

# Plasma Polymer Deposition from Mixture of Tetramethoxysilane and Oxygen on PET Films and their Oxygen Gas Barrier Properties

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**ABSTRACT:** Plasma polymerization of silane compounds has been discussed for deposition of SiOx positron emission tomography (PET) films at room temperature. A mixture of tetramethoxysilane (TMOS) and oxygen containing 60 mol % O<sub>2</sub> is a preferable raw material for SiOx formation by plasma polymerization. The deposited plasma polymers consist mainly of Si—O networks with small amount of Si—OH and Si—C groups. A part of Si—O networks in the plasma polymers is distorted by the Si—OH and Si—C groups. The oxygen permeability coefficient for the plasma polymer itself is  $2.1 \times 10^{-15}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg, which is lower than that for hydrolyzed ethylene-vinylacetate copolymer (Eval) and poly(vinylidene chloride) (Saran). Conclusively, the plasma polymer deposited from the mixture of TMOS and oxygen containing 60 mol % O<sub>2</sub> is a material with good oxygen barrier properties. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1031–1039, 1997

## INTRODUCTION

Silicon oxide film (SiOx) is a thermally stable and good electrical insulator. As a result, SiOx film is an important material in electronics technology and is frequently used as an insulator for protection of LSI devices. Recently, many investigators have taken interest in the coating of polymeric material surfaces with SiOx film to improve wear resistance and gas barrier properties.

SiOx film is synthesized from alkoxysilane by means of sol-gel, chemical vapor deposition (CVD), and plasma CVD methods.<sup>1</sup> Conventionally, tetraethoxysilane, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEOS), is used as a raw compound for SiOx formation from the viewpoint of convenient handling. In chemistry, the SiOx formation proceeds essentially in two reactions: TEOS is hydrolyzed into silanol, Si(OH)<sub>4</sub>; and two silanols are polycondensed to build up Si—O—Si bonds. The complete polycondensation reaction gives hard SiOx

films. Since the complete polycondensation reaction requests high temperature above 500°C,<sup>2</sup> it is a serious problem in the application of the SiOx deposition to surfaces of polymeric materials how completely the polycondensation reaction proceeds at low temperature below 100°C. At low temperature near 100°C, carbon residues will be incorporated into the deposited SiOx films because of incomplete pyrolysis of alkyl residues hydrolyzed from TEOS.

In this study, plasma polymerization has been used for formation of SiOx film at room temperature. We have expected that hydrolysis of alkoxysilanes and elimination of alkyl residues from deposited plasma polymers will be promoted by plasma action. Choice of silane compounds suitable for the SiOx formation by plasma polymerization and oxygen gas barrier properties of the deposited plasma polymers will be discussed.

## EXPERIMENTAL

### Materials

Poly(ethylene terephthalate) (PET) film (trade name, BOPET; *T<sub>m</sub>* 256°C; *T<sub>g</sub>* 67°C), 500 mm wide

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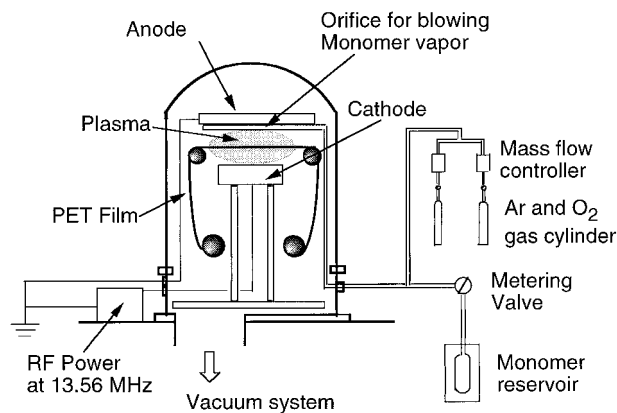
and 38  $\mu\text{m}$  thick, provided by Toyobo Co. Ltd., was used as a substrate for plasma polymer deposition. The PET film was washed with acetone in an ultrasonic washer prior to the plasma polymer deposition. Tetraethoxysilane (TEOS), triethoxysilane (TrEOS), tetramethoxysilane (TMOS), dimethyldimethoxysilane (DMDMOS), and tetramethylsilane (TMS) were purchased from Petrarch Systems Co. and were used as starting materials for plasma polymerization without purification. The purity of these silanes was 98–99%.

### Reactor Used for Plasma Polymerization of Silanes

A commercial vacuum deposition apparatus (Ulvac Co., Japan; model EBH6), which had a bell jar chamber (400 mm diameter, 590 mm high) and a vacuum system with a combination of a rotary pump (320 lit/min) and a diffusion pump (550 lit/s), was remodeled into a special reactor for plasma polymerization. Stainless steel electrodes for initiating a glow discharge (a circular anode electrode 380 mm in diameter and a rectangular cathode electrode 50 mm wide and 200 mm long, with an electrode gap of 50 mm), 22 orifices (1 mm diameter) for blowing off monomer vapor (mounted in the wall of the anode electrode), a rolling machine for reeling PET films (variable reeling rates of 33 to 994 mm/min), a thickness monitor (Ulvac Co., Japan; model CRTM-1000) for monitoring the deposition rate of plasma polymers, and a pressure gauge were installed in the bell jar chamber. An electrical energy input system for initiating a glow discharge and a gas flow rate-controlling system were annexed to the reactor. The electrical energy input system was an radio frequency (rf) generator with a frequency of 13.56 MHz and a maximum capacity of 200 W (Samco Co., Japan; model RFG-200). The gas flow rate controlling system was a combination of a metering needle valve (Nupro Co.; model BM-4BMG) for the silane compounds and a mass flow controller (Estec Co., Japan; model SEC-400 MARK3) for oxygen gas. A schematic diagram of the plasma reactor used in this study is shown in Figure 1.

### Plasma Polymerization of Silanes

The PET films (200 mm wide) were set up on reels of the rolling machine. The silane as a starting material for plasma polymerization was poured in a reservoir. Air dissolved in the silane in the reservoir was removed by a repeated freezing-fu-



**Figure 1** Schematic presentation of the reaction chamber for plasma polymerization.

sion procedure, and the reservoir was kept in temperature-controlled oven at 60°C to increase the vapor pressure of the silane. Air in the reaction chamber was displaced with argon, and the reaction chamber was evacuated to approximately 0.13 Pa. Afterwards, the silane vapor whose flow rate was adjusted to 20  $\text{cm}^3/\text{min}$  by the metering valve; and if necessary, oxygen gas adjusted by the mass flow controller were blown off from the orifices of the anode electrode surface to the reaction chamber. The plasma polymerization was performed at a system pressure of 13.3 Pa at rf powers of 50 W. The deposition rate of plasma polymers was determined from reading of the thickness monitor (model CRTM-1000). Plasma polymers deposited on the PET film surface at the anode side but did not deposit on the PET film surface at the cathode side. After the plasma polymerization, the reaction chamber was evacuated to less than 0.13 Pa for 30 min, and then argon gas was introduced into the reaction chamber up to atmospheric pressure. The PET films were taken out from the reaction chamber and served as specimens of chemical composition (XPS) analyses, atomic force microscopy (AFM) measurements, and oxygen permeation rate measurements.

### Infrared Spectra of Plasma Polymers

Plasma polymers deposited on aluminum foils were used as specimens for measurement of infrared (IR) spectra. IR spectra were recorded in the attenuated total reflection (ATR) mode on a Horiba FT300 Fourier transform spectrometer with an MCT detector. A crystal of KRS-5 was used as a prism for the ATR technique, and the incident

angle of the IR light against the prism was 45 degrees. The spectral resolution was  $1.0 \text{ cm}^{-1}$ , and 300 scans were recorded on each specimen.

### X-ray Photoelectron Spectra of Plasma Polymers

XPS spectra of the plasma polymers deposited on the PET films were obtained on a Shimadzu ESCA K1 using a nonmonochromatic  $\text{MgK}_{\alpha}$  photon source. The anode voltage was 10 kV, the anode current was 30 mA, and the background pressure in the analytical chamber was  $1.5 \times 10^{-6}$  Pa. A size of the x-ray spot was 2 mm diameter, and the take-off angle of photoelectrons was 90 degrees with respect to the sample surface. The XPS spectra were referenced with respect to the 285.0 eV carbon 1s level observed for hydrocarbon to eliminate charge effects. The spectra were not smoothed. The spectra were 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. The sensitivity factors (S) for the core levels were  $S(\text{C}_{1s}) = 1.00$ ,  $S(\text{Si}_{2p}) = 0.87$ , and  $S(\text{O}_{1s}) = 2.85$ . C/Si and O/Si atomic ratios of the plasma polymers were estimated from the spectra intensity, and the sensitivity factor of corresponding core level within an experimental error of  $\pm 0.05$ .

### Atomic Force Microscopy

Plasma polymers deposited on the PET films were scanned with an atomic force microscopy (Seiko Instrument SFA-300) to observe their surface morphology. A triangular-pyramidal silicon nitride tip was used as a probe, and an area of  $2 \times 2 \mu\text{m}$  square was scanned under a probe pressure of  $8.7 \times 10^{-11} \text{ N/m}^2$ . An arithmetic mean of the surface roughness ( $R_a$ ) and a root mean square of the surface roughness ( $R_{ms}$ ) were calculated from the roughness profile determined by AFM. When a roughness profile is written as a function of  $Z(x)$ ,  $R_a$  and  $R_{ms}$  are defined by the following equations:

$$R_a = \frac{1}{L} \int_0^L |Z(x)| dx \quad (1)$$

$$R_{ms} = \sqrt{\frac{1}{L} \int_0^L Z(x)^2 dx} \quad (2)$$

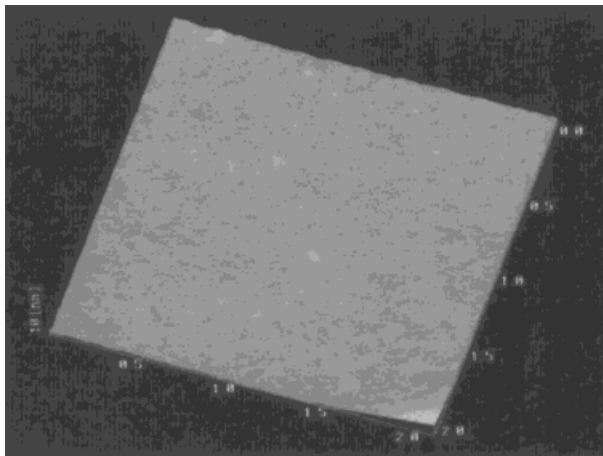
where  $L$  is the scanning distance ( $2 \mu\text{m}$ ).

### Oxygen Permeation Rate Through Plasma Polymer-Deposited PET Film

A gas barrier tester (Mocon Co.; model OX-TRAN 2/20) was used for measurement of the oxygen permeation rate (in  $\text{cm}^3/\text{m}^2/\text{day}/\text{atm}$ ) through plasma polymer-deposited PET films (area of 78 mm diameter) at  $30^\circ\text{C}$  and at relative humidity of 0 and 70% RH. Three or five specimens were used for the measurement, and the oxygen permeation rate was determined from an average of the measurements within an experimental error of  $0.1 \text{ cm}^3/\text{m}^2/\text{day}/\text{atm}$ . From the oxygen permeation rate, the oxygen permeability coefficient (in (STP)  $\text{cm}^3/\text{cm}/\text{cm}^2/\text{sec}/\text{cm Hg}$ , (STP)  $\text{cm}^3$  means volume at standard temperature ( $0^\circ\text{C}$ ) and pressure (76 cm Hg) for the plasma polymer film deposited on the PET film was estimated under assumption of two layer model. The two layer model will be described in a section of oxygen permeation rate through plasma polymer deposited PET films in the Results and Discussion.

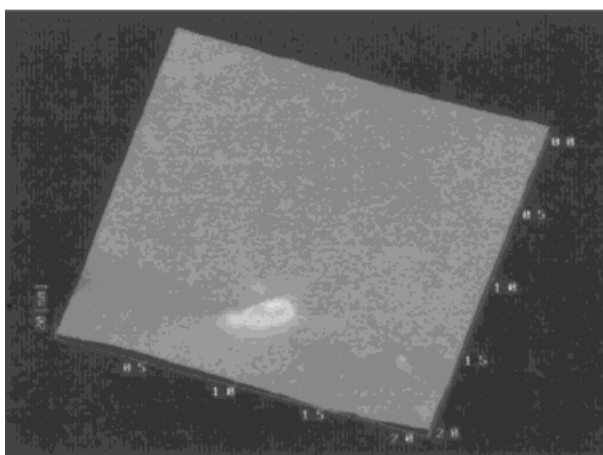
## RESULTS AND DISCUSSION

Preliminary experiments showed that plasma polymers deposited on the PET films were varied in appearance from powder-like to filmy surface by changing plasma polymerization conditions such as rf power, flow rate of the silane compounds, and operating pressure in the reaction chamber. Filmy plasma polymers deposited under following operating conditions: an rf power of 50 W, a flow rate of the silane compounds of  $20 \text{ cm}^3/\text{min}$ , and an operating pressure of 13.3 Pa. Thickness distribution of the plasma polymers deposited on the PET film in the direction of the film width was almost symmetrical against the center of the PET film and was within 5% deviation in areas of at least 5 cm width from the center of the films, when the plasma polymerization was operated at an rf power of 50 W, a flow rate of the silane compounds of  $20 \text{ cm}^3/\text{min}$ , and an operating pressure of 13.3 Pa. Therefore, a part of 10 cm width from the film center was cut off as a specimen for measurement of the oxygen permeation rate. Furthermore, the PET film surfaces were scanned by scanning electron microscopy (SEM) and AFM to make sure of uniformity of the deposited plasma polymers. SEM pictures showed monotone surfaces with less contrast, and there was no grain at the film surfaces. AFM pictures



PET original

$R_a = 1.0 \text{ nm}$   
 $R_{ms} = 1.2 \text{ nm}$



SiOx-deposited  
 PET

$R_a = 1.3 \text{ nm}$   
 $R_{ms} = 1.5 \text{ nm}$

**Figure 2** AFM pictures of the plasma polymer-deposited PET film. (The deposition of plasma polymers is 80 nm thickness).

showed less change in surface roughness by deposition of the plasma polymers. Typical AFM pictures are shown in Figure 2. The surface roughness ( $R_a$  and  $R_{ms}$ ) of the original PET film is 1.0 and 1.2 nm, respectively, and that of the plasma polymer deposited PET film (an average thickness of the deposited plasma polymers is 80 nm) is 1.3 and 1.5 nm, respectively. Less change in the surface roughness indicates that the plasma polymers deposited uniformly at a constant thickness on all the PET surface. Therefore, we conclude that the plasma polymer deposited PET films can serve the measurement of the oxygen permeation rate as specimens without apprehension of heterogeneity in plasma polymer thickness.

#### Choice of Silane Compounds for Formation of SiOx Films by Plasma Polymerization

Plasma polymerization of silane compounds deposits polymer films containing Si—O, Si—C, and CH<sub>2</sub>—CH<sub>2</sub> bonds. The deposition of SiOx films requires the elimination of carbon residues from the silane compounds and the Si—O network formation during the plasma polymerization. Many researchers have applied a heating procedure of plasma polymers at high temperature of more than 500°C to eliminate the carbon residues. The heating procedure is not applicable to the deposition toward PET films because of poor thermal resistance of the PET films. It is indispensable to the deposition of SiOx films on the

**Table I Atomic Composition of Plasma Polymers Formed from Silane Compounds**

Silane Compounds	C/Si and O/C Atomic Ratio			
	In Monomers		In Plasma Polymers	
	C/Si	O/Si	C/Si	O/Si
(C <sub>2</sub> H <sub>5</sub> O) <sub>4</sub> Si	8	4	3.2	1.9
(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> SiH	6	3	1.9	1.4
(CH <sub>3</sub> O) <sub>4</sub> Si	4	4	1.5	1.5
(CH <sub>3</sub> O) <sub>2</sub> Si(CH <sub>3</sub> ) <sub>2</sub>	4	2	1.7	1.1
Si(CH <sub>3</sub> ) <sub>4</sub>	4	0	2.5	0.3

PET film surface that elimination reactions of carbon residues from the silane compounds occur effectively at lower temperatures than the glass transition temperature (67°C) of the PET film. Table I compares the C/Si atomic ratio among plasma polymer films deposited from the five silane compounds—TEOS, TrEOS, TMOS, DDMOS, and TMS—to discuss how many elimination reactions occurred by the plasma polymerization. The five silane compounds have different C/Si atomic ratios of 8 to 4 and different bond structures (Si—O—C and Si—C bonds) between Si and C atoms. The plasma polymerization of these silane compounds was performed under the same plasma conditions (an rf power of 50 W, a flow rate of the silane compounds of 20 cm<sup>3</sup>/min, and an operating pressure in the reaction chamber of 13.3 Pa) and plasma polymers deposited on the PET film surface at room temperature. The C/Si atomic ratio in the deposited plasma polymers, as shown in Table I, depends on the C/Si atomic ratio and the bond structure in the original silane compounds; small C/Si atomic ratios in the deposited plasma polymers are given from plasma polymerization of silane compounds with small C/Si atomic ratios and with Si—O—C bond structure. Therefore, TMOS is preferable to TEOS, DDMOS, and TMS as a silane compound for deposition of plasma polymers with small C/Si atomic ratio. However, TMOS is not a satisfactory compound because the plasma polymers of TMOS possess still a large C/Si atomic ratio of 1.5.

Oxygen gas was mixed with TMOS, and the mixture was plasma-polymerized to accelerate elimination of carbon residues. Table II shows C/Si atomic ratio in the plasma polymers as a function of the oxygen concentration in the mixture. The C/Si atomic ratio decreases with increasing the oxygen concentration and reaches a minimum of 0.5 at an oxygen concentration of 60 mol %.

Mixing of oxygen gas is an effective way to decrease carbon residues. However, further elimination of carbon residues was impossible by changing the operating conditions.

#### Oxygen Permeation Rate Through Plasma Polymer-deposited PET Films

Oxygen permeation rate through the plasma polymer-deposited PET films was determined, and typical results are shown in Table II. The deposited plasma polymers are 80 nm thick, which is considered to be sufficient for complete covering of the PET film surface with the plasma polymers. How the thickness of plasma polymers is requested for complete coating of the PET film surface will be discussed later in this article. Deposition of the plasma polymers formed from the TMOS/O<sub>2</sub> mixture containing 60 mol % O<sub>2</sub> contributes to improvement of the oxygen gas barrier properties. The oxygen permeation rate decreases approximately one-third the time from 44 for the original PET film to 14 cm<sup>3</sup>/m<sup>2</sup>/day/atm. However, the plasma polymers of the TMOS or TMOS/O<sub>2</sub> mixture containing 10 mol % O<sub>2</sub> do not contribute to decrease in the oxygen permeation rate. This comparison suggests that the plasma polymer of the TMOS/O<sub>2</sub> mixture containing 60 mol % O<sub>2</sub> is an effective material for improvement of oxygen gas barrier properties.

To estimate the oxygen permeability coefficient of the plasma polymer itself, we assume that the structure of the plasma polymer-deposited PET film is lamination of two layers, the PET film layer and the plasma polymer layer (Fig. 3). The thickness of the PET film layer and its oxygen permeability coefficient are  $d_1$  and  $P_1$ , respectively. The thickness and oxygen permeability coefficient of the plasma polymer layer are also  $d_2$  and  $P_2$ , respectively. The total oxygen permeability coefficient

**Table II** Effects of Oxygen-mixing on Atomic Composition of Plasma Polymer of TMOS

Oxygen Concentration in TMOS/O <sub>2</sub> Mixture (mol %)	Atomic Composition		Oxygen Permeation Rate at 80 nm Thickness at 30°C (cm <sup>3</sup> /m <sup>2</sup> /day/atm)
	C/Si	O/Si	
0	1.5	1.5	38
10	0.8	1.7	40
30	0.6	1.7	—
60	0.5	1.5	14
80	0.6	1.6	—

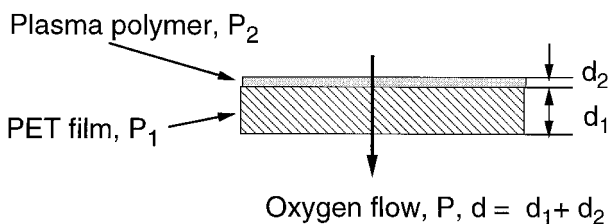
cient for the plasma polymer-deposited PET film is  $P$ , and its thickness is  $d = d_1 + d_2$ . A relationship among  $P$ ,  $P_1$ , and  $P_2$  is given by eq. (3).<sup>3</sup>

$$\frac{d}{P} = \frac{d_1}{P_1} + \frac{d_2}{P_2} \quad (3)$$

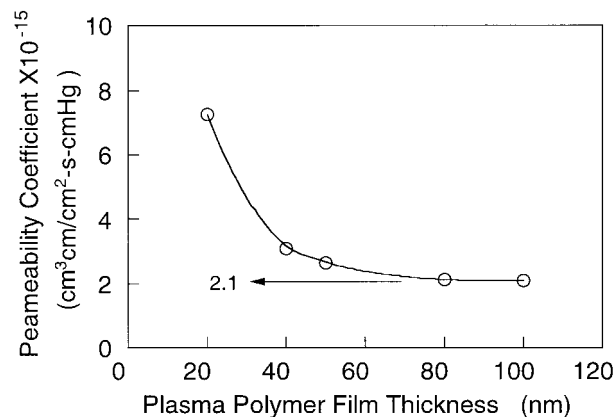
In this study,  $d_1$  is extremely larger than  $d_2$ :  $d_1$  is 38  $\mu\text{m}$ , and  $d_2$  is less than 100 nm. Therefore, equation (3) is modified as follows:

$$\frac{1}{P} = \frac{1}{P_1} + \frac{d_2}{d_1 + d_2} \frac{1}{P_2} \quad (4)$$

From eq. (4) and an oxygen permeation rate at 30°C of 44 (STP) cm<sup>3</sup>/m<sup>2</sup>/day/atm, the oxygen permeation coefficient of the original PET film was calculated to be  $2.5 \times 10^{-12}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg. The oxygen permeability coefficients of PET films are distributed widely, from 1.8 to  $5.9 \times 10^{-12}$  cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg, depending on crystallinity and orientation.<sup>3-5</sup> The calculated coefficient ( $2.5 \times 10^{-12}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg) for the original PET film is not an unreasonable one. From the data of Table II, the apparent oxygen permeability coefficient for the plasma polymers of the TMS/O<sub>2</sub> mixture containing 60 mol % O<sub>2</sub> was calculated according to

**Figure 3** Two layers model for oxygen permeation through the plasma polymer-deposited PET film.

eq. (4) and is plotted in Figure 4 as a function of the plasma polymer thickness. In the calculation, a value of  $2.5 \times 10^{-12}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg was used as the oxygen permeability coefficient  $P_1$  for the original PET film. The calculated oxygen permeability coefficient for the plasma polymers decreases with an increase in the plasma polymer thickness and reaches an almost constant value of  $2.1 \times 10^{-15}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg at 80 and 100 nm thickness. When homogeneous plasma polymers deposit on the PET film surface and the deposition covers all PET film surface in a constant thickness, the oxygen permeability coefficient calculated from equation (4) should be an intrinsic value of the plasma polymers themselves, independent of the plasma polymer thickness. We believe that complete covering of the PET film surface with the plasma polymer may be accomplished at more than 80 nm thickness because of a constant oxygen permeability coefficient. Therefore, the oxygen permeability coefficient at 30°C for the plasma polymers of the TMS/O<sub>2</sub> mixture containing 60 mol % O<sub>2</sub> may be 2.1

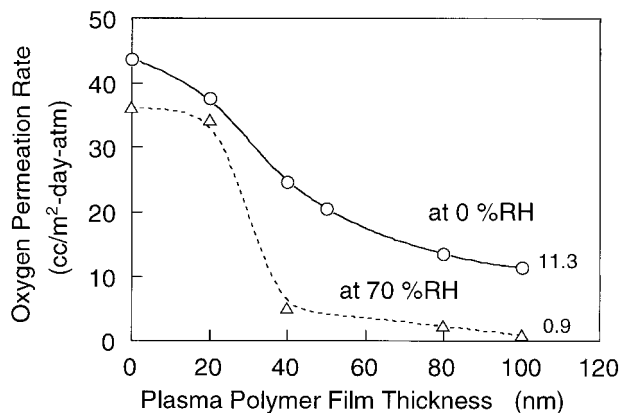
**Figure 4** Oxygen permeability coefficient for plasma polymers of TMOS/O<sub>2</sub> mixture as a function of the plasma polymer thickness.

**Table III** Oxygen Permeability Coefficient of Plasma Polymers

Polymers	Oxygen Permeability Coefficient (STP) cm <sup>3</sup> -cm/cm <sup>2</sup> -s-cmHg)		Reference
	At 0% RH	At 70% RH	
PET	$2.53 \times 10^{-12}$ (at 30°C)	$2.09 \times 10^{-12}$ (at 30°C)	this study
Plasma polymer of (80 nm thick)	$2.1 \times 10^{-15}$ (at 30°C)	$0.27 \times 10^{-15}$ (at 30°C)	this study
TMOS/O <sub>2</sub> mixture (100 nm thick)	$2.1 \times 10^{-15}$ (at 30°C)	$0.13 \times 10^{-15}$ (at 30°C)	this study
Hydrolyzed (ethylene-vinylacetate copolymer) (Eval F)	$1.2 \times 10^{-14}$ (at 25°C)		3 and 5
Polyvinylidene chloride (Saran)	$5.1 \times 10^{-14}$ (at 30°C)		4
	$3.0 - 8.9 \times 10^{-14}$ (at 25°C)		3
	$6.2 \times 10^{-14}$ (at 25°C)		5

$\times 10^{-15}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg, which is about three orders less than that of the original PET film ( $2.5 \times 10^{-12}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg). In food engineering, hydrolyzed ethylene-vinylacetate (Eval) copolymer and polyvinylidene chloride (Saran) are typical oxygen gas barrier materials. The oxygen permeability coefficient is  $1.2 \times 10^{-14}$  for Eval and  $3.0 - 8.9 \times 10^{-14}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg at 25°C for Saran (Table III).<sup>3-5</sup> The plasma polymer of the TMS/O<sub>2</sub> mixture containing 60 mol % O<sub>2</sub> ( $2.1 \times 10^{-15}$  (STP) cm<sup>3</sup>/cm/cm<sup>2</sup>/s/cm Hg) is lower by 5.7 times in the oxygen permeability coefficient than Eval, and is 14–42 times lower than Saran. Therefore, we conclude that the plasma polymer of the TMS/O<sub>2</sub> mixture is an effective oxygen gas barrier material.

In the practical use of packages for foods, drinks, and liquors, oxygen permeation through



**Figure 5** Oxygen permeation rate through the plasma polymer-deposited PET films as a function of the plasma polymer thickness and relative humidity.

packaging hardly occurs at a relative humidity (RH) of 0%, but at some humidity. Figure 5 compares the oxygen permeation rate at 0 and 70% RH for the plasma polymer-deposited PET films. The oxygen permeation rate at 70% RH is slower than that at 0% RH, and there is large difference between the oxygen permeation rates at 0 and 70% RH. The oxygen permeation rate at 0% RH was measured; then using the same specimen, the oxygen permeation rate at 70% RH was measured; the large difference between the oxygen permeation rates at 0 and 70% RH is not due to different specimens but is due to effects of humidity. Using equation (4), the oxygen permeability coefficients at 0 and 70% RH for the plasma polymers were calculated. The PET films deposited with the plasma polymers of 80 and 100 nm thickness were used for the calculation because of complete coating with the plasma polymers. The calculation result is shown in Table III. The oxygen permeability coefficients at 70% RH are eight or sixteen times less than those at 0% RH. This indicates that some interaction between the plasma polymer and water molecule occurs to retard oxygen molecule traveling through the plasma polymer layer. Such retarding effect by humidity has not been observed in conventional polymers. Generally, humidity effect increases rather than decreases the oxygen permeability coefficient.<sup>3</sup> We cannot interpret what interaction between the plasma polymer with water molecules occurs to decrease oxygen permeability.

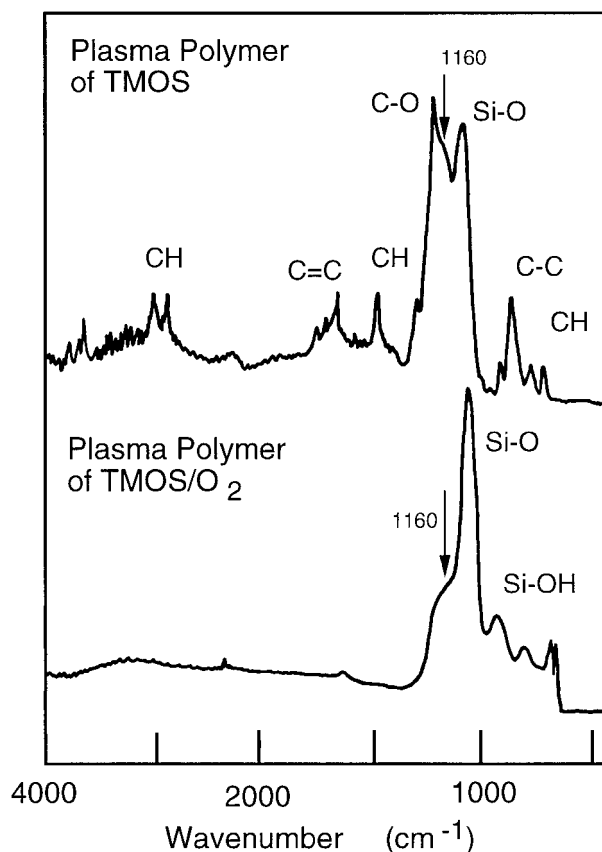
#### Chemical Composition of Plasma Polymers

The chemical composition, especially Si—O networks in plasma polymers of the TMOS/O<sub>2</sub> mix-

ture containing 60 mol %  $O_2$  was analyzed by IR and XPS. In a previous section, we have discussed the chemical composition of the plasma polymers from viewpoint of atomic composition and have pointed out an advantage of the TMOS/ $O_2$  mixture containing 60 mol %  $O_2$  as a starting compound for the plasma polymerization. However, even when the TMOS/ $O_2$  mixture containing 60 mol %  $O_2$  was plasma-polymerized, complete SiOx without carbon residue did not deposit, but the deposited plasma polymers contained some carbon residues.

XPS spectra show useful information with regard to the state of Si atoms in the plasma polymer of the TMOS/ $O_2$  mixture. The  $Si_{2p}$  spectrum for the plasma polymer of the TMOS/ $O_2$  mixture appeared at 103.8 eV with a narrow full width at half-maximum (FWHM) value of 1.7 eV. The binding energy of  $Si_{2p}$  core level depends on the oxidation state of Si atoms: the  $Si_{2p}$  core level in  $SiO_2$ , SiO, and SiC appears at 103.3, 102.1, and 100.4 eV, respectively.<sup>6-8</sup> Therefore, most of Si atoms in the plasma polymers exist in a state of  $SiO_2$ , and no SiO and SiC exist in the plasma polymers.

Figure 6 shows IR spectrum for the plasma polymers of the TMOS/ $O_2$  mixture. A strong absorption peak due to Si—O stretching vibration at  $1055\text{ cm}^{-1}$ , weak absorption peaks due to Si—OH, and Si—C groups at  $927$  and  $801\text{ cm}^{-1}$ , and a shoulder at  $1160\text{ cm}^{-1}$  appear.<sup>9</sup> The shoulder at  $1160\text{ cm}^{-1}$  has been explained to be due to extrinsic distortions of Si—O networks by impurities such as carbon and silanol groups.<sup>10</sup> Therefore, we can say that the plasma polymer of the TMOS/ $O_2$  mixture consists mainly of Si—O networks with a small amount of Si—OH and Si—C groups. However, part of the Si—O network is distorted by the Si—OH and Si—C groups. On the other hand, the Si—O networks in the plasma polymer of TMOS are more heavily distorted than those of the TMOS/ $O_2$  plasma polymer. Figure 6 compares IR spectra for both plasma polymers. The absorption at  $1160\text{ cm}^{-1}$  for the plasma polymer of TMOS is more intense than that for the plasma polymer of the TMOS/ $O_2$  mixture; and intense absorption peaks due to CH (at  $2964$ ,  $2849$ ,  $1455$ , and  $760\text{ cm}^{-1}$ ), C=C (at  $1543\text{ cm}^{-1}$ ), and C—O groups (at  $1200\text{ cm}^{-1}$ )<sup>9</sup> appear, although an intense absorption peak due to Si—O stretching vibration at  $1055\text{ cm}^{-1}$  can be observed. We can speculate that the distortion of the Si—O networks may disturb the oxygen gas barrier properties from comparison in the oxygen permeation



**Figure 6** IR spectra for the plasma polymers of TMOS/ $O_2$  mixture and TMOS.

rate between the plasma polymers of the TMOS/ $O_2$  mixture and TMOS.

## CONCLUSION

Plasma polymerization of silane compounds has been discussed for deposition of SiOx PET films at room temperature. Deposited plasma polymers were analyzed by IR and XPS, and their oxygen gas barrier properties were compared with those of the hydrolyzed ethylene-vinylacetate copolymer (Eval) and poly(vinylidene chloride) (Saran). The main results are summarized as follows.

- 1) A mixture of TMOS and oxygen containing 60 mol %  $O_2$  is a preferable raw material for SiOx formation by plasma polymerization.
- 2) Complete coating of the PET film surface is accomplished by the plasma polymer deposition of 80 nm thickness. The plasma



polymer deposition gives no change in surface roughness on the PET film surface.

- 3) Oxygen barrier properties are improved by the plasma polymer deposition. The oxygen permeability coefficient for the plasma polymer is calculated to be  $2.1 \times 10^{-15}$  (STP)  $\text{cm}^3/\text{cm}/\text{cm}^2/\text{s}/\text{cm Hg}$ , which is lower by that for Eval and Saran.
- 4) The plasma polymer consists mainly of Si—O networks with small amount of Si—OH and Si—C groups. However, a part of the Si—O network is distorted by the Si—OH and Si—C groups.

From results, we conclude that the plasma polymer deposited from the mixture of TMOS and oxygen containing 60 mol %  $\text{O}_2$  is a material with good oxygen barrier properties. Release of distorted Si—O networks will contribute to improvement of the oxygen gas barrier properties.

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