substrate temperature was measured by using a thermocouple bead, electrically shielded from the plasma that contacted the backside of the substrate holder. Ammonia (NH₃) and 5% silane in argon (SiH₄/Ar) were used as source gases. During the growth process, the total gas flow rate was maintained at 150 sccm. All of the samples studied were deposited at 150 °C to prevent any deformation of the PES substrates. The molded PES substrates were 0.2 mm in thickness with a glass-transition temperature of 220 °C and a surface roughness of ~0.7 nm.

The SiNₓ/PES samples used here were 100 nm in thickness. The refractive index and transmittance of the nitride films were obtained with a thin-film measurement system (model: 1280, N and K Tech.). The film thickness and deposition rate were measured directly on the coated PES, or on small pieces of Si wafer used as reference substrates, by a Tencor-KLA (P-10) profilometer. A Fourier transform infrared (FTIR) spectrometer (FTS 40, Bio-Rad) was employed to analyze the chemical bonding within the films.
material and to give insight into their composition and structure. The detection limit of this equipment is given by an integrated area of ~2.5 cm$^{-1}$ with a resolution of 2 cm$^{-1}$.

Surface morphology of the SiN$_x$ film was analyzed by atomic force microscopy (AFM, PSI Auto Probe). The measurements were accomplished with a Si cantilever for contact AFM (contact mounted ultralever; force constant of 4 N/m and resonance frequency of 45 Hz), and the scan rate and area were 1–2 Hz and 5×5 $\mu$m$^2$, respectively. Finally, permeation was measured for both untreated control sample and for coated samples. Measurements of OTR and WVTR permeation were carried out on a 10-cm$^2$ active sample area, at 25 °C, using MOCON “Ox-tran 2/61” and “Permatran-W3/61” instruments, respectively; for OTR measurements, we used 0% relative humidity. Frequent calibrations were performed with a standard PET film sample supplied by MOCON.

### 3. Results and discussion

Fig. 1 shows the FTIR spectra of the SiN$_x$ samples deposited under different NH$_3$/SiH$_4$ flow ratios, where the total gas flow is kept constant. The peaks including (1) N–H stretching at 3330 cm$^{-1}$; (2) Si–H stretching at 2159 cm$^{-1}$; (3) N–H bending at 1169 cm$^{-1}$; and (4) Si–N stretching at 828 cm$^{-1}$ [11,12]. Since the temperature is reduced in plasma deposition on polymer substrates, the energy required for desorbing hydrogen becomes less available, leading to more hydrogen incorporation and reduced film density. On decreasing the NH$_3$/SiH$_4$ flow ratio during the SiN$_x$ deposition, the H-related bonds are changed from N–H to Si–H and the main absorption peak (Si–N) is shifted to low wavenumbers suggesting a more silicon-rich composition for high silane fluxes [13]. It was found that the refractive index increased from 1.69 to 1.94 and the transmittance decreased from 90% to 81% as the NH$_3$/SiH$_4$ flow ratio decreased from 10 to 1.43. The higher Si–H bonding content can be related to the higher refractive index and lower transmittance. Moreover, as the NH$_3$/SiH$_4$ flow ratio increased above 7.0, the N–H and Si–H stretching vibrations became weaker and a band centered at 1067 cm$^{-1}$ was observed, which corresponded Si–O stretching vibrations. This indicates that some nitride films deposited under high NH$_3$ content are extremely porous, showing oxidation after only a few minutes in air [12].

The deposition rate and adhesion of the nitride barrier film as functions of the NH$_3$/SiH$_4$ flow ratio are presented in Fig. 2. As the NH$_3$/SiH$_4$ increased from 1.43 to 5.0, the deposition rate first decreased because of the decrease of the silane supply. Further increasing the NH$_3$/SiH$_4$ flow ratio resulted in the increase of deposition rate due to the increase of Si–O bonding content in the SiN$_x$ film. The nitride coatings prepared by higher NH$_3$/SiH$_4$ flow ratios are seen as...
to possess good adhesion characteristics presumably related to generative Si–O bond of the film. Fig. 3 illustrates the effect of NH₃/SiH₄ flow ratio on the OTR and WVTR data of the nitride barrier films. As the NH₃/SiH₄ flow ratio decreased from 10 to 1.43, the WVTR and OTR data decreased to a value of near 0.01 g/m²/day and 0.01 cm³/m²/day, respectively. During the WVTR measurement (water soaking), the water exposed surface of SiNₓ could be partially oxidized, because the Si–O bond is thermodynamically more stable (8.26 eV) than the Si–N bond (5.2 eV) [9]. Under higher NH₃/SiH₄ flow ratios (>7.0), the oxidation of SiNₓ in water and oxygen will be enhanced as described in Fig. 1.

In the following, the SiNₓ/PES samples were deposited under a NH₃/SiH₄ flow ratio of 3.7 to obtain a high transparent barrier film. The effect of chamber pressure on the OTR and WVTR of the SiNₓ barrier films is shown in Fig. 4. As the chamber pressure increased from 26.7 to 133.3 Pa, no evident variations in the OTR/WVTR data were observed. Generally, the PECVD coatings prepared under high chamber pressures are seen to possess higher roughness presumably related to higher deposition rate generative less dense of the film. A higher deposition rate does not give atoms enough time to reach the lower energy sites. From the AFM measurements (Fig. 5), the corresponding surface roughness of the coated PES increased from 1.04 to 3.51 nm, a little higher than that of the bare PES substrate (0.7 nm). These indicate that the grain size of all SiNₓ films is very fine, contributing to the present OTR/WVTR result.

4. Conclusions

SiNₓ barrier coatings on flexible PES substrates by PECVD for oxygen and water resistant applications are described. The NH₃/SiH₄ flow ratio has played an important role in SiNₓ films such as bond configuration, transmittance, refractive index, deposition rate, adhesion, WVTR, and OTR. Under optimum conditions, the WVTR and OTR for PES after coating a 100-nm-thick SiNₓ barrier can be reduced to a level of near 0.01 g/m²/day and 0.01 cm³/m²/day, respectively. It was found that the deposition rate, adhesion and roughness of the SiNₓ film increased as the chamber pressure increased from 26.7 to 133.3 Pa. However, no evident variations in WVTR and OTR properties were observed under these chamber pressures. These results indicate that the SiNₓ/PES barrier coatings have high potential for flexible organic light-emitting-diode applications.

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