Properties of SiO$_2$-like barrier layers on polyethersulfone substrates by low-temperature plasma-enhanced chemical vapor deposition

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Abstract

We investigated the characterization of silicon oxide (SiO$_2$) films on polyethersulfone (PES) substrates by plasma-enhanced chemical vapor deposition for transparent barrier applications. The film properties, such as deposition rate, etch rate, roughness, and water vapor transmission rate (WVTR), were found to increase as the plasma power increased from 10 to 120 W. As the pressure of chamber increases from 75 to 375 mbar, the deposition rate, etch rate, and roughness increase while the WVTR decreases. Under optimum conditions, the WVTR for PES can be reduced from a level of 50 g/m$^2$/day (bare substrate) to 0.31 g/m$^2$/day after application of a 100-nm-thick SiO$_2$ coating at 150 °C. A more efficient way to improve permeation of PES was carried out by using a double-side coating of a 100-nm-thick SiO$_2$ film. It was found that the WVTR can be reduced to a level of 0.1 g/m$^2$/day. The double-side coating on PES could contribute to the lower stress of oxide film, which greatly improves the WVTR data. These results indicate that the SiO$_2$/PES barrier coatings have high potential for flexible organic light-emitting diode (OLED) applications.

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1. Introduction

Transparent barrier coatings, such as silicon oxide (SiO$_2$), on polymers are receiving much attention in industries for pharmaceutical, food, and beverage packaging 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. The oxidation of the active organic material is critical as well. In order to reduce the rate of permeation of vapors through polymers, several barrier options have been proposed and utilized. Thin, glassy coatings of silicon compounds, SiO$_2$ or Si$_3$N$_4$, which are optically transparent, can be deposited by plasma-enhanced chemical vapor deposition (PECVD) [4–6]. PECVD is one of the techniques that allow industrial-scale deposition of high-quality barrier coatings with good uniformity and good adherence to the substrate. The PECVD coatings have some important advantages over the current metallization technology: they are transparent and permit recycling of the coated polymer while providing a diffusion barrier of similar quality to the metallized one. Furthermore, it is well known now that one of the main advantages of PECVD is that applying an ion bombardment on the surface is equivalent to increasing the temperature of this surface [7]. This contributes to the film’s densification and improved adhesion, allowing the possibility of depositing high-quality coatings at lower temperatures.

Most of the previous reports about barrier coating were focused on the polyethylene terephthalate (PET) substrate [8–10]. Recently, high-temperature resistant polymers like polyethersulfone (PES) are becoming increasingly important for many applications [11]. Although the water vapor transmission rate (WVTR) of PES (~ 50 g/m$^2$/day; thickness: 200 μm) is higher than that of PET (~ 16 g/m$^2$/day; thickness: 188 μm), the PES substrate can withstand process temperatures of up to 180 °C, a range which is higher than...
that of PET (\(\sim 120^\circ\)). Higher process temperatures provide more flexibility in device process design and better quality deposited films. In this study, we investigated the properties of SiO\(_2\) films on flexible PES substrates deposited by PECVD for transparent barrier applications. Details of the effects of deposition parameters (gas ratio, pressure of chamber, and plasma power) on oxide film properties in terms of deposition rate, refractive index, roughness, etch rate, and WVTR will be discussed.

2. Experimental details

Silicon oxide 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 (6 in 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 \times 10 \text{ cm}^2. The substrate temperature was measured by using a thermocouple bead, electrically shielded from the plasma, that contacted the backside of the substrate holder. SiH\(_4\) (5\%) in Ar and N\(_2\)O was used as a source gas. 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 \(0.7 \text{ nm}\).

Most of the SiO\(_2\)-on-PES samples used here were 100 nm in thickness, except for the discussion on thickness effects. The refractive index was obtained with a thin-film measurement system (model: 1280, N\&K Tech.) by measuring the reflectance spectra of the samples deposited on Si substrates. 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. The etch rate of the SiO\(_2\) film was measured directly on the coated PES, or on small pieces of Si wafer used as reference substrates, by a Tencor-KLA (P-10) profilometer. The etch rate of the SiO\(_2\) film was determined by the 6:1 buffer–oxide–etch solution, and the etching depth was measured by a profilometer. A Fourier transform infrared (FTIR) spectrometer (FTS 40, Bio-Rad) was employed to analyze the chemical bonding within the film and to give insight into their composition and structure. The detection limit of this equipment is given by an integrated area of \(\sim 2.5 \text{ cm}^{-1}\) with a resolution of 2 cm\(^{-1}\). Surface morphology of the SiO\(_2\) film was analyzed by atomic force microscopy (AFM, PSI Auto Probe). The measurements were accomplished with a Si cantilever for contact AFM (ULCT-AUMT-B, contact-mounted ultralever, force constant of 4 N/m, and resonance frequency of 45 Hz), and the scan rate and area were \(1–2 \text{ Hz and } 5 \times 5 \text{ \mu m}^2\), respectively. Permeation was measured for both untreated control samples and for coated samples. WVTR of the barrier film on PES was carried out on a 10-cm\(^2\) active area, at 25 °C/100% RH, using a MOCON W3/61 instrument. 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 SiO\(_2\) samples deposited under different N\(_2\)O/SiH\(_4\) flow ratios, where the total gas flow is kept constant. As the flow ratio decreased to 10, a widened band centered at 1067 cm\(^{-1}\) was observed, which corresponded to Si–O stretching vibrations. Its intensity decreased due to the enhanced structural disorder and to an increase in the intensity of the band centered at 875 cm\(^{-1}\), assigned to Si–N stretching vibrations. Moreover, a band in the 3382 cm\(^{-1}\) spectral region corresponded to stretching vibrations of the N–H bonds. A band centered at 2258 cm\(^{-1}\) appeared, indicating the presence of Si–H stretching vibrations. Under higher N\(_2\)O/SiH\(_4\) ratios, the samples presented spectra very similar to thermally grown SiO\(_2\) from Si, exhibiting only the characteristics of Si–O stretching and bending modes. It was found that the refractive index dramatically decreased from 1.973 to 1.438 as the flow ratio increased from 10 to 105. Typically, the stoichiometric silicon oxide film (\(n = 1.46\)) by PECVD at 300–350 °C can be obtained under a N\(_2\)O/SiH\(_4\) ratio below 10 [12]. The higher flow ratio required for stoichiometric silicon oxide in this study could have been due to the lower deposition temperature (150 °C), which resulted in insufficient dissociation of N\(_2\)O. In the following, the SiO\(_2\)-like samples were deposited under a N\(_2\)O/SiH\(_4\) ratio of 40.

Fig. 2 shows the influence of the chamber pressure on the deposition rate, etching rate, surface roughness, and WVTR of the oxide barrier film. The deposition rate initially increased with chamber pressure but decreased at higher
pressure above 375 mbar. The etching rate and roughness at various chamber pressures also showed an increase-maximum-decrease behavior. Faster film growth results in lower density and rougher film (75 to 375 mbar). The etch rate, in turn, increases correspondingly. The locus of the maximum etching rate in Fig. 2(b) shifted to a higher pressure of 600 mbar. The behavior can be explained by the presence of competing or parasitic gas phase reaction channels in this pressure range (375 to 750 mbar). Particle formation was observed on the chamber walls and windows at deposition pressures above 375 mbar. This is an obvious reaction pathway for depletion of the deposition species, which become more prevalent at higher pressures. Further increasing the chamber pressure (600 to 750 mbar) yielded a very low deposition rate, resulting in the decrease of etch rate.

The WVTR of the SiO$_2$-on-PES samples as a function of chamber pressure is also illustrated in Fig. 2(a). An increase in process pressure to 600 mbar achieved lowest WVTR data. There are two possible explanations for the decrease of WVTR as the chamber pressure increases from 75 to 600 mbar. One of those may be the decrease of kinetic energy of active species due to the longer residence time in the gas phase. The lower kinetic energy of active species could result in a barrier layer with lower residual stress, which would result in fewer defects (e.g., pinholes, microcracks, etc.). However, it is controversial that the etching rate increases with increasing chamber pressure. Another explanation is that the film coated at higher pressure is less hydrophilic than that at lower pressure. The higher pressure induces not only the larger particles but also the more stable bonding state at the surface of particles. This decreases the wettability of water on the film and hinders the penetration of water vapor.

Fig. 3 shows the influence of the radio-frequency (RF) power on the deposition rate, etching rate, surface roughness, and WVTR of the SiO$_2$ barrier film. Here, the pressure of chamber was kept at 150 mbar although various pressures (200–750 mbar) had been attempted and showed similar trends. The deposition rate, etching rate, and roughness increased with the RF power level and reached a maximum of 120 W. When the RF power increases, the energy of the plasma generates significant amounts of O$^*$ [6]. A higher deposition rate does not give atoms enough time to reach the lower energy sites. This leads to the increase of etching rate and roughness. It is worth mentioning that the WVTR also increases with the RF power level. This could be attributed to the barrier layer with higher residual stress and increase the defects (e.g., pinholes, microcracks, etc.). The film formed at higher RF power may also be more hydrophilic due to the rougher surface and this enhances the penetration of water.

It has been proposed that gas and water vapor transport in barrier films is comprised of contributions from three components: unhindered transport through ‘macrobeaks’ (>1 nm) in the oxide layer, hindered transport through ‘nanodefects’ (<1 nm), and hindered transport through...
the amorphous lattice of the oxide (interstice < 0.3 nm) [13]. The permeation data indicate that the oxide layer is more similar to a nanoporous solid (such as zeolite) than to SiO2 glass and that all three components contribute to the total permeation. Under optimum conditions (N2O/SiH4 = 40, chamber pressure = 600 mbar, RF power = 30 W), the WVTR for PES can be reduced from a level of 50 g/m2/day (bare substrate) to 0.31 g/m2/day after surface coating of a 100-nm-thick SiO2 film. However, the surface roughness of the coated PES will increase to 2.71 nm, a little higher than the bare PES substrate (0.68 nm). Further increasing the thickness of oxide barrier is expected to improve WVTR, but it also makes a rougher surface, which is not suitable for flexible OLED display applications. A more efficient way to improve WVTR of PES was carried out by using a double-side coating of a 100-nm-thick SiO2 film. Although the barrier thickness was doubled, it was found that the WVTR can be reduced to a level of 0.1 g/m2/day. The double-side coating on PES could contribute to the lower stress of oxide film, which greatly improves the WVTR data.

4. Conclusions

The characteristics of SiO2 films on flexible PES substrates by PECVD are described. In spite of the defects, the WVTR of the coated PES substrate can be reduced by two orders of magnitude lower than that of uncoated ones. It was observed that the higher chamber pressure and lower RF power favor the better WVTR data. The kinetic energy of active species could have resulted in the residual stress and defects of the barrier layer (e.g., pinholes, microcracks, etc.). Under optimum conditions, the WVTR for PES can be reduced to a level of 0.1 g/m2/day after a double-side surface coating of a 100-nm SiO2 layer at 150 °C. Further improvement in permeation of the SiO2 coating on PES is still needed for flexible OLED applications (<10^{-5} g/m2/day) [3].

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References