Ultrathin DLC and SiO$_x$ Layer Deposition on Poly(ethylene terephthalate) and Restriction of Surface Dynamics

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ABSTRACT: The hydrophilicity of oxygen plasma-reated polymer surfaces decays with storing time in air environments. Because they are dense, highly crosslinked, and chemically stable, diamond-like carbon (DLC) films and silicon oxide films (SiO$_x$) were deposited on poly(ethylene terephthalate) by plasma-enhanced chemical vapor deposition to restrict polymer surface dynamics. In this study, the effects of ultrathin films on surface dynamics of these polymers were investigated. The layers were deposited on substrates with thickness below 100 Å. The thickness of films was measured with a scanning analyzer ellipsometer, while ATR-IR spectroscopy and Raman spectroscopy were performed to observe the chemical structure of the films. Films below 50 Å were also shown to be effective in stabilizing the plasma treated polymer surfaces. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1158–1164, 2000

Key words: plasma; DLC (diamond-like carbon); SiO$_x$ (silicon oxide); ellipsometry; surface dynamics

INTRODUCTION

The most widely used effect of a plasma is the chemical surface modification of polymers.[1–3] This phenomenon occurs when the outside layer of the polymer is altered to create chemical groups capable of interacting with materials deposited on the polymer. The inherently low surface energy of untreated polymers hinders their wetting and interaction with adhesive systems or deposited metals. Typically, plasma treatments are used to add polar functional groups that dramatically increase the surface energy of polymers. Any change in the surface energy can be easily detected by a change in the contact angle of water with the surface of the modified polymer.[4,5] However, the surface properties of a polymer may change in response to changes in their surrounding environments to minimize their interfacial tension. The hydrophobic recovery phenomenon occurs with most plasma-treated surfaces either partially or completely.[6,7]

Several studies, such as ion beam treatments, repeated plasma treatments, and the control of storing conditions, have been reported for restricting the surface dynamics. The predeposition of dense and highly crosslinked layers may also be a possible techniques for this purpose. However, earlier studies concerning the effective thickness of the deposited layer have not been performed.

In the last few years there was a trend to deposit SiO$_x$ films by using PVD or PECVD techniques. These films are used for applications, such as protective coatings for ophthalmic lenses, barrier films for food and pharmaceutical packaging, corrosion protection layers, and coatings for biocompatible materials and dielectric layers in microelectronic applications. Because SiO$_x$ films are chemically inert, transparent, and dense, they exhibit properties that could make them successful in reducing chain mobility of polymer surfaces.
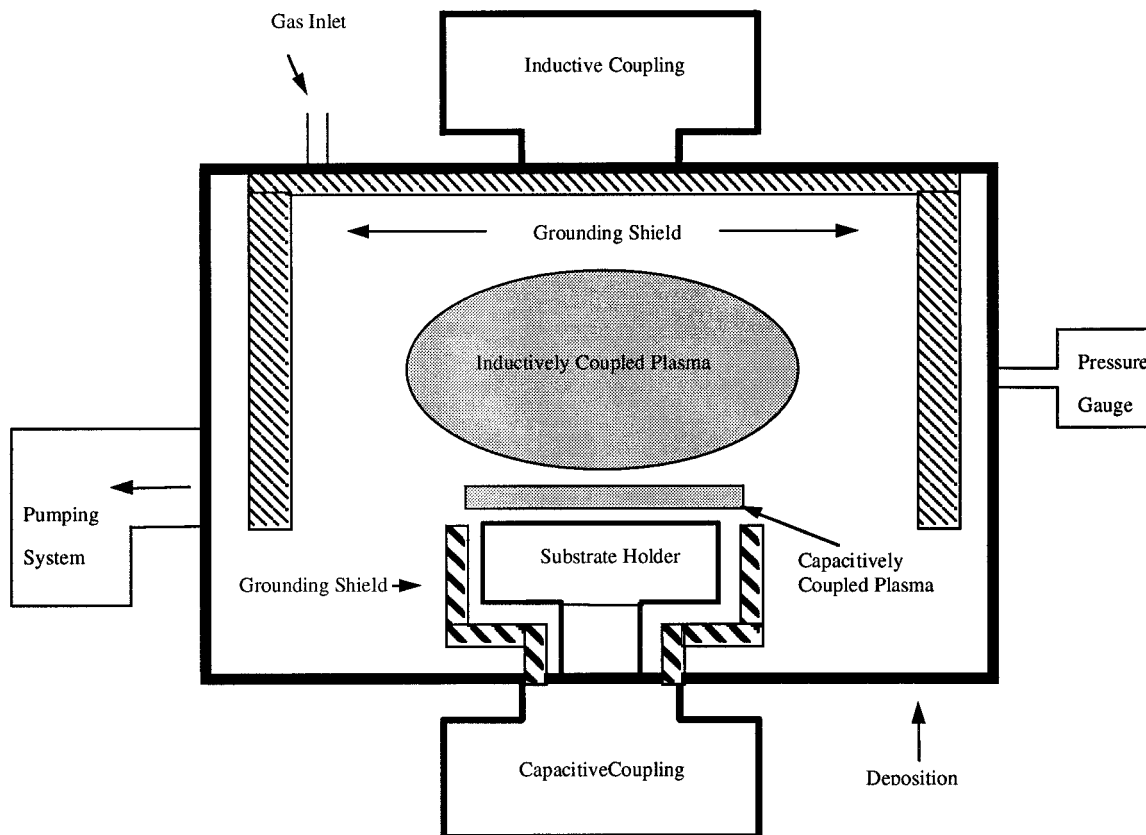
Figure 1   Schematic diagram of an RF PECVD system.

The exact meaning of the term diamond-like has been somewhat controversial, due to its many historical uses. Although this term is still used to describe a broad range of carbon containing materials, the current usage describes a class of amorphous, hydrogenated carbon films that are both hard and electrically insulating, lending to the term diamond-like.

The properties represented by a diamond-like carbon film are due to a mixture of tetragonal (sp^3) and trigonal (sp^2) carbon bonding. While the sp^2 bonds can be found in graphite, the sp^3 bonds are found only in diamond.[23] DLC films are generally formed by condensation of high energy carbon species and exhibit high density, hardness, electrical resistivity, chemical inertness, IR transparency, nanosmoothness, and no long range structural order. The DLC films formed by plasma polymerization display a higher density, thermal stability, and chemical stability than other conventionally made polymer films. It results from their high crosslinked and chemically complex structure. Therefore, the layers on a polymer can be considerably effective in reducing

hydrophobic recovery. In this study, the effective thickness of ultrathin films and the surface dynamics after an oxygen plasma treatment are discussed.

EXPERIMENTAL

Ultrathin Layer Deposition

Ultrathin films were deposited on a commercial PET (ROHM and HAAS, 0.005 × 40″ × 10FT Clear Polyester) film with an inductively coupled RF plasma system shown in the Figure 1. Prior to treatment, PET specimens were ultrasonically washed in ethanol and deionized water for 5 min.[7]

PET films were cut and placed on a copper plate for the treatment. The thickness of a plasma-deposited layer was controlled according to the experimentally determined calibration curve. Specimens were mounted on the flat sample holder and the chamber was evacuated to a base pressure of 10^{-6} Torr or better. Treatment was performed at an operating pressure of 5 × 10^{-2}
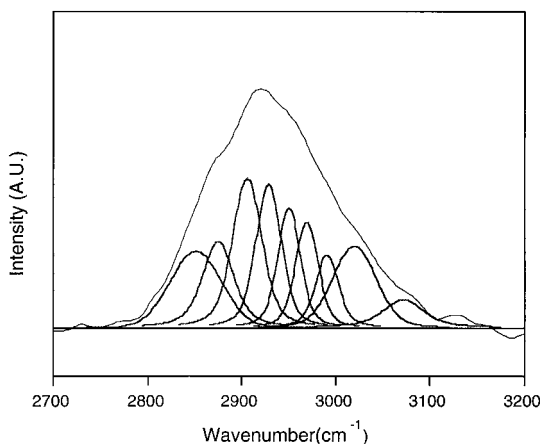
Figure 2 FTIR spectra of the bulk DLC film.

Torr, while using only ethylene for the precursor of the DLC films.

Ultrathin silicon oxide films were deposited from a mixture of tetramethylsilane (TMS) and oxygen under the same deposition conditions of the DLC films.

Oxygen Plasma Treatment

The RF plasma system is a commercially available, capacitively coupled equipment with 13.54 MHz RF power and a quartz made reaction chamber (inner diameter 26 cm, length 19 cm). Pumping down was performed with a Trivac® rotary pump, coupled with a mass trap. All RF plasma treatments were carried out at 100 mTorr gas pressure.

Characterization

The contact angles between the distilled water and the plasma or ion beam modified polymer films were measured at room temperature using a Goniometer (RAME-HART, MODEL100-00 115 1119), using the sessile droplet technique. A drop of deionized water is introduced on the surface of a sample by a microsyringe. At equilibrium, the contact angle is measured with a telescope equipped with a goniometer eyepiece.[8]

The thicknesses of DLC and SiO_x films below 100 Å were estimated using the ellipsometric spectra. The ellipsometric spectra were recorded from 1.5 to 6.0 eV to obtain information about the dielectric response of the polymer surfaces with the Rotating Analyzer Ellipsometer.[9] FTIR spectroscopy was performed on the films with a Biorad spectrometer (FTS 375°C). The incoming

source was a KBr laser, and 100 scan spectra were recorded from 400 to 4000 cm at 4 cm resolution using a Ge ATR crystal.[10] Raman spectroscopy was carried out by using an Ar^+ ion laser operated at 514.5 nm (2.41 eV) at a power of 200 mW. The Raman spectra were detected from 1200 to 1800 cm^{-1}.

RESULTS AND DISCUSSION

Effect of Ultrathin DLC Film

FTIR-ATR was carried out to observe the chemical structure of ultrathin films with a Ge crystal. DLC films exhibit a wide FTIR absorption band at 2900 cm^{-1}, indicating relatively high hydrogen content in the film as shown in Figure 2. The broad band, which is a superposition of various stretching vibrations of a C—H bond, can be deconvoluted into different individual peaks corresponding to the types of a bond. The assignments of the peaks are in Table I.[11–13]

It is well known that the sp^2 CH bonds show absorptions at about 3000 cm^{-1} (olefinic) and 3050 cm^{-1} (aromatic). The absorption peak of a sp^2 CH_2 (olefinic) vibration mode also exists at 3020 cm^{-1} (olefinic). The region of the broad band mainly shows the existence of sp^3 CH_2 vibrations at 2855 (symmetric), 2925 cm^{-1} (asymmetric) and 2950 cm^{-1} (olefinic) as well as sp^3 CH_3 vibrations at 2870 cm^{-1} (symmetric) and 2960 cm^{-1} (asymmetric). The ratio of sp^3 and sp^2 carbon networks can be considered from the relative intensity of the peaks. However, quantitative analysis of the ratio was not performed due to the difficulty of accurate deconvolution of the FTIR spectra.

DLC films deposited on a silicon wafer were examined by Raman spectroscopy. Because Raman spectroscopy is sensitive to changes in trans-

Table I Assignments of Absorption Peaks in the C—H Stretching Region

Wavenumber (cm^{-1})	Assignment
2855	sp^3CH_2 (sym.)
2870	sp^3CH_3 (sym.)
2925	sp^3CH_2 (asym.)
2950	sp^3CH_2 (olef.)
2960	sp^3CH_3 (asym.)
3000	sp^2CH (olef.)
3020	sp^2CH_2 (olef.)
3050	sp^2CH (arom.)

lational symmetry, it is useful for observing the disorder or crystallite formation and structural modifications in DLC films. The first-order Raman spectrum for diamond and graphite consists of a single line at 1332 and 1580 cm^{-1}, respectively. Because losing of the long-range translational symmetry causes a different crystal momentum, the spectrum changes drastically in disordered graphite. A Raman spectrum for a hydrogenated amorphous carbon film commonly shows another disorder or D (disordered) peak at 1350 cm^{-1} in addition to G (graphitic) peak at 1530 cm^{-1}. The scattering of carbon atoms with sp^2 bond results in the both peaks.

Figure 3(a) represents that the DLC film has a relatively high sp^3 bonded carbon. From the previous research, it was seen that the samples prepared with a high bias voltage began to change the shape of G peak at 1530 cm^{-1} and D peak appeared at 1350 cm^{-1}, as shown in Figure 3(b).[24]
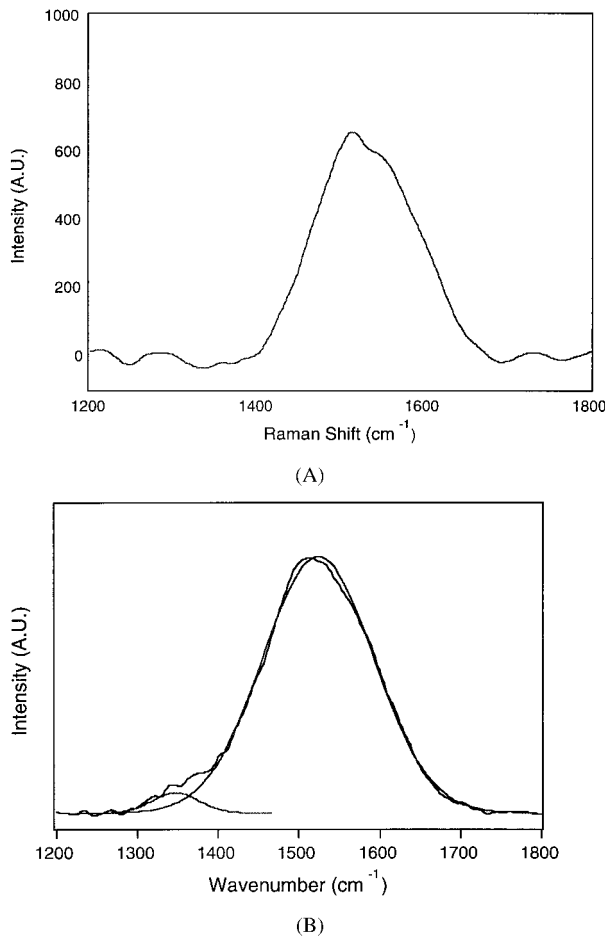

(A)

(B)

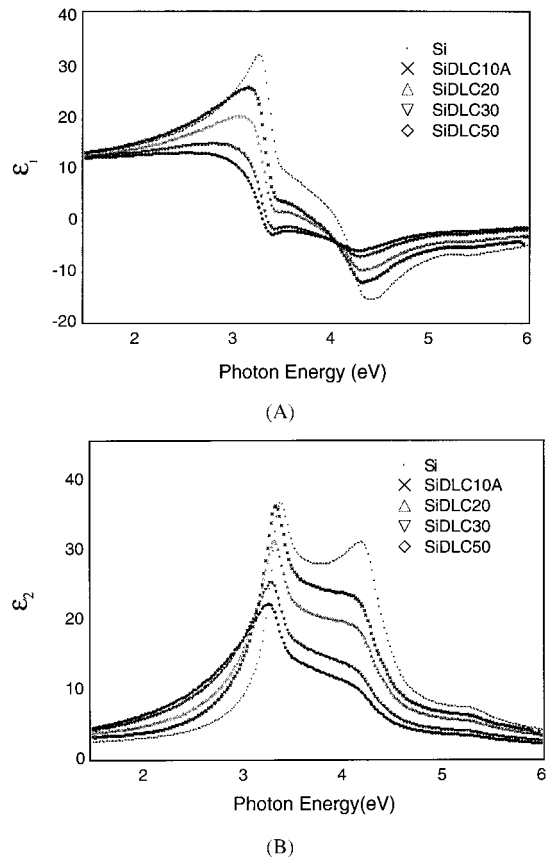**Figure 3** Raman spectra of the bulk DLC film. (A) Experimental; (B) typical DLC.

(A)

(B)

Figure 4 Ellipsometric spectra of ultrathin DLC films. (A) Real part; (B) imaginary part.

However, no peaks from the scattering caused by the sp^3 carbon bond were observed because the sp^2 sites have a much greater scattering cross-section than the sp^3 sites.

To restrict the surface dynamics, ultrathin DLC films were applied on polymers under the same deposition condition of a bulk film excluding the deposition times. However, because it is difficult to differentiate the peaks from the noise level, rotating analyzer ellipsometry was proposed for the measurement of film thickness below 100 Å.

In general, the silicon spectra show the characteristic shape of dielectric response in the range of 1.5 to 6.0 eV, provided by an Xe lamp. When the silicon is covered with the other materials, the dielectric response makes the spectrum shape change at certain photon energies. The change of the shape depends on the thickness of layers on a silicon surface. Figure 4 represents the dielectric functions of silicon and ultrathin DLC films on silicon. Ellipsometry was performed at the different detecting positions and with rotating samples on the sample holder. Because the spectra were
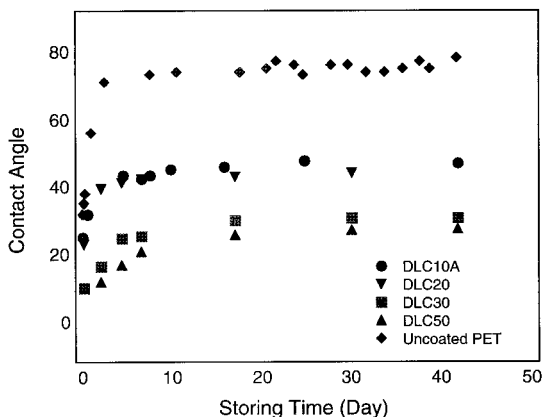
Figure 5 Water contact angles of DLC-coated PET as a function of time.

the same in the cases, the film was considered optically isotropic.

Ellipsometric response was obtained with the films of a different thickness calculated from the calibrated deposition rate. The shape was shown to change as a function of the thickness of the deposited films. The thickness between the known films, which were taken with AFM, was inferred from the difference of shape change. The thickness of DLC10, DLC20, DLC30, and DLC50 were 10, 20, 30, and 50 angstroms, respectively.

Diamond like carbon is a mildly hydrophobic surface, with a water contact angle around 60°. Recent investigations have shown that elements like silicon, fluorine, oxygen, and nitrogen influence the contact angle of water when they are incorporated into the network structure of a DLC coating. Silicon and fluorine increase the hydrophobicity, indicating a lower surface energy. On the other hand, oxygen and nitrogen increase the hydrophilicity, indicating an higher surface energy.[20,21] Oxygen plasmas form oxygen containing hydrophilic functional groups such as CO, COOH, OH, etc., which are responsible for the drastic change in the water contact angles.[14,15] However, the surface properties of a polymer may change in response to changes in the surrounding medium

to minimize the interfacial tension. The hydrophobic recovery phenomenon occurs either partially or completely with most plasma treated surfaces.[16,17] Due to the high mobility of the chains, the surface dynamics of polymer solids are significantly different from those of more rigid materials such as metals and ceramics. Because polymer chains on the surface have more free volume than the bulk, those in the surface region can be oriented in a different manner than the bulk.[18] Therefore, it is extremely difficult to predict the surface properties from the nature of chemicals of which the polymers are composed. The aging, which takes place due to the surface dynamics, is believed to be due to the reorientation of mobile chains near the modified surface. For example, hydrophilic polymer surface becomes hydrophobic in exposure to hydrophobic mediums such as air or a nonpolar liquid, whereas a hydrophobic polymer surface becomes hydrophilic in hydrophilic mediums such as water or polar liquid.[1,6,7]

Figure 5 also shows the aging phenomena, which is also called hydrophobicity recovery, of ultrathin DLC-deposited PET films. The surface morphology was considered with AFM for the possible effect on the water contact angles. The surfaces are smooth enough not to influence the results from the surface characterization. As can be expected, an uncoated PET film recovered its original hydrophobicity in a few days, but coated PET films are still wettable and stabilized even 50 days later. This effect is due to the highly crosslinked carbon layers that restrict the chain mobility from responding to a different environment.[19]

From the previous results it was believed that the hydrophobicity recovery followed an exponential function with a critical point of a characteristic value. Table II shows the hydrophobicity recovery of oxygen plasma treated PET films quantitatively. The contact angle of "after aging" was obtained by curve fitting the original data and predicting at the infinite time. Although the hydrophobicity recovery is large as the contact angle of "after aging" increases, the hydrophobicity recovery is fast as the

Table II   Aging of DLC-Deposited PET Films

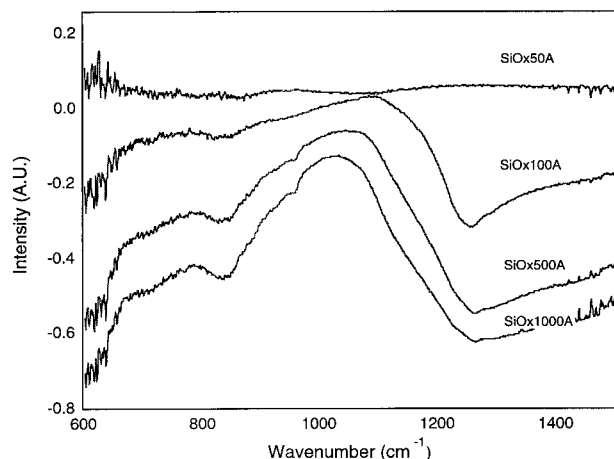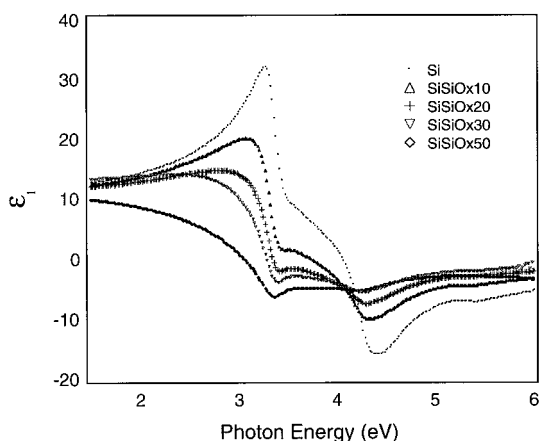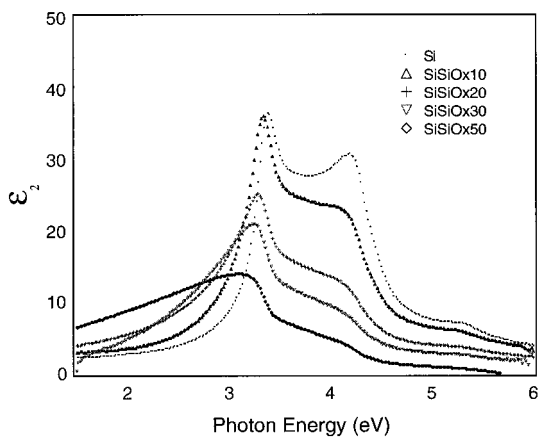| Contact Angle	DLC2	DLC5	DLC10	DLC15	Uncoated PET
Before aging	25	23	10	11	25
After aging	46	43	30	27	75
Characteristic value (day)	3.4	1.7	5.1	10.6	1.1

Figure 6   FTIR-ATR spectra of the bulk SiO$_x$ films.

"characteristic value" is small. From the results, the hydrophobicity recovery of the uncoated PET is faster than the other DLC-precoated PET films, and

(A)

(B)

Figure 7   Ellipsometric spectra of ultrathin SiO$_x$ films. (A) Real part; (B) Imaginary part.

recovered its original hydrophobicity completely for a short time. DLC precoating is significantly effective in reducing the surface dynamics. The water contact angle of DLC films taken just after an oxygen plasma treatment is lower than the water contact angle of an uncoated PET film for a dense and highly crosslinked DLC structure. A thicker DLC precoated PET film shows relatively longer aging time; the wettability is still higher than a thinner DLC or an uncoated PET film.

Effect of Ultrathin SiO$_x$ Film

FTIR-ATR spectroscopy was performed with 50, 100, 500, and 1000 Å-thick SiO$_x$ films for obtaining characteristic spectra. When oxygen rich feeds are utilized, the C—H and Si—(CH$_3$)$_x$ vibrations are dramatically reduced, and the FTIR spectra are characterized by a strong Si—O—Si stretching vibration near 1070 cm^{-1} and by a Si—O—Si bending vibration at 800 cm^{-1}. Figure 6 represents the infrared spectra taken on the SiO$_x$ films deposited on the PET films. The ultrathin SiO$_x$ film of 50 Å exhibits no significant peak at around 800 and 1070 cm^{-1} because of the small intensity compared to noise level, while thicker SiO$_x$ films exhibit distinct peaks. The peaks assigned for O—H stretching at 3600 cm^{-1} and Si—OH bending at 930 cm^{-1} were not observed. These results can be supported by the water contact angles of about 60° performed on the films. The surfaces showed hydrophobic properties, which indicate few O—H groups in the films. It can be inferred that the films deposited on the substrate are silicon-like or SiO$_2$-like films.[22]

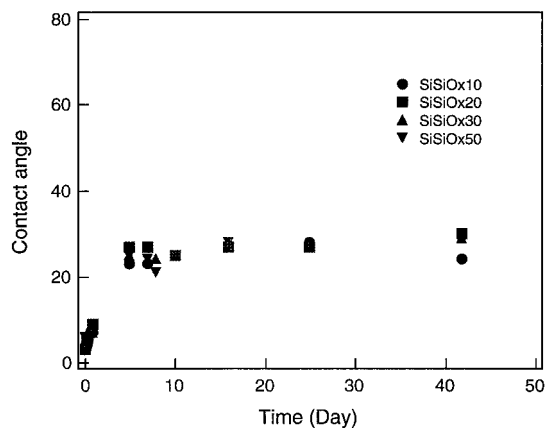The dielectric response from ellipsometry can be an indicator for measuring the thickness of

Figure 8   Water contact angles of SiO$_x$-coated PET as a function of time.

Table III   Aging of SiO$_x$-Deposited PET Films

Contact Angle	SiO$_x$50	SiO$_x$100	SiO$_x$500	SiO$_x$1000	Uncoated PET
Before aging	4	3	5	6	25
After aging	27	28	28	28	75
Characteristic value (day)	4.2	2.4	3.6	5.5	1.1

ultrathin SiO$_x$ films on the Si substrate. As ultrathin DLC films have a reliable trend of spectra change, SiO$_x$ films also show the trend in the Figure 7. As the thickness of the deposited layers increase, the shapes of dielectric functions change, exhibiting a certain trend. Because the thicker films over 100 Å showed interference patterns, only SiO$_x$ films below 50 Å was shown in the figure.

Ultrathin SiO$_x$ films were deposited on the PET surface to restrict the surface dynamics of oxygen plasma-treated polymers. As can be seen in Figure 8, SiO$_x$ precoating is effective for stabilizing the surface. The characteristic values and contact angles are shown in Table III. The wettability is relatively higher, and aging time is also longer than even ultrathin DLC precoated PET films. This may result from the higher crosslinked and denser layer of SiO$_x$.

CONCLUSIONS

Because DLC and SiO$_x$ films show the highly crosslinked, isotropic, and transparent properties, they were deposited on polymers for restricting the chain mobility of oxygen plasma treated surfaces during storage in air condition. The thicknesses of ultrathin films were characterized with AFM and ellipsometry. DLC and SiO$_x$ films were precoated by PECVD systems before the oxygen plasma treatments. The surfaces treated with oxygen plasma were highly wettable and stabilized in a hydrophobic storing condition for a long time. SiO$_x$ precoating was more effective in keeping wettability for the highly crosslinked and denser structure. The DLC films below 50 Å thick were also applied on the PET surface. The films showed significant wettable behavior and kept the property permanently in an air condition.

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