Preparation of Oxygen Gas Barrier Poly(ethylene terephthalate) Films by Deposition of Silicon Oxide Films Plasma-Polymerized from a Mixture of Tetramethoxysilane and Oxygen

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ABSTRACT: To prepare silicon oxide (SiOx)-deposited poly(ethylene terephthalate) films with high oxygen gas barrier capability, SiOx deposition by plasma polymerization has been investigated from the viewpoint of chemical composition. Tetramethoxysilane (TMOS) is suitable as a starting material for the synthesis of the SiOx films. The SiOx deposition under self-bias, where the etching action occurs around an electrode surface, is effective in eliminating carbonaceous compounds from the deposited SiOx films. There is no difference in the chemical composition between the SiOx films deposited under self-bias and under no self-bias. The SiOx films are composed of a main component of Si—O—Si networks and a minor component of carbonized carbons. The SiOx films deposited under no self-bias from the TMOS/O_2 mixture show good oxygen gas barrier capability, but the SiOx films deposited under the self-bias show poor capability. The minimum oxygen permeation rate for poly(ethylene terephthalate) films deposited SiOx film is 0.10 cm^3 m^{-2} day^{-1} atm^{-1}, which corresponds to an oxygen permeability coefficient of 1.4×10^{-17} cm^3-cm cm^{-2} s^{-1} cm^{-1} Hg for the SiOx film itself. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2091–2100, 1999

Key words: silicon oxide films; oxygen gas barrier; poly(ethylene terephthalate); tetramethoxysilane

INTRODUCTION

Silicon oxide (SiOx) film, which is a thermally stable and good electrical insulator, is an important material in microelectronics technology, and is frequency used as a passivating film for protecting the surface of large-scale integrated circuit devices. Recently, applications of SiOx film are being extended to the food and pharmaceutical technologies besides the microelectronics technology. Polymeric packing materials with good oxygen-gas barrier properties are sought for protecting foods or medicines from deterioration of their quality by oxidation. SiOx-coated and biaxially stretched polyester [poly(ethylene terephthalate)] films are possible materials for this purpose.

Usually, SiOx film is synthesized from a mixture of tetraethoxysilanes (TEOS) and oxygen by the plasma chemical vapor deposition (plasma CVD) method,[1] and deposited on the heating surface at > 500°C to eliminate carbonaceous compounds from the deposited SiOx films (pyrolysis of the carbonaceous compounds). The plasma CVD method is a good process for preparing the SiOx-deposited PET film, because the synthesis of SiOx and the coating of the PET film surface with SiOx occur simultaneously in one process. However, the plasma CVD method is difficult to apply for

the preparation of SiOx-deposited PET film, because of low thermal resistance of the PET film. SiOx preparation should proceed at lower temperatures than the glass transition temperature ($\sim$ 70°C) of the PET film.

In the plasma CVD method, we believe that SiOx films are formed in two reactions: (1) the bond scission of Si—O—C bond in TEOS to form Si · or SiO · radicals, and (2) the recombination between two radicals to form Si—O—Si linkage. The repetitious combination of the two reactions leads to the Si—O—Si network and, as a result, SiOx film deposits. On the other hand, fragments, ethyl or ethoxy radicals, eliminated from TEOS also recombine to form carbonaceous compounds, and are incorporated into the deposited SiOx film. In the conventional plasma CVD process, the carbonaceous compounds in the deposited SiOx film are eliminated by the pyrolysis of the deposited SiOx film at high temperature (500°C).[2] Therefore, in preparation of the SiOx-deposited PET film, some special process for the elimination of the carbonaceous compounds, instead of the pyrolysis treatment, should be found. The elimination process should operate at low temperatures below 70°C, which is the glass transition temperature of PET films.

In this study, we have investigated two factors for the elimination of the carbonaceous compounds from the deposited SiOx films. (1) tetramethoxysilane (TMOS) instead of TEOS is used as a starting silane material for SiOx synthesis by the plasma CVD method. TMOS (C/Si = 4) has a lower C/Si atom ratio than TEOS (C/Si = 8). We expect that the plasma CVD of TMOS will deposit SiOx films having a small amount of carbonaceous compounds. (2) An etching process occurring on an electrode surface is used for the elimination of the carbonaceous compounds from the deposited SiOx films. In a glow discharge at 13.56 MHz frequency, electrode A is grounded, and electrode B is connected to the electrical power generator. Electrons and ions are oscillated by changing the polarity of the electrical field. As a result, the ion sheath is formed around electrode B, due to much lower speed of ion species than electrons, and electrode B is charged negatively (self-bias) against electrode A, which is grounded.[3] The self-bias reaches from a few tens to hundreds of volts, depending on the plasma operating conditions. As a result, the ion bombardment occurs powerfully in the ion sheath region. From this viewpoint, we expect that light carbonaceous components incorporated into the SiOx films will be sputtered out

from the deposited SiOx films, and dense SiOx films with less carbonaceous component will remain. The self-bias effects have been already applied for the formation of amorphous silicon.[4]

We have discuss herein the appropriateness of the selection of TMOS and the self-bias effect for the preparation of the SiOx-deposited PET film from the viewpoint of chemical composition. The oxygen gas barrier capability of the SiOx-deposited PET films also has been evaluated and is discussed.

EXPERIMENTAL

Materials

Biaxially stretched PET film (trade name: BOPET, 38 μm thick) kindly provided by Toyobo Co. Ltd., was used as a substrate for SiOx deposition. The PET film was washed with acetone in an ultrasonic washer before SiOx deposition. TMOS and TEOS, which were purchased from Petrarch Systems Co. and whose purity was 99%, were used as starting materials for the SiOx film deposition without purification.

Reactor Used for SiOx Deposition

A commercial vacuum deposition apparatus (Ulvac Co., Japan; model EBH6), which had a bell-jar chamber (400 mm diameter $\times$ 590 mm high) and a vacuum system with a combination of a rotary pump (320 L min^{-1}) and a diffusion pump (550 L s^{-1}), was remodeled into a special reactor for SiOx film deposition. A diode planar electrode made of stainless steel for glow discharge, inlets of the TMOS and TEOS vapors and oxygen or argon gas, a rolling machine for reeling the PET film (variable reeling rates of 33–994 mm min^{-1}), a thickness monitor (Ulvac Co.; model CRTM-1000) for monitoring the SiOx deposition rate, and a pressure gauge was installed in the bell-jar chamber. An electrical energy input system for initiating a glow discharge (Samuco Co., Japan; model RFG-200), a digital voltmeter with a matching box (Samuco Co.; model MU-2) for measuring the self-bias voltage, and a flow rate controlling the system for the TMOS and TEOS vapors and oxygen and argon gases were annexed to the reactor. The diode electrode contained a circular electrode (electrode A), with a dimension of 380 mm diameter and a rectangular electrode (electrode B) with a dimension of 50 mm wide and

Figure 1 Schematic presentation of the reaction chamber for SiOx deposition.

100 mm long. The relative area of the two electrodes is 22.7 : 1. The gap between the electrodes was 60 mm. Electrode A was grounded, and electrode B was connected to an electrical power generator at 13.56 MHz (Samuco Co.; model RFG-200). The PET film was run between the electrodes, and the film was reeled by the rolling machine. The gas flow rate controlling system was a combination of a metering needle valve (Nupro Co.; model BM-4BMG) for the TMOS and TEOS vapors and a mass flow controller (Estec Co., Japan; model SEC-400 MARK3) for oxygen and argon gases. A schematic diagram of the plasma reactor used in this study is shown in Figure 1.

SiOx Deposition from TMOS and TMOS/O_2 Mixtures

The PET film (110 mm wide) running between electrodes A and B was set up on reels of the rolling machine. Two setting-up positions for the PET film were used for the SiOx deposition. One position was within 5 mm distance of electrode B surface (deposition on the electrode surface), and the other position was midway between electrodes A and B (30 mm away from the electrode B surface). TMOS was poured in a reservoir, and air dissolved in the TMOS was removed by a repeated freezing-fusion procedure. The reservoir

was kept in a temperature-controlled oven at 60°C to increase the vapor pressure of TMOS.

Air in the reaction chamber was displaced with argon, and the reaction chamber was evacuated to ∼ 0.13 Pa. Afterwards, TMOS vapor whose flow rate was adjusted to a given flow rate (15–6 cm^3 min^{-1}) by the metering valve and oxygen gas adjusted by the mass flow controller (0–9 cm^3 min^{-1}) were blown off from the inlets to the reaction chamber. The combined flow rate of the TMOS vapor and oxygen gas was kept at a constant 15 cm^3 min^{-1}. The plasma CVD of the TMOS/O_2 mixtures was performed at a system pressure of 39.9 Pa at radiofrequency (RF) powers of 40–100 W. The deposition rate of SiOx films was determined from a reading of the thickness monitor (model CRTM-1000). After the SiOx deposition, the reaction chamber was evacuated to <0.13 Pa for 30 min, and then argon gas was introduced into the reaction chamber up to atmospheric pressure. The PET film was taken from the reaction chamber, and served as specimens for X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and oxygen permeation rate measurements.

X-Ray Photoelectron Spectra of SiOx Films

XPS spectra of the SiOx films deposited on the PET films were obtained on a Shimadzu ESCA K1 using a nonmonochromatic MgK$_\alpha$ photon source. The anode voltage was 12 kV, the anode current was 20 mA, and the background pressure in the analytical chamber was 1.5×10^{-6} Pa. The size of the X-ray spot was 2 mm diameter, and the take-off angle of photoelectrons was 90°, with respect to the sample surface. Spectra were not smoothed and decomposed by fitting a Gaussian–Lorentzian mixture function (80 : 20 mixture ratio) to an experimental curve using a nonlinear, least-squares curve fitting program, ESCAPAC, supplied by Shimadzu (Kyoto, Japan). The sensitivity factors (S) for the core levels were S(C_{1S}) = 1.00, S(Si_{2p}) = 0.87, and S(O_{1S}) = 2.85. C/Si and O/Si atomic ratios of the deposited SiOx films were estimated from the spectral intensity and the sensitivity factor of the corresponding core level within an experimental error of ±0.05.

Oxygen Permeation Rate Through SiOx-Deposited PET Film

A gas barrier tester (Mocon Co., model OX-TRAN 2/20) was used for measuring the oxygen perme-

Table I Chemical Composition of SiOx Films Deposited from TMOS and TEOS

	Plasma CVD Conditions		Chemical Composition	
Starting Compound	RF Power (W)	Pressure (Pa)	C/Si Atom Ratio	O/Si Atom Ratio
TEOS	60	13.3	3.2	1.9
TMOS	40	13.3	1.4	1.7
	60	13.3	1.5	1.8
	100	13.3	1.7	1.8

ation rate (in cm^3 m^{-2} day^{-1} atm^{-1}) through SiOx-deposited PET films (area of 78 mm diameter) at 30°C and at a relative humidity (RH) of 70% RH. Three or five specimens were used for measurement, and oxygen permeation rate was determined from an average of the measurements within an experimental error of 0.1 cm^3 m^{-2} day^{-1} atm^{-1}. From the oxygen permeation rate, the oxygen permeability coefficient for the deposited SiOx film in (STP) cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg was estimated under assumption of the two-layer model.

The SiOx-deposited PET film is a laminated structure consisting of the PET film layer and SiOx film layer. For the two-layer model, the following equations [(1) and (2)] are given,[5]

$$d = d_1 + d_2 \tag{1}$$

$$\frac{d}{P} = \frac{d_1}{P_1} + \frac{d_2}{P_2} \tag{2}$$

where subscripts 1 and 2 are the original PET film layer and the SiOx film layer deposited on the PET film surface, respectively. P and d are the oxygen permeability coefficient and film thickness, respectively. For the original PET film, P_1 is 2.5×10^{-12} (STP) cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg and d_1 is 38 μm. For the SiOx film, d_2 is 100 nm. Equation (2) is modified into eq. (3).

$$\frac{1}{P} = \frac{1}{P_1} + \frac{d_2}{d_1 + d_2}\frac{1}{P_2} \tag{3}$$

The oxygen permeability coefficient, P_2, for the SiOx film in the SiOx-deposited PET film can be calculated from eq. (3).

RESULTS AND DISCUSSION

Chemical Composition of SiOx Films Deposited from TMOS

TMOS instead of TEOS was used as a starting compound, and effects of TMOS on the chemical composition of the deposited SiOx films was in-

Table II Chemical Composition of SiOx Films Deposited from TMOS/O_2 Mixtures Under No Self-Bias and Under Self-Bias

TMOS/O_2 Mixture O_2 Concentration (mol %)	RF Power (W)	Chemical Composition of SiOx Films			
		Deposited Under No Self-bias		Deposited Under Self-bias	
		C/Si Atom Ratio	O/Si Atom Ratio	C/Si Atom Ratio	O/Si Atom Ratio
0	40	1.4	1.7	0.90	1.6
20	40	0.44	1.5	0.39	1.7
40	40	0.30	1.5	0.24	1.5
60	40	0.25	1.5	0.35	1.5
0	60	1.5	1.8	1.2	1.7
20	60	0.39	1.4	0.45	1.4
40	60	0.42	1.4	0.31	1.6
60	60	0.49	1.4	0.59	1.3
0	100	1.7	1.8	—	—
60	100	0.26	1.4	—	—

vestigated by XPS. Carbon, oxygen, and silicon concentration in the deposited SiOx films were determined as the C/Si and O/Si atom ratio from the relative intensities of the XPS spectra, and a typical result is shown in Table I. There are large differences in the C/Si atom ratio between the SiOx films deposited from TMOS and TEOS. The C/Si atom ratio is 1.4–1.7 for the SiOx films deposited from TMOS, and 3.2 for that from TEOS. This comparison shows that the usage of TMOS as a starting material rather than TEOS is preferable to decrease the carbon content of the deposited SiOx films. On the other hand, the O/Si atom ratio shows only a small difference between the SiOx films deposited from TMOS and TEOS. The O/Si atom ratio in the SiOx films deposited from both silanes is 1.7–1.9. From these results, we conclude that TMOS is more suitable as a starting material for the synthesis of the SiOx films than TEOS.

To eliminate carbonaceous compounds from the deposited SiOx films, a mixture of TMOS and oxygen gas was used for the synthesis of the SiOx films. Table II shows the C/Si and O/Si atom

Figure 3 XPS (Si2p) spectra of SiOx films deposited under no self-bias from the TMOS/O_2 mixtures as a function of oxygen concentration in the TMOS/O_2 mixture.

ratios in the deposited SiOx films as functions of oxygen concentration in the TMOS/O_2 mixture. Mixing of oxygen gas leads to large decreases in the C/Si atom ratio of the deposited SiOx films. When an oxygen gas of 20 mol % O_2 was mixed with TMOS, the C/Si atom ratio in the deposited SiOx films decreases from 1.4 to 0.44 at a RF power of 40 W and from 1.5 to 0.39 at 60 W. On the other hand, changes in the O/Si atom ratio by mixing oxygen gas is small. The O/Si atom ratio decreases from 1.7 to 1.5 at an RF power of 40 W, and from 1.8 to 1.4 at 60 W, even when the oxygen concentration increases from 0 to 60 mol %.

XPS (C1s and Si2p) spectra give detailed information regarding influences of the mixing of oxygen gas. Figures 2 and 3 compare C1s and Si2p spectra among three SiOx films deposited from the TMOS/O_2 mixtures of 0, 20, and 40 mol % O_2 at an RF power of 60 W. The SiOx film deposited from TMOS (no oxygen mixing) shows an intensive and complex C1s spectrum on which a maximum peak appears at 286.9 eV (due to C—O

Figure 2 XPS (C1s) spectra of SiOx films deposited under no self-bias from the TMOS/O_2 mixtures as a function of oxygen concentration in the TMOS/O_2 mixture.

groups whose relative concentration is 83%), and a shoulder appears at 285 eV (due to CH groups whose relative concentration is 17%).[6] The Si2p spectrum shows a maximum peak appears at 103.4 eV (due to SiO_2 groups). The full width at half-maximum (FWHM) value of the Si2p spectrum is 1.79 eV. On the other hand, for the two SiOx films deposited from the $TMOS/O_2$ mixtures of 20 and 40 mol % O_2, the C1s spectra distributes from 283 to 286 eV, and a maximum peak appears at 284.3–284.7 eV (due to carbonized carbon). The Si2p spectra show a peak at 103.4 eV (due to SiO_2) whose FWHM value is 1.65 eV which is smaller than that for the SiOx film deposited from TMOS (1.79 eV).

This comparison indicates that the chemical composition of the carbonaceous compounds incorporated into the deposited SiOx film is distinctly altered by the mixing of oxygen gas. The carbonaceous compound in the SiOx film deposited from TMOS consists mainly of C—O and CH groups, whereas the film deposited from the

Figure 5   Self-bias voltage at a constant oxygen concentration in $TMOS/O_2$ mixture as a function of RF power.

$TMOS/O_2$ mixtures is composed of carbonized carbons. Furthermore, the Si—O—Si network in the SiOx films deposited from the $TMOS/O_2$ mixture may be denser than that deposited from TMOS, because of small FWHM value.

Chemical Composition of SiOx Films Deposited Under Self-Bias

The electrode system that we used for the SiOx film deposition is a diode planar electrode system that contains electrodes A and B. Electrode A has a larger surface area by 22.7 times than electrode B. Electrode A is grounded, and electrode B is connected to the RF generator. As described in the "Introduction," when an electrical field with high frequency is applied between electrodes A and B, self-bias occurs around electrode B due to large differences in the drift rate between ion species and electrons and, as a result, electrode B is charged negatively against electrode A. Figures 4 and 5 show typical results of the self-bias voltage as functions of the RF power and the

Figure 4   Self-bias voltage at a constant RF power as a function of oxygen concentration in $TMOS/O_2$ mixture.

TMOS/O_2 mixture composition. Self-bias voltage increases linearly with increasing both oxygen concentration in the TMOS/O_2 mixture and RF power. Self-bias voltage reaches from -36 to -125 V at oxygen concentrations of $0-60$ mol % at RF powers of $40-100$ W. Therefore, we expect that etching will occur powerfully on electrode B.

Table II compares the C/Si and O/Si atom ratios between the SiOx films deposited under self-bias and under no self-bias. The deposition under self-bias leads to large decreases in the C/Si atom ratio. The C/Si atom ratio for the SiOx films deposited at RF powers of 40 and 60 W decreases from 1.4 to 0.90 and from 1.5 to 1.2, respectively. However, the O/Si atom ratio is scarcely influenced by self-bias. The O/Si atom ratio is $1.6-1.8$. Mixing of oxygen gas with TMOS leads to further decreases in the C/Si atom ratio. When an oxygen feed of 20 mol % is mixed with TMOS, the C/Si atom ratio for the SiOx films deposited at RF powers of 40 and 60 W decreases from 0.90 to 0.39 and from 1.2 to 0.45, respectively. Minimum C/Si atom ratios of 0.24 and 0.31 are reached at oxygen concentrations of 40 mol % at 40 and 60 W, respectively.

Figure 6 XPS (C1s) spectra of SiOx films deposited under self-bias from TMOS/O_2 mixtures as a function of oxygen concentration in the TMOS/O_2 mixture.

Figure 7 XPS (Si2p) spectra of SiOx films deposited under self-bias from TMOS/O_2 mixtures as a function of oxygen concentration in the TMOS/O_2 mixture.

From this result, we conclude that self-bias is effective in eliminating carbonaceous compounds from the deposited SiOx films. A combination of the self-bias and oxygen gas-mixing is more effective for carbon elimination.

The chemical composition of the SiOx films deposited under self-bias was analyzed with XPS. Figures 6 and 7 show typical C1s and Si2p spectra for the SiOx films deposited under self-bias. The C1s spectrum for the SiOx films deposited from TMOS under self-bias shows a narrow distribution, which contains a peak at 287.0 eV due to C—O groups and a small shoulder near 285 eV due to CH groups whose relative concentration is estimated to be 87% and 13%, respectively. The relative concentrations of the C—O and CH components in the SiOx film deposited under self-bias corresponds almost to those in the SiOx film deposited under no self-bias (83% for the C—O component and 17% for the CH component), although the SiOx film deposited under self-bias, as shown

Table III   Oxygen Permeation Rate Through SiOx-Deposited PET Films and Oxygen Permeability Coefficient for SiOx Films

RF Power (W)	Self-bias	Oxygen Concentration (%) in TMOS/O_2 Mixture	Oxygen Permeation Rate for SiOx-Deposited PET Film (cm^3 m^{-2} day^{-1} atm^{-1})	Oxygen Permeation Coefficient for Deposited SiOx Film ($\times 10^{-14}$ cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg)
40	No	0	28	1.7
	Yes	0	28	1.7
60	No	0	27	1.5
	No	20	27	1.5
	No	40	0.60	8.4×10^{-3}
	No	60	0.10	1.4×10^{-3}
60	Yes	0	29	2.1
	Yes	20	28	1.7
	Yes	40	21	3.9×10^{-1}
	Yes	60	14	3.2×10^{-1}
100	No	0	29	2.1
	No	60	0.34	4.7×10^{-3}
	Yes	0	29	2.1

in Table II, possesses lower carbon content (C/Si atom ratio = 1.2) than that deposited under no self-bias (C/Si = 1.5). This comparison means that the etching action by self-bias removes carbonaceous components, independent of the kind of components (C—O and CH components) from the SiOx film surface. The Si2p spectrum is symmetrical and has a narrow distribution whose FWHM value is 1.68 eV, which is smaller than that for the SiOx film deposited under no self-bias (1.79 eV) (shown in Fig. 3).

Oxygen-mixing with TMOS gives great changes in the C1s spectrum, but a small change in the Si2p spectrum. When oxygen contents of 20 and 40 mol % are mixed with TMOS, the C1s spectra becomes very weak, and the peak position of the spectra shifts from 287 to 284.5 eV due to carbonized carbons (Fig. 6). The Si2p spectra become intense, and the peak appears at 103.4 eV due to SiO_2 groups (Fig. 7). For study of self-bias effects on chemical composition, four SiOx films, that is, each two SiOx films deposited from the TMOS/O_2 mixtures of 20 and 40 mol % O_2 under self-bias and under no self-bias, were compared. Their C/Si atom ratio is 0.45 and 0.31 for the SiOx films deposited under self-bias, and 0.39 and 0.42 for SiOx films under no self-bias. Their C1s and Si2p spectra are shown in Figures 2 and 3 for the SiOx films under no self-bias, and in Figures 6 and 7 for the SiOx films under self-bias. All four SiOx films show very weak C1s spectra, but intense Si2p spectra. There is no

difference in C1s and Si2p spectra between the SiOx films deposited under self-bias and under no self-bias. All C1s spectra show a peak at 284.3–284.7 eV (carbonized carbon groups). All Si2p spectra show a peak of 103.4 eV (due to SiO_2 groups). Their FWHM values of the Si2p spectra are small (1.59–1.65 eV), indicating that Si—O—Si networks in the SiOx films may become dense, because of the narrow FWHM value of 1.59–1.65 eV.

From this result, we conclude that there is no difference in the chemical composition between the SiOx films deposited under self-bias and under no self-bias, although the C/Si atom ratio is different between these SiOx films.

OXYGEN GAS BARRIER PROPERTIES OF SiOx-DEPOSITED PET FILMS

SiOx films (100 nm thickness) were deposited from TMOS and the TMOS/O_2 mixtures on the surface of the PET films under self-bias and under no self-bias, and the SiOx-deposited PET films were provided for the evaluation of the oxygen gas barrier properties. Table III shows typical results of the oxygen permeation rate (in a dimension of cm^3 m^{-2} day^{-1} atm^{-1}) at 30°C at a RH of 70% RH through the SiOx-deposited PET films. The oxygen permeation rate of the original PET film is 44 cm^3 m^{-2} day^{-1} atm^{-1}, which corresponds to an oxygen permeability coefficient of 2.5

$\times$ 10^{-12} cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg. All SiOx-deposited PET films, as shown in Table III, show oxygen permeation rate from 0.10 to 29 cm^3 m^{-2} day^{-1} atm^{-1}, which are smaller than that of the original PET film (44 cm^3 m^{-2} day^{-1} atm). This comparison indicates that the SiOx film deposition is effective in improving the oxygen gas barrier properties of the PET films, and that the gas barrier capability is strongly dependent on what starting material (the oxygen concentration in TMOS/O$_2$ mixture) was used for the SiOx film deposition and what operational plasma conditions were used.

When TMOS alone is used as a starting material, the SiOx-deposited PET films show low oxygen gas barrier capability. Their oxygen permeation rate is an almost constant 28–29 cm^3 m^{-2} day^{-1} atm^{-1} independent of the magnitude of the RF power and the self-bias. On the other hand, when the TMOS/O$_2$ mixture is used as a starting material, the SiOx-deposited PET films show much higher oxygen gas barrier capability than the SiOx-deposited PET films from TMOS alone. The oxygen permeation rate, as shown in Table III, is 0.60 and 0.10 cm^3 m^{-2} day^{-1} atm^{-1} for the SiOx-deposited PET films from TMOS/O$_2$ mixtures of 40 and 60 mol % O$_2$, at an RF power of 60 W. Another SiOx-deposited PET film from the TMOS/O$_2$ mixture of 60 mol % O$_2$ at an RF power of 100 W also shows a low oxygen permeability rate of 0.34 cm^3 m^{-2} day^{-1} atm^{-1}. From these results, we conclude that the SiOx films deposited from the TMOS/O$_2$ mixture possess high oxygen gas barrier capability.

On the other hand, the SiOx films deposited under self-bias give low contributions to improving the oxygen gas barrier properties. The SiOx films were deposited under the self-bias from TMOS/O$_2$ mixtures of 40 and 60 mol % O$_2$ at an RF power of 60 W on the PET film surface, and their oxygen permeation rate was examined (Table III). The SiOx-deposited PET films with self-bias, as shown in Table III, show extremely high oxygen permeation rates of 21 and 14 cm^3 m^{-2} day^{-1} atm^{-1}, compared with the PET films deposited SiOx films under no self-bias (0.60 and 0.10 cm^3 m^{-2} day^{-1} atm^{-1}). The SiOx films deposited under self-bias, as discussed in a previous section, are almost the same in chemical composition as those deposited under no self-bias. Both SiOx films consist mainly of Si—O—Si network with a small amount of carbonized carbon groups. Therefore, we believe that a large difference in the oxygen gas barrier capability between the SiOx

(a)

(b)

Figure 8 SEM pictures of SiOx films deposited under self-bias and under no self-bias from the TMOS/O$_2$ mixture with 60 mol % O$_2$.

films deposited under self-bias and under no self-bias may be due to physical factors, such as cracks and voids in the SiOx films rather than chemical factors, such as the chemical composition of the deposited SiOx films. Figure 8 shows SEM pictures of the SiOx-deposited PET films under self-bias and under no self-bias from the TMOS/O$_2$ mixtures of 60 mol % O$_2$ at an RF power of 60 W. The surface of the SiOx-deposited PET film under no self-bias is smooth, and has no defects, such as cracks and holes, whereas the surface of the SiOx-deposited PET film under self-bias shows defects: there are many cracks in the SiOx film. We believe that the extremely low oxygen gas barrier capability of the PET films deposited SiOx films under self-bias may be due to the formation of

cracks in the SiOx films. The cracks may be formed during the elimination process of carbonaceous compounds from the SiOx films by the etching action of self-bias.

Finally, using eq. (3), the oxygen permeability coefficient for the deposited SiOx film itself was estimated, and the result of the estimation is listed in Table III. The SiOx film deposited under no self-bias from the TMOS/O_2 mixtures of 60 mol % O_2 at an RF power of 60 W shows a very small oxygen permeability coefficient of 1.4×10^{-17} cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg, which is 860–6360 times smaller than conventional polymers with good gas barrier capability, EVAL F (hydrolyzed ethylene-vinylacetate copolymer, 1.2×10^{-14} cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg) and Saran (polyvinylidene chloride, $3.0–8.9 \times 10^{-14}$ cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg).[7] Therefore, the SiOx film deposited under no self-bias from TMOS/O_2 mixtures of 60 mol % O_2 at an RF power of 60 W is good material with high oxygen gas barrier capability. We believe that the SiOx-deposited PET films will be useful in food and pharmaceutical technology, because of the low oxygen permeation rate of < 1 cm^3 m^{-2} day^{-1} atm^{-1}.

CONCLUSIONS

In this study, the preparation of SiOx-deposited PET films with high oxygen gas barrier capability was investigated. The main results are summarized as follows.

1. TMOS rather than TEOS is suitable as a starting material for the synthesis of the SiOx film. The TMOS/O_2 mixture is more suitable as a starting material than TMOS alone.
2. The SiOx deposition under self-bias gives SiOx films with a smaller amount of carbonaceous compounds in the deposited film than that under no self-bias.

3. There is no difference in the chemical composition between the SiOx films deposited under self-bias and under no self-bias, although the C/Si atom ratio is different between these SiOx films. The SiOx films are composed of a main component of Si—O—Si networks and a minor component of carbonized carbons.
4. The SiOx films deposited under no self-bias from the TMOS/O_2 mixture give good films with high oxygen gas barrier capability, but the SiOx films deposited under self-bias give poor films. The minimum oxygen permeation rate for PET films deposited SiOx film under no self-bias is 0.10 cm^3 m^{-2} day^{-1} atm^{-1}, which corresponds to an oxygen permeability coefficient of 1.4×10^{-17} cm^3 cm^{-1} cm^{-2} s^{-1} cm^{-1} Hg for the SiOx film itself.

We believe that the SiOx-deposited PET films will be useful in the food and pharmaceutical technology, because of their low oxygen permeation rates of < 1 cm^3 m^{-2} day^{-1} atm^{-1}.

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