

# Suppression of Radiation-Induced Oxidation of Polymers by Sputtered Silicon Oxide Coating

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Received 21 February 2001; accepted 21 May 2001

**ABSTRACT:** Oxygen barrier coating on polymers was attempted to obtain polymeric composite materials with improved radiation resistance. Silicon oxide (SiO<sub>1.6</sub>) films ranging from 120 to 240 nm thick were formed on polypropylene (PP) and polyethylene (PE) by radio frequency (RF) magnetron sputtering. Oxygen permeability after SiO<sub>1.6</sub> deposition was reduced significantly in all samples studied, indicating that silicon oxide is a useful gas barrier. The oxygen permeability coefficient of deposited films for PP was  $1.7\text{--}2.2 \times 10^{-14}$  cm<sup>3</sup>-cm/cm<sup>2</sup>/s/cmHg and that for PE was  $2.8\text{--}4.8 \times 10^{-13}$  cm<sup>3</sup>-cm/cm<sup>2</sup>/s/cmHg. We studied the effect of such films on the radiation resistance of polymers in the presence of oxygen by microscopic infrared (IR) absorption spectroscopy. Silicon oxide films 180 nm thick were deposited on the surfaces of PP and PE, and the formation of carbonyl groups after irradiation in air was measured as a function of depth from the surface. Results compared with those for uncoated PE and PP showed that the radiation-induced polymer oxidation is dramatically suppressed by silicon oxide coating. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 186–190, 2002

**Key words:** sputtering deposition; silicon oxide; oxygen permeation; irradiation; polymer oxidation

## INTRODUCTION

Organic polymers irradiated with high-energy radiation in the presence of oxygen are gradually oxidized by chemical reactions between free radicals and oxygen. Koyama et al. studied the degradation of polyethylene (PE) by the combined effects of oxygen and  $\gamma$ -irradiation.<sup>1</sup> They found a good correlation between the amount of carbonyl groups formed as a result of  $\gamma$ -irradiation in air or water and the reduction in tensile strength of the polymer. Because oxygen permeation into a polymer is responsible for radiation-induced oxida-

tion, an oxygen barrier coating on a polymer may effectively suppress oxidation and improve radiation resistance in the presence of oxygen.

Several authors successfully formed gas barrier coatings of silicon oxide on polypropylene (PP),<sup>2</sup> poly(ethylene terephthalate) (PET),<sup>3</sup> and oriented polypropylene (OPP)<sup>4</sup> by plasma-enhanced chemical vapor deposition (PECVD). Agres et al. noted that the high density and low free volume of silicon oxide is responsible for its good oxygen barrier property.<sup>2</sup> Attempts to form gas barrier coatings by postdeposition oxygen-plasma treatment of a plasma-polymerized siloxane layer on PE were not, however, very successful.<sup>5</sup>

Among the different thin-film deposition techniques, radio frequency (RF) magnetron sputtering is often used to prepare silicon oxide and

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*Journal of Applied Polymer Science*, Vol. 83, 186–190 (2002)  
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nitride films for different applications in electronics and optics.<sup>6,7</sup> The advantage of this technique over others is that it produces films with a high density close to the bulk value, good mechanical properties, and superior moisture resistance. Nevertheless, RF magnetron sputtering has not, to our knowledge, been applied in the formation of gas barrier coatings on polymers. We report on the usefulness of sputter-deposited silicon oxide as a gas barrier that effectively suppresses radiation-induced polymer oxidation.

## EXPERIMENTAL

### Film Deposition

Film was deposited with a RF magnetron sputtering system (L-332S-FHS, ANELVA, Tokyo, Japan) by using a SiO<sub>2</sub> target 75 mm in diameter. The distance between the target and substrate was fixed at 90 mm. Before film deposition, the chamber was evacuated with a diffusion pump to a vacuum of about  $1.3 \times 10^{-4}$  Pa. Under a steady flow of argon of a purity exceeding 99.9995%, stable RF plasma was generated at a frequency of 13.56 MHz.

Films were deposited on silicon wafers 0.38 mm thick and 75 mm in diameter at different Ar pressures and discharge powers up to 450 W to determine the deposition rate and composition. Films then were deposited on PP 40  $\mu\text{m}$  thick and PE 30  $\mu\text{m}$  thick to measure oxygen permeability. Carbonyl groups formed after  $\gamma$ -irradiation in air were measured for 3-mm-thick PP and 1-mm-thick PE samples with and without silicon oxide coating on both of the surfaces. Most PP and PE substrates (Goodfellow Cambridge Ltd. Co., Cambridge, UK) were cleaned with ethanol or acetone before film deposition.

### Determination of Film Thickness and Deposition Rate

A spectroscopic ellipsometer (Model FTM-5000, Otsuka Electronic Co., Osaka, Japan) was used to measure the thickness and refractive index of films deposited on Si. Spectra recorded at a light incident angle of 55° were analyzed by least-squares fitting. The error of the determined thickness was about 1 nm and film thickness uniformity was better than 3%. Film deposition rates under different conditions were determined by dividing the measured thickness by deposition

time. The thickness of films deposited on PP and PE substrates was estimated, assuming that the deposition rate was the same as that for Si substrates.

### Determination of Film Composition

Film composition was determined by Rutherford backscattering spectroscopy (RBS) at RIKEN. Samples were bombarded with 1.5 MeV He<sup>+</sup> ions generated by a tandem accelerator. The beam spot was about 1 mm in diameter and the ion current 10–30 nA. The energy distribution of backscattered He<sup>+</sup> ions was measured at a scattering angle of 160°.

### Oxygen Permeability Measurement

A Model OX-TRAN 2/20 Tester (Mocon Co., USA) was used to determine oxygen permeability of PP films with and without silicon oxide coating and PE films with silicon oxide coating. Data for uncoated PE were obtained at Mocon Co. All measurements were done at room temperature, 90% relative humidity, 100% oxygen, and 100% nitrogen at 1 atm.

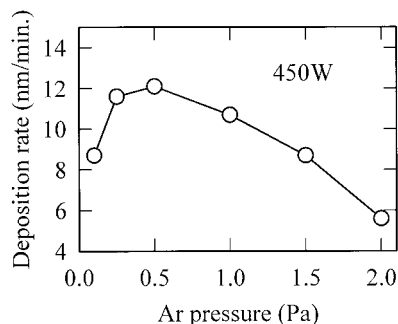
### $\gamma$ -Irradiation and Microscopic IR Absorption Spectroscopy

Three-millimeter-thick PP and 1-mm-thick PE samples with and without 180-nm-thick silicon oxide coating on the surfaces were irradiated with <sup>60</sup>Co  $\gamma$ -rays in air at the National Institute of Advanced Industrial Science and Technology. The dose rate was 110 Gy/h and the accumulated total dose was 100 kGy. About 2 months after irradiation, sample cross sections were cut into films 100  $\mu\text{m}$  thick. A microscopic IR spectrometer (JIR-6000, JEOL, Tokyo, Japan) was used to measure carbonyl (C=O) group IR absorption at 1716 cm<sup>-1</sup> as a function of depth from the surface.

## RESULTS AND DISCUSSION

### Deposition Rate

Variation of film deposition rate as a function of Ar pressure at 450 W discharge is shown in Figure 1. The deposition rate peaks at an intermediate Ar pressure of 0.5 Pa. As the deposition rate increased in proportion to RF power, the maximum deposition rate was obtained at 0.5 Pa and 450 W. The refractive index of films determined



**Figure 1** Silicon oxide deposition rate versus Ar pressure at 450 W.

by ellipsometry was independent of discharge power.

### Film Composition

Figure 2 shows the RBS spectrum of silicon oxide film 1092 nm thick deposited on Si at 0.5 Pa and 450 W. Similar spectra were observed for different samples prepared at different Ar pressures and discharge powers. The spectrum clearly showed that the film was composed of silicon and oxygen; no other elements were observed. The energy dependence of  $\text{He}^+$  ions scattered by the film is very similar to that of the ions scattered by bulk Si and  $\text{SiO}_2$ , indicating that film composition is uniform as a function of depth from the surface. By comparing the number of the ions scattered by silicon and oxygen in the film with that in bulk  $\text{SiO}_2$  based on the zeroth-order approximation,<sup>8</sup> film composition was determined to be  $\text{SiO}_{1.6}$ . The maximum error of the composition determined by this method is about 10%.<sup>8</sup>

### Oxygen Permeability

Silicon oxide films with thicknesses ranging from 120 to 240 nm were deposited on PP films 40  $\mu\text{m}$  thick and PE films 30  $\mu\text{m}$  thick at an Ar pressure of 0.5 Pa and 450 W discharge. Oxygen permeability was measured for samples with and without  $\text{SiO}_{1.6}$  coating. Results are listed in Table I.

Silicon oxide deposition significantly reduces the oxygen permeability of PP and PE films. Upon deposition of 180-nm-thick  $\text{SiO}_{1.6}$ , the oxygen permeability of PP decreases from 2881 to 60  $\text{cm}^3/\text{m}^2/\text{day}/\text{atm}$  by a factor of about 50. The corresponding permeability of PE decreases from 5372 to 858  $\text{cm}^3/\text{m}^2/\text{day}/\text{atm}$ .

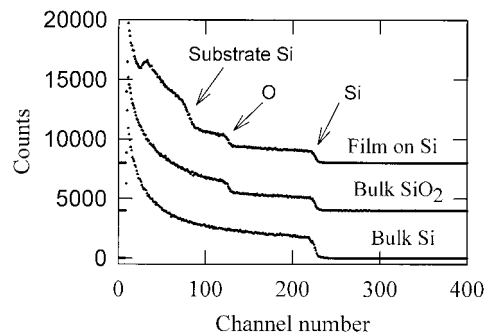
We estimated the oxygen permeation coefficient of deposited  $\text{SiO}_{1.6}$  film by using the following equations derived from the two-layer model<sup>4</sup>

$$d/P = d_1/P_1 + d_2/P_2$$

$$d = d_1 + d_2$$

Here  $P$  and  $d$  represent the oxygen permeability coefficient and total thickness of the composite film.  $P_1$  and  $P_2$  are the individual permeability coefficients of the polymer and  $\text{SiO}_{1.6}$  layer, respectively, and  $d_1$  and  $d_2$  are corresponding layer thicknesses. In our case,  $d_1$  is 40  $\mu\text{m}$  for PP and 30  $\mu\text{m}$  for PE. For uncoated PP and PE, we obtained permeation coefficients of  $1.8 \times 10^{-10}$  and  $2.4 \times 10^{-10}$   $\text{cm}^3\text{-cm}/\text{cm}^2/\text{s}/\text{cmHg}$ , respectively. The last column of Table I shows calculated oxygen permeation coefficients of silicon oxide films deposited on PP and PE. The permeability coefficient of  $\text{SiO}_{1.6}$  on PP ranged from  $1.7 \times 10^{-14}$  to  $2.2 \times 10^{-14}$  (STP)  $\text{cm}^3\text{-cm}/\text{cm}^2/\text{s}/\text{cmHg}$ . The permeability coefficient of  $\text{SiO}_{1.6}$  on PE ranged from  $2.8 \times 10^{-13}$  to  $4.8 \times 10^{-13}$  (STP)  $\text{cm}^3\text{-cm}/\text{cm}^2/\text{s}/\text{cmHg}$ . Sputter-deposited silicon oxide thus has at least three orders of magnitude smaller oxygen permeation coefficients than the original PP and PE films. Our values for films on PP are close to the values of silicon oxide films formed on surface-treated OPP by PECVD.<sup>4</sup>

A comparison of oxygen permeation coefficients of silicon oxide films on PP with those on PE showed that  $\text{SiO}_{1.6}$  deposition on PE was not so effective in lowering oxygen permeability as that on PP. Inagaki et al. found that the oxygen per-



**Figure 2** Rutherford backscattering spectrum of 1092-nm-thick silicon oxide film on Si deposited at 0.5 Pa Ar pressure and 450 W discharge power. Bulk Si and  $\text{SiO}_2$  spectra are included for comparison. For clarity, the spectra of bulk  $\text{SiO}_2$  and film on Si are shifted upward by 4000 and 8000 counts, respectively. By comparing the number of ions scattered by silicon and oxygen in the deposited film with that in bulk  $\text{SiO}_2$  on the basis of the zeroth-order approximation, film composition was determined to be  $\text{SiO}_{1.6}$ .

**Table I Oxygen Permeation Data for 40- $\mu\text{m}$ -thick PP and 30- $\mu\text{m}$ -thick PE Films With and Without Silicon Oxide Coating**

Sample	Deposition Time (min)	SiO <sub>1.6</sub> Thickness (nm)	O <sub>2</sub> Permeation Rate (cm <sup>3</sup> /m <sup>2</sup> /day/atm)	O <sub>2</sub> Permeation Coefficient of SiO <sub>1.6</sub> [(STP)cm <sup>3</sup> -cm/cm <sup>2</sup> /s/cmHg]
PP-0	0	0	2881	—
PP-1	10	120	114	$2.2 \times 10^{-14}$
PP-2	15	180	60	$1.7 \times 10^{-14}$
PP-3	20	240	49	$1.8 \times 10^{-14}$
PE-0	0	0	5372	—
PE-1	10	120	1344	$3.3 \times 10^{-13}$
PE-2	15	180	858	$2.8 \times 10^{-13}$
PE-3	20	240	1055	$4.8 \times 10^{-13}$

Note. SiO<sub>1.6</sub> films were deposited at 0.5 Pa Ar pressure and 450 W discharge power to achieve the maximum deposition rate. The O<sub>2</sub> permeation rate through uncoated PE was obtained at Mocon Co., USA. The permeation coefficients of the original PP and PE were  $1.8 \times 10^{-10}$  and  $2.4 \times 10^{-10}$  cm<sup>3</sup>-cm/cm<sup>2</sup>/s/cmHg, respectively.

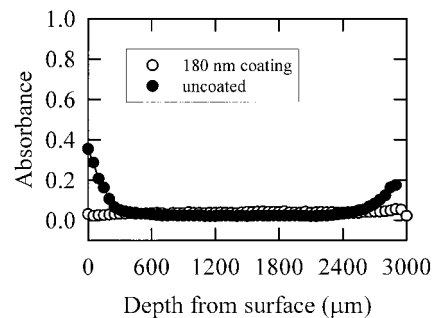
meation coefficient of silicon oxide films deposited on PET by PECVD is much lower than that of films on OPP.<sup>4</sup> These authors pointed out the importance of adhesion at the interface between the deposited film and polymer substrate. The glass transition temperature of PET is higher and the glass transition temperature of PP lower than room temperature. OPP is rubbery at room temperature and the film deposition on it occurs on a thermally mobile surface. The adhesion of silicon oxide to OPP may thus be poorer than that to PET and, hence, the oxygen permeation coefficient higher. Because the glass transition temperature of PE is lower than that of PP, the adhesion of the deposited film with the PE surface may be poorer than that with the PP surface. It is also likely that the film on PE contains defects and pinholes which facilitate oxygen permeation.<sup>3</sup> A study is under way at the authors' laboratory to characterize the defects and holes in sputter-deposited silicon oxide by means of positron annihilation lifetime spectroscopy<sup>9,10</sup> and other techniques.

#### Formation of Carbonyl Groups After $\gamma$ -Irradiation in Air

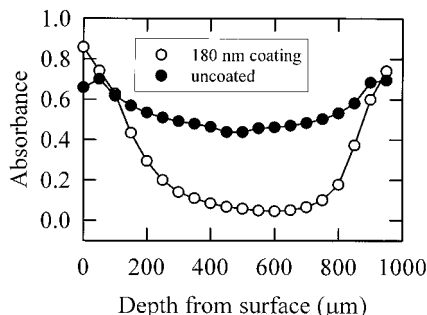
As mentioned above, PP and PE samples with and without SiO<sub>1.6</sub> 180 nm thick on the surfaces were irradiated with <sup>60</sup>Co  $\gamma$ -rays at a dose rate of 110 Gy/h, up to a total dose of 100 kGy in air. The intensity of the IR absorption peak due to carbonyl groups at 1716 cm<sup>-1</sup> formed by radiation-induced oxidation is shown as a function of depth from the surface in Figures 3 and 4, which clearly show that silicon oxide deposition is useful in suppressing radiation-induced oxidation of PP and PE.

The oxidation of the uncoated PP sample after  $\gamma$ -irradiation in air is limited to the near-surface region, because the oxygen permeation rate through uncoated PP is not so high as that of PE (Table I). Carbonyl absorption in the near-surface region almost disappears upon the deposition of SiO<sub>1.6</sub> 180 nm thick on the surfaces of PP. This means that oxygen permeation in the near-surface region of oxygen permeation is well suppressed by the deposited silicon oxide layer with a small permeability coefficient of  $1.6 \times 10^{-14}$  (STP) cm<sup>3</sup>-cm/cm<sup>2</sup>/s/cmHg (Table I).

Figure 4 shows that PE without a silicon oxide coating is highly oxidized in the near-surface region and deep inside the polymer after  $\gamma$ -irradiation in air. Obviously this is due to the higher oxygen permeability of PE (Table I). The result



**Figure 3** Variation of carbonyl absorbance (per 100  $\mu\text{m}$ ) at 1716 cm<sup>-1</sup> as a function of depth from the surface for 3-mm-thick polypropylene with and without 180-nm-thick SiO<sub>1.6</sub> deposited at an Ar pressure of 0.5 Pa and 450 W discharge. Data were obtained by microscopic IR absorption spectroscopy by line-scanning the sample at 50  $\mu\text{m}$  steps under an excitation beam of 50  $\times$  50  $\mu\text{m}$  in size.



**Figure 4** Variation of carbonyl absorbance (per 100  $\mu\text{m}$ ) at  $1716\text{ cm}^{-1}$  as a function of depth from the surface for 1-mm-thick polyethylene with and without 180-nm-thick  $\text{SiO}_{1.6}$  deposited at 0.5 Pa Ar pressure and 450 W discharge. Data were obtained by microscopic IR absorption spectroscopy by line-scanning the sample at 50  $\mu\text{m}$  steps under an excitation beam of  $50 \times 50\ \mu\text{m}$  in size.

for the sample with silicon oxide coating showed that the formation of carbonyl groups is effectively suppressed by the deposition of  $\text{SiO}_{1.6}$  films 180 nm thick. Note that carbonyl absorption is very weak at depths exceeding 0.3 mm from the surfaces, indicating that oxygen in air did not reach that area and its reaction with free radicals therein was almost completely prevented.

## CONCLUSION

Gas barrier coatings can be formed on polymers such as PP and PE using RF magnetron sputtering to deposit thin silicon oxide films. Such coat-

ings very effectively suppress radiation-induced oxidation of polymers and may be useful in improving their radiation resistance in the presence of oxygen.

We thank Dr. N. Minoura and Dr. C. L. Wang for help in ellipsometric measurements. This work was conducted as part of the Nuclear Crossover Project of the Science and Technology Agency (STA).

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