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Deposition of SiO_x barrier films by O_2/TMDSO RF-PECVD*

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This paper reports that the SiO_x barrier films are deposited on polyethylene terephthalate substrate by plasma-enhanced chemical vapour deposition (PECVD) for the application of transparent barrier packaging. The variations of O_2/ Tetramethyldisiloxane (TMDSO) ratio and input power in radio frequency (RF) plasma are carried out to optimize barrier properties of the SiO_x coated film. The properties of the coatings are characterized by Fourier transform infrared, water vapour transmission rate (WVTR), oxygen transmission rate (OTR), and atomic force microscopy analysers. It is found that the O_2/TMDSO ratio exceeding 2:1 and the input power over 200 W yield SiO_x films with low carbon contents which can be good to the barrier (WVTR and OTR) properties of the SiO_x coatings. Also, the film properties not only depend on oxygen concentration of the inlet gas mixtures and input power, but also relate to the surface morphology of the coating.

Keywords: RF-PECVD, TMDSO, SiO_x films, barrier property
PACC: 5275, 8115H

1. Introduction

Transparent barrier coatings on polymer surface have received much more attention from industries of the pharmaceutical, food and beverage packaging applications recently.[1,2] Now a novel application area has appeared for this technology, namely polymer-based organic light-emitting diode display, which requires a perfect encapsulation against inward permeation of water and oxygen.[3] Plasma acting as a versatile tool can polymerize a coating and perform innovative properties. The materials formed by plasma polymerization are very different from conventional ones and demonstrate a novel characterization. Because of the advantage of such polymers, the formation of organic solids or films in plasma has attracted considerately,[4] and the plasma-enhanced chemical vapour deposition (PECVD) becomes one of the techniques that allow industry-scale deposition functional films, where a high bombardment on the surface will contribute to the film densification and adhesion. These films have the advantage of recycling usage without pollution. Furthermore, it is well known that in PECVD the ions cause a quality barrier coating with good uniformity and good adherence to the substrates.[5] It is well known that SiO_x coatings have more important advantages than the currently metallized high-quality coatings deposited at lower temperatures.[6]

2. Experimental

Figure 1 shows the schematic diagram of the plasma setup employed in this work. During the experiment the background pressure of the film deposition system is normally evacuated less than 3Pa. Tetramethyldisiloxane (TMDSO) was used as the precursor and oxygen gas was used as the dilution gas. SiO_x coatings were deposited on polyethylene terephthalate (PET) (12-μm thickness), KBr and silicon (100) wafer substrates. The SiO_x films deposited in different O_2/TMDSO ratios and input plasma powers (50–300 W) were investigated, respectively. The chemical structure and surface morphology of the coatings were characterized by Fourier transform infrared spectroscopy analysis (Shimadzu, FTIR-8400, Japan) and atomic force microscopy (AFM, CSPM3000, BenYuan China). And the barrier properties of the films were tested by water vapour trans-

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mission rate (WVTR, Labthink, Jinan) and oxygen transmission rate (OTR, model 8000, Illinois, American, supplied by Guangzhou Biaoji Co.) analysers. The OTR test was carried out at a fixed condition (temperature at 23 °C and humidity at 50 %).

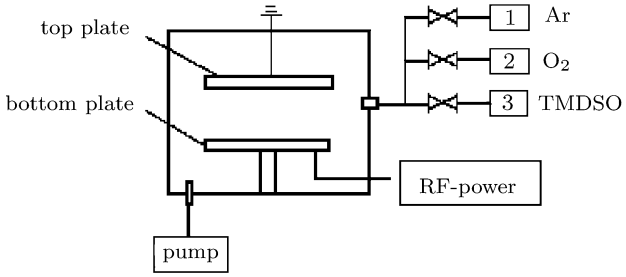


Fig.1. Schematic diagram of the plasma setup.

3. Results and discussion

3.1. FTIR spectra

Figure 2(a) shows the FTIR spectra of the SiO_x coatings deposited under different plasma powers when the total gas pressure and discharge time were kept constant and the discharge in the continuous mode. As the power increased from 50 W to 250 W, FTIR spectra shows that the main adsorption peaks in the band 1060–1070 cm^{-1} become much more intense, and the Si–O–Si stretching vibrations and bending vibration around 805–810 cm^{-1} are more obvious in the figure. The band centred at 1067 cm^{-1} was widened with the increase of the power and a nearby shoulder peak was also appeared in the higher plasma power. But the band near 1274 cm^{-1} assignment for Si–CH_3 stretching vibration dramatically reduced with the increase of the power. It is known that carbon negatively affects the barrier properties of the deposited coating.[7] When the power exceeded 200 W, moreover, the peak of carbon disappeared, which means that the high pure Si–O coating was generated. The same trend was observed when the oxygen content was increased.

Figure 2(b) shows that the Si–CH_3 component decreased with the increase of O_2/TMDSO ratio in the mixture gases, and the purity of Si–O in the film getting higher meanwhile. The possible reason is that the discharge generates a large quantities of atomic oxygen in plasma,[8] which combine with active radicals and cause a high deposition rate with pure SiO_x component.

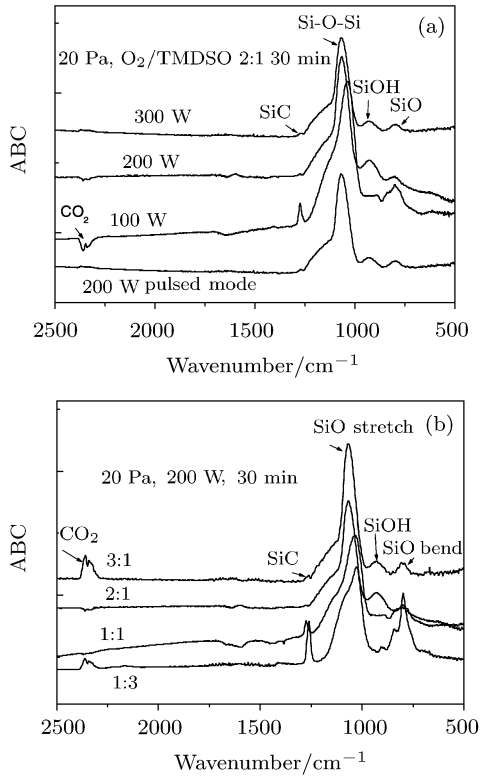


Fig.2. Dependence of FTIR spectra on a-incident powers, b-O_2/TMDSO ratio.

3.2. Barrier properties

Figure 3 shows the WVTR and OTR properties of SiO_x coated PET film. Normally it is considered that the gas /water vapour transport in films comprised of three paths: unhindered transport through 'macrodefects' (> 1 nm) in the oxide coating; hindered transport through 'nano-defects' (< 1 nm); and hindered transport through the amorphous lattice of the oxide (the porous < 0.3 nm).[9] From the WVTR and OTR results it can be considered that the total three tracks of the coatings have contribution to the gas and water permeation in this film. So the surface topography of the deposition coatings can definitely affect the barriers performance.When the O_2/TMDSO ratio was increased in the mixture gases, the high efficient oxidation reaction concentrates the inorganic component SiO_xin the film, which can improve the barrier properties.

It is also noticed in these figures that WVTR and OTR for SiO_x coated PET films were optimized at the condition of 200 W, O_2/TMDSO ratio of 2:1. When the input power rises up, however, the WVTR and OTR begin to decrease.

Figure 3(a) demonstrates that at the beginning the WVTR value decreased strongly from 30.25 g/m^{2}day for the uncoated PET to 2.15 g/m^{2}day for SiO_x coated film. The OTR value, under the same condition, also decreased dramatically from 170 cm^3/(m^2·day) for the virgin PET to 6.7 cm^3/(m^2·day) for coated one, respectively, in Fig.3(b). When the oxygen content in the mixture gases kept increasing, Fig.2 shows that the WVTR and OTR abnormally increased after minimization, not continuously decreased as expected. The reason may be attributed to the etching effects of atomic oxygen on the film surface and inducing the surface topography coarse, or because of the high temperature on the ground electrode caused by high discharge power which is harmful to the surface topography uniformity.

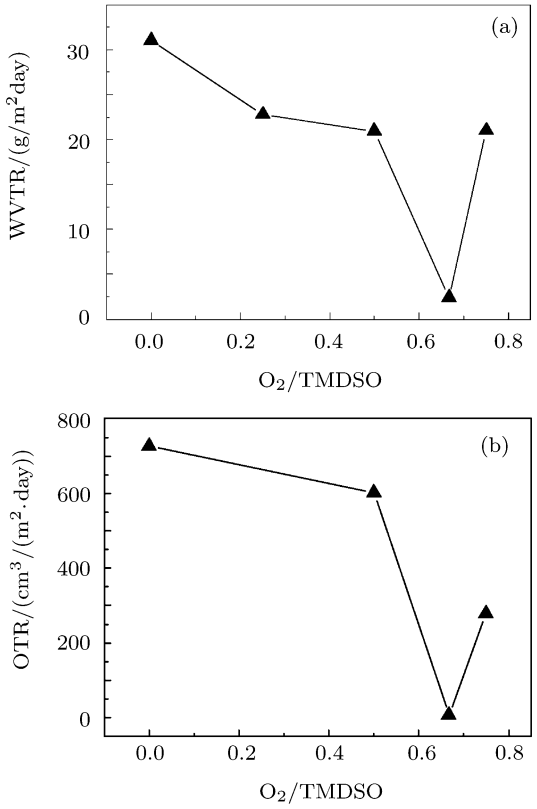


Fig.3. The relationship of WVTR and OTR in SiO_x coated PET films with O_2/TMDSO ratio. a-WVTR, b-OTR (20Pa, 200 W, 30 min).

In addition, the comparison of the discharge mode (the continuous and pulsed modes) on the properties, in the same discharge parameters: 200 W, O_2/TMDSO=2:1, concludes that the purity of Si–O is similar in two cases as shown by the FTIR spectra, but not the properties of WVTR and OTR. There is a big difference between them. In the continuous mode the film showed a higher value of WVTR and OTR as 2.4 g/m^{2}day and 6.7 cm^3/(m^2·day), respectively, than that one deposited in the pulse mode: 13.58 g/m^{2}day for WVTR and 15.2 cm^3/(m^2·day) for OTR. Generally the pulsed mode is prior to the continuous one,[10,11] but from above the conclusion is not so.

3.3. AFM

Figure 4 was the AFM photos of SiO_x barrier coating prepared in different plasma modes. Figure 4(a) is the film deposited in the continuous mode with 200 W, 20Pa working pressure, 30 min and the O_2/TMDSO rate of 2:1 which obtained WVTR of 2.65 g/m^{2}day and OTR of 11.1 cm^3/(m^2·day). Figure 4(b) is in the pulse mode, the WVTR (13.58 g/m^{2}day) and the OTR (15.2 cm^3/(m^2·day) are visually higher. By a close investigation of Fig.4(a) and Fig.4(b), we notice that the size of grain is uniform in CW plasma deposited film and the grain is arranged compactly in the surface. In pulsed plasma deposited film, on the other hand, it was not so. It may be the exact reason that the film barrier characteristic in Fig.4(a) is superior to that in the Fig.4(b) according to the penetration principle.[11]

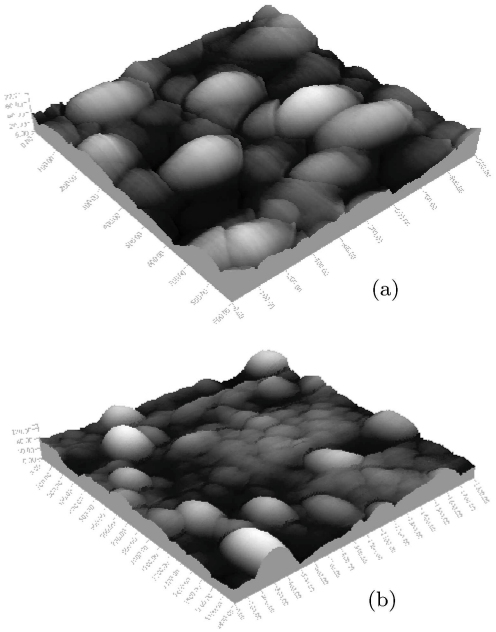


Fig.4. AFM photos of the barrier coating deposited in different discharge modes (a-CW, b-pulsed plasma).

4. Conclusion

By the PECVD method, under the mild condition, SiO_x barrier films were deposited on PET sur-

face. In continuous discharge condition, the inlet gas content and the plasma power affect the composition of the deposited coatings. With the increase of O_2 content and the power, the pure SiO_xcan be deposited. In 200 W, O_2/TMDSO ratio at 2:1 and continuous discharge mode, the optimized high water and oxygen gas barrier films can be obtained. And from the AFM and FTIR analysis it can conclude that the compact structure of the coatings deposited in CW plasma is of benefit to the better barrier characterization than that obtained in pulsed plasma.

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