Deposition of Silicon Oxide Hard Coatings by Low-Temperature Radio-Frequency Plasmas

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ABSTRACT: In this study, the deposition of silicon oxide (SiOx) hard coatings on polycarbonate (PC) substrates was attempted with low-temperature radio-frequency (RF) plasmas from tetramethyldisiloxane (TMDSO) with the addition of oxygen. The coating uniformity and deposition rate were investigated in terms of substrate size, glow uniformity, and RF power input. The hardness of the resulting SiOx plasma coatings was examined by the ASTM pencil hardness test method. The hardness of the resulting SiOx plasma coatings was mainly determined by the TMDSO–O_2 ratio in the plasma gas mixture. Ultraviolet–visible transmission spectra showed that these plasma coatings were transparent in the visible light region. Fourier transform infrared–attenuated total reflection analysis results indicated that the resulting SiOx plasma coatings were inorganic in nature. The interfacial adhesion, which is a common problem in the deposition of hard protective coatings on polymeric substrates, was also significantly improved by the deposition of an ultrathin plasma polymer interlayer from TMDSO before the deposition of the SiOx plasma coatings on the PC substrates. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 245–251, 2010

Key words: films; coatings; plasma polymerization; polycarbonates

INTRODUCTION

In recent years, plastic glass materials, such as polycarbonates (PCs) and poly(methyl methacrylate), have progressively been substituted for inorganic glasses because of their light weight, low cost, and safety features as shatterproof windows. Many commercial products, such as optical lenses, digital electronic panels, and automotive headlamp lenses, are made of plastic glass. Moreover, the miniaturation of the next generation display panel has naturally required skinnier and more flexible panel substrates, such as plastic materials. However, the components of plastic glass materials are intrinsically soft, and thus, the use of plastic is limited to moderately mild applications. To refine the inherent restrictions of plastic substrates, a variety of protective coating fabrication methods have recently been used.[1–5] The wet-chemistry method, which consists of curing by UV radiation or oven heating, is easily accessible and the most commonly used. Nevertheless, it is hard to obtain ultrathin protective coatings and to control the thickness uniformity from the wet-chemistry processes.[6] These coating techniques are also considered uneconomical and environmentally hazardous because toxic materials are involved.

For many technological applications, protective coatings need to be ultrathin, uniform, and adhesive and have antiscratch strength. Silicon oxide (SiOx) films have attracted much attention because of their specific chemical structure and admirable electrical insulation characteristics. The unique properties of SiOx films make it applicable as an intermetal dielectric, gas barrier layer, and protective coating. For most protective coatings for modern technologies, SiOx films must be ultrathin, uniform, and adhesive and have antiscratch strength. The plasma chemical vapor deposition process is a very promising technique for protective coating fabrications.[7–11] Over the traditional wet-chemistry method, the plasma-deposition technique has many advantages, including its process simplicity, environmental friendliness, and its ease in the preparation of uniform, ultrathin, pinhole-free coatings through a single-step process. The low-temperature plasma process in the deposition of hard coatings on plastic substrates would not alter the substrate bulk properties. Among many investigations into the successful development of plasma protective coatings on plastic substrates, there has been a need to develop a

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plasma chemical vapor deposition process that is capable of handling large-size substrates. In addition, it is desired that the plasma reactor system be widely available, easily cleaned, and simple to operate.

To meet these demands, we developed a radiofrequency (RF) plasma reactor system for hard-coating deposition. With such a plasma reactor system, we were able to deposit uniform SiOx hard coatings on PC substrates from a gas mixture of tetramethyldisiloxane (TMDSO) and oxygen as the precursors. The resulting SiOx coatings were transparent and hard. The effects of the process parameters, including TMDSO–O_2 ratio, plasma pretreatment, RF input power, and adhesion-promoting interlayer on the quality of the resulting coatings were investigated.

EXPERIMENTAL

The precursors used for plasma deposition was TMDSO, which was purchased from Pfaltz & Bauer, Inc. (Waterbury, CT). Before it was introduced into the reactor system, TMDSO was degassed by a freezing–thawing process three times. PC films were used as substrates and cleaned ultrasonically in deionized water for 15 min to remove surface contamination before they were loaded into the plasma reactor. These substrates were individually placed into the plasma reactor. The plasma reactor system used in this study was a bell-jar-type reactor, with dimensions of 46 cm in height and 44.5 cm in diameter. An electrode assembly with a proprietary design was connected to an RF power source. A TMDSO and oxygen gas mixture was used as a precursor for plasma deposition. The plasma reactor was first pumped to a base pressure of 1 mTorr or below; the TMDSO and oxygen mixture was then introduced into the chamber at a preset flow rate and mixing ratio. The system pressure in the reactor was controlled with an MKS pressure controller. When the system pressure reached a preset value, plasma power was applied at 13.56 MHz with a required match network unit (RFX-600 generator Advanced Energy Industries, Inc. Fort Collins, CO).

The silicon wafer samples were also cleaned with an acetone wipe and attached to the substrate surfaces with double-layer tape. For the purpose of thickness and refractive index measurements, a null-seeking type AutoEL-II automatic ellipsometer (Rudolph Research Corp., Flanders, NJ) with a 632.8-nm helium–neon laser light source was used. In this study, Fourier transform infrared (FTIR)–attenuated total reflection (ATR) spectra were recorded on a Nicolet FTIR 460 spectrometer from Thermo Electron Corp. (Waltham, MA) to determine the chemical structures of the resulting plasma coatings. The instrument was purged with dry nitrogen to prevent the interference of atmospheric moisture. The Nicolet FTIR 460 spectrophotometer was connected to a computer running standard OMNIC software from Thermo Electron Corp. In total, 256 scans were accumulated to obtain high signal–noise levels for the final spectra in the spectral range 4000–400 cm^{-1}. The substrate used for ATR–FTIR in this study was a silicon wafer. Ultraviolet–visible (UV–vis) transmission detection was carried out with a Varian Cary 50 UV spectrophotometer with an 80-Hz flash lamp (Varian, Inc. Palo Alto, CA). UV–vis spectra of the uncoated and plasma-coated PC substrates were measured in absorption mode with the Varian Cary 50 UV spectrophotometer in the wavelength range 300–800 nm at room temperature.

The surface hardnesses of both the untreated and plasma-coated PC substrates were examined by the pencil hardness testing method according to ASTM D 3363-05. The pencils, which were obtained from Derwent, Inc. (Cambria, UK), had hardnesses from 6H to 6B (hard to soft). In this method, the flat pencil head was placed against the PC substrates at a 45° angle and pushed forward to make a scratch on the substrate. The tested pencils, with hardness levels from hard to soft, were used until one pencil was found that could not make a scratch on the substrate. The hardness level of the final test pencil defined the hardness of the plasma coatings on the PC substrate. The adhesion of the SiOx coating was tested by the ASTM 3359-93B tape adhesion test. This testing method provides semiquantitative results given in levels of 0–5. The level of adhesion is graded by the pattern of coating lifting with a rating of 0 for greater than 65% coating liftoff and a rating of 5 for no coating liftoff, along with the level described in the ASTM standard. The method was applied to the dry surface. Poor adhesion can be easily detected by this simple test. When the test result reaches the grade of 5, this simple test cannot distinguish between results. However, if the samples are exposed to some adhesion-damaging environment before the tape test, it is possible to further distinguish the level or nature of adhesion. A wet-tape test is a modification of the tape adhesion test. In this process, test samples were prepared consistent with the standard procedure described previously. Instead of undergoing the tape test directly, samples were placed in hot water (65°C) for a prearranged period of time. In this study, periods of 1, 2, 4, 8, 24, and 72 h were used. Samples initially immersed in hot water (with prescribed marks) were subjected to the tape test. Because the interface between the coating and the substrate was exposed to hot water, the water sensitivity of the adhesion could easily be detected by this test.

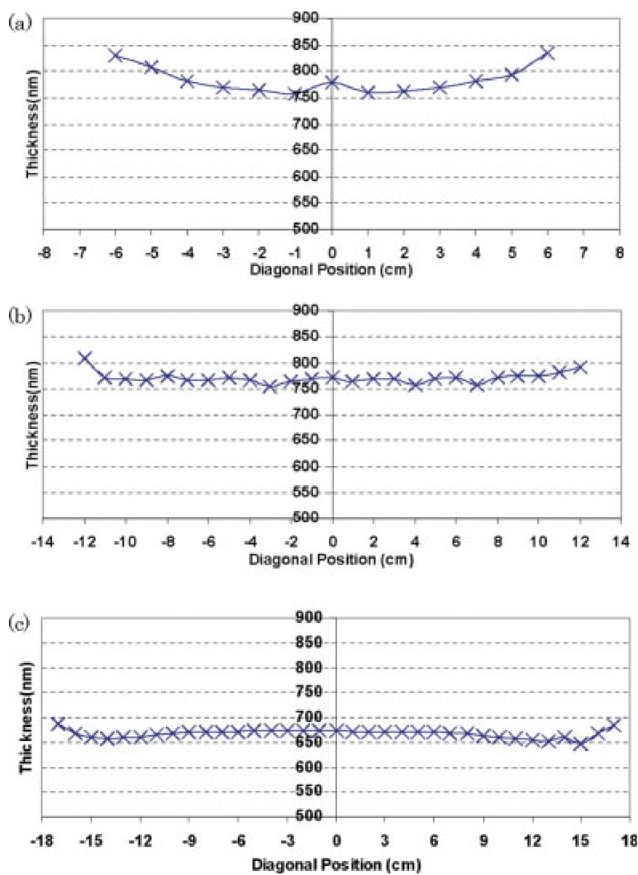


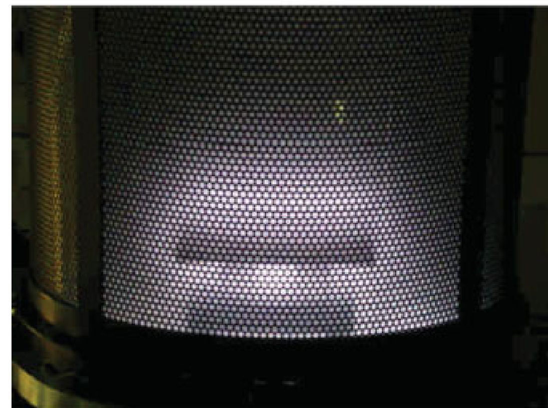
Figure 1 Thickness profile of the resulting SiOx plasma coatings in the diagonal direction on square-shaped PC substrates with different sizes: (a) 3 × 3, (b) 7 × 7, and (c) 10 × 10 $in.^2$. Plasma conditions: 1-sccm TMDSO, 10-sccm O_2, 30 mTorr of pressure, 40 W of RF power input, and 25-min deposition time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Uniformity of the SiOx plasma coatings

During the plasma-deposition process, the uniformity of the plasma-deposited coatings was important for their successful application. Figure 1 shows the deposition profiles of the plasma-deposited SiOx coating on different sized power electrodes as substrates. The refractive indices of the plasma-deposited SiOx coatings were consistent with a value of about 1.45. The deposition profile of the plasma-deposited SiOx coatings were relatively more uniform on large size substrates than those on the small size substrate, as shown in Figure 1. Figure 2 represents the luminous gas phase in the RF glow discharge of the TMDSO+O_2 mixture with the power electrode as a substrate located in the center of a bell-jar-type plasma reactor. We clearly observed the effect of the substrate size on the RF glow discharge of the TMDSO+O_2 mixture: the glow intensity and glow volume decreased with increasing substrate size (see Fig. 2). Also, the decrease in deposition thickness with increasing substrates size was consistent with the decrease in the glow intensity and the increase in the glow volumes in the RF glow discharge of the TMDSO+O_2 mixture, as shown in Figure 2.

(a)



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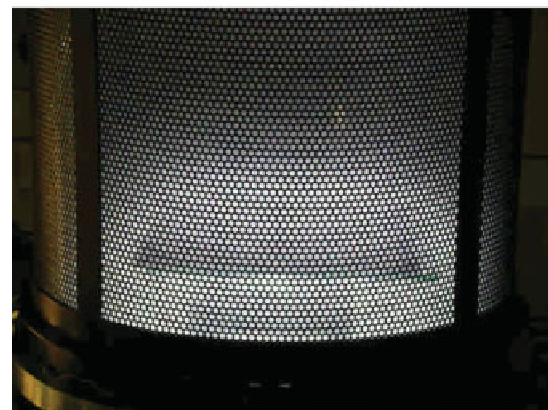


(c)

Figure 2 Pictorial views of the luminous gas phase in RF plasmas of TMDSO+O_2 gas mixtures with different size PC substrates loaded inside the reactor: (a) 3 × 3, (b) 7 × 7, and (c) 10 × 10 $in.^2$. Plasma conditions: 1-sccm TMDSO, 10-sccm O_2, 30 mTorr of pressure, and 40 W of RF power input. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

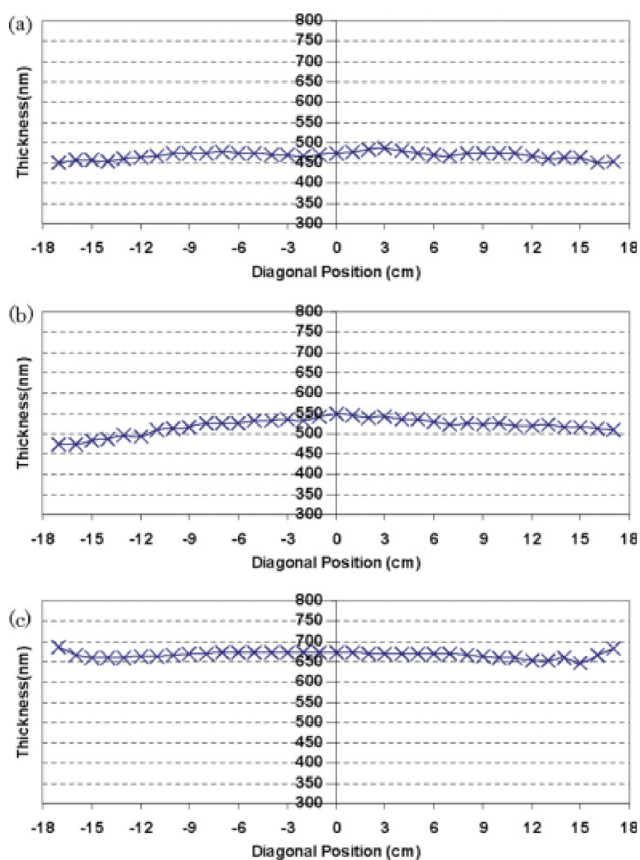
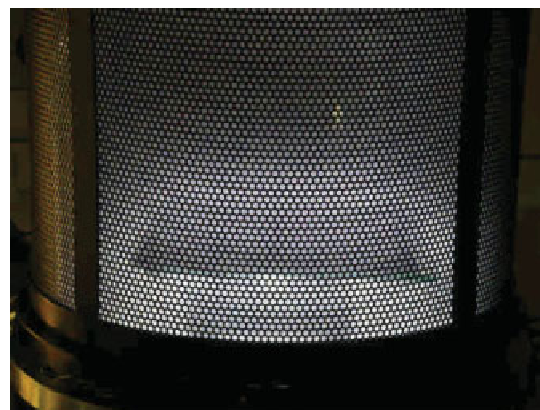
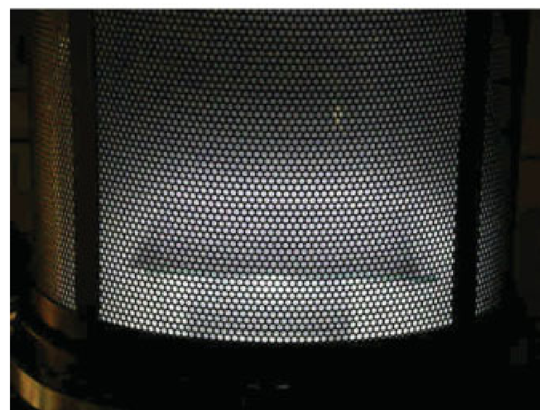


Figure 3 Thickness profile of the resulting SiOx plasma coatings in the diagonal direction on square-shaped PC substrates prepared under different RF power inputs: (a) 10, (b) 20, and (c) 40 W. Plasma conditions: 1-sccm TMDSO, 10-sccm O_2, 30 mTorr of pressure, 40 W of RF power input, 25-min deposition time, and 10 × 10-in.^{2} substrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 shows the deposition profiles of plasma-deposited SiOx coatings with different RF plasma power inputs. The refractive index of the plasma-deposited SiOx coatings in all of the plasma treatments were also consistent with a value of about 1.45. With increasing RF plasma power input, the uniformity of the plasma-deposited SiOx coating was improved, and the thickness of the plasma-deposited SiOx coating increased. In contrast to the effect of the substrates sizes on the RF glow discharge of TMDSO+O_2 mixture, the glow intensity and the glow volume increased with increasing RF plasma power input, as shown in Figure 4. In other words, Figure 4 also elucidates the significant relationship between the luminous gas phase and plasma deposition in the RF TMDSO+O_2 chemical vapor deposition system.[12] As shown in Figures 1–4, a deposition process was achieved at well-controlled operational parameters of the RF plasma chemical vapor deposition system. As a result, the results of this study indicate that this plasma chemical vapor deposition system has the potential to attain uniform SiOx coatings on large-scale plastic substrates.



(a)



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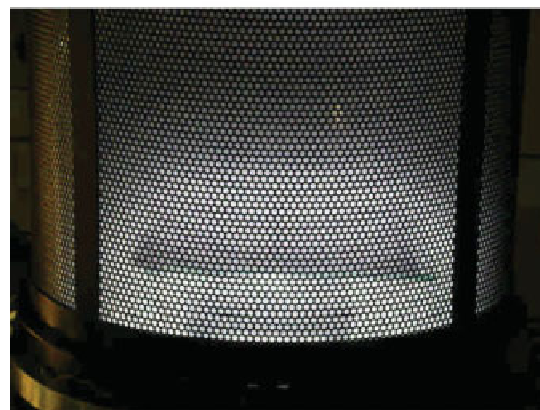

(c)

Figure 4 Pictorial views of the luminous gas phase in the RF plasmas of TMDSO+O_2 gas mixtures under different RF power inputs: (a) 10, (b) 20, and (c) 40 W. Plasma conditions: 1-sccm TMDSO, 10-sccm O_2, 30 mTorr of pressure, 40 W of RF power input, and 10 × 10-in.^{2} substrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

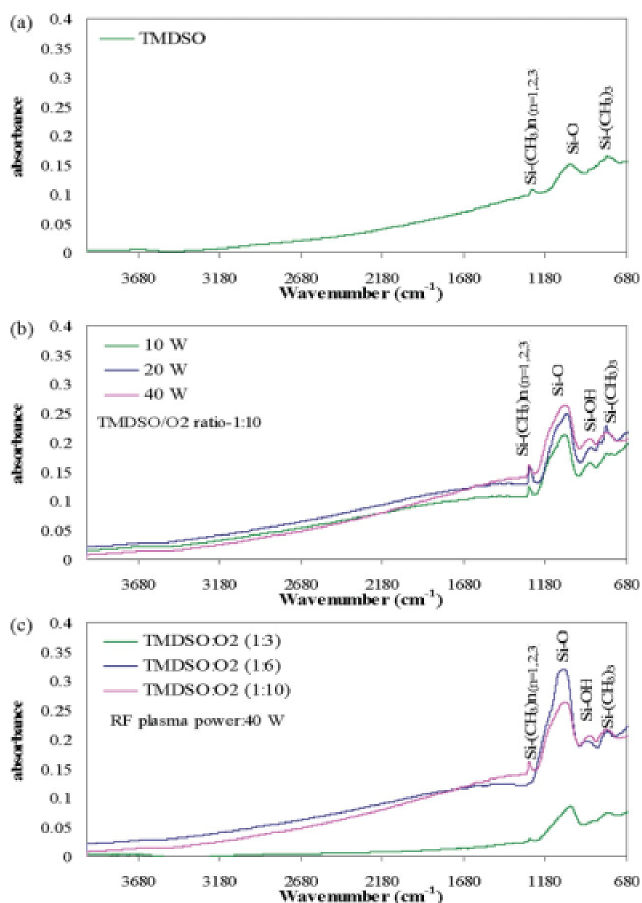

Figure 5 FTIR–ATR spectra for low-temperature plasma coatings with coating thicknesses of 0.45–0.80 μm: (a) plasma-polymerized TMDSO coating, (b) plasma-deposited SiOx coatings with different RF power inputs, (c) plasma-deposited SiOx coatings with different TMDSO–O_2 ratios. Plasma conditions: 1-sccm TMDSO, 30 mTorr of pressure, and 25-min deposition time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FTIR–ATR characterization results

FTIR–ATR spectra of the plasma-deposited TMDSO interlayer and plasma-deposited SiOx coatings with different plasma powers and TMDSO–O_2 ratios are shown in Figure 5(a–c). It was obvious that the plasma interlayer deposited from TMDSO without oxygen addition retained the organic structure of the starting TMDSO precursors. New absorption peaks [Si—OH stretching at 930 cm^{-1} and Si—$(CH_3)_3$ stretching at 800 cm^{-1}] appeared in the plasma-deposited interlayer, and these new absorption peaks were not present for the TMDSO precursors. The Si—OH peaks of the plasma-deposited SiOx coatings' FTIR–ATR spectra could have been caused by the chemical structures resulting from the plasma phase reactions.[13] Particularly, the relative intensity ratio of Si—O over the Si—$(CH_3)_3$ absorption peaks significantly increased with more O_2 addition. This indicated the formation of the SiOx inorganic nature of the resulting plasma coatings.

Also, no peaks were detected at 2900 and 1730 cm^{-1} due to C—H and C=O stretching vibrations. Therefore, the plasma-deposited SiOx coatings obtained inorganic characteristics at the low substrate temperature of 35–40°C, and the Si—O absorption peaks at 1078 cm^{-1} were more pronounced with increasing RF plasma power. Furthermore, the strongest intensity of the Si—O absorption peak in the FTIR–ATR spectrum obtained at a TMDSO–O_2 ratio of 1 : 6 implied that reasonably more Si—O groups occurred in the RF TMDSO–O_2 mixture (1 : 6) plasma chemical vapor deposition system. Consequently, Si—O groups were indicated as the major structure in the resulting plasma coatings because of the decomposition of the TMDSO–O_2 mixture in the plasma-deposition process; this gave rise to SiOx coatings with relatively high inorganic characteristic, as characterized by FTIR–ATR analysis.[13]

SiOx plasma coatings on the PC substrates

The dependences of the deposition rate and refractive index on different oxygen–TMDSO ratios on PC substrates are shown in Figure 6. The typical plasma-deposition rate was about 21–32 nm/min. The plasma-deposited SiOx coating was characterized as

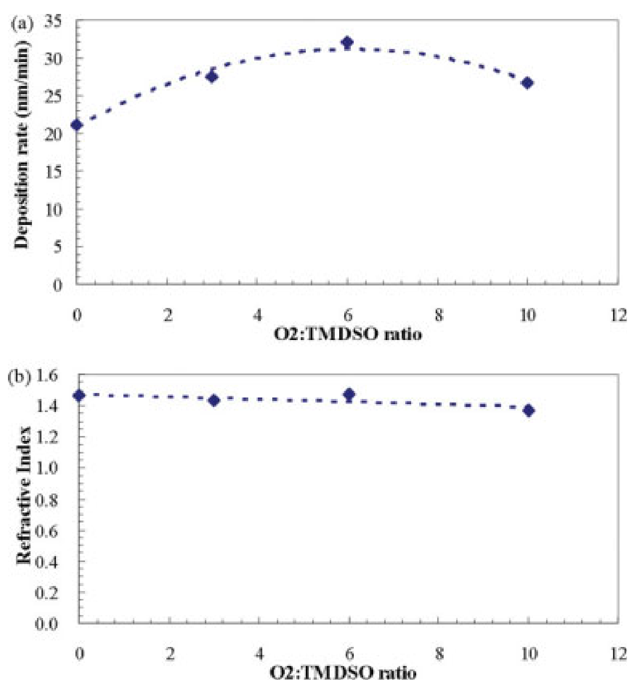

Figure 6 Change in the average deposition rate and refractive index of plasma-deposited SiOx coatings with different TMDSO–O_2 ratios used in the gas mixture for plasma deposition. Plasma conditions: 1-sccm TMDSO, 30 mTorr of pressure, 40 W of RF power input, and 25-min deposition time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

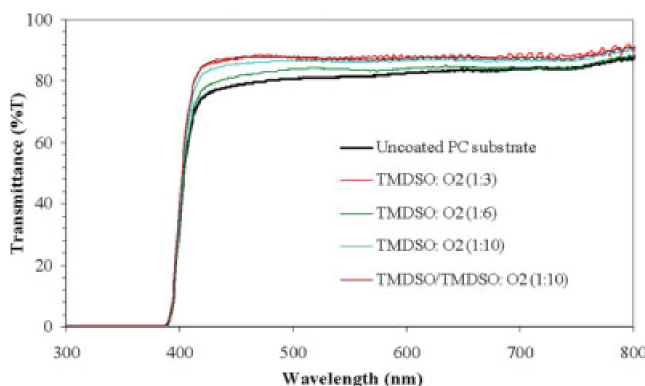

Figure 7 UV–vis transmission spectra of SiOx plasma coatings deposited on PC substrates from gas mixtures with different TMDSO–O_2 ratios. Plasma conditions: 1-sccm TMDSO, 30 mTorr of pressure, 40-W RF power input, and 25-min deposition time. The coating thicknesses were in the range 0.66–0.79 μm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

a hard and transparent film on the PC substrates. With increasing oxygen addition in plasma deposition, the deposition rate increased initially and then leveled off. The refractive indices of the plasma-deposited SiOx on the PC substrates were maintained around 1.4–1.5 with increasing oxygen addition. The deposition rate increased with more oxygen addition. However, an excessive amount oxygen could have diluted the TMDSO concentration in the gas mixture and, thus, reduced the deposition rate of the resulting SiOx plasma coatings.

Because the transparency of protective coatings is essential to the advanced plastic development for optical applications, UV–vis transmission analysis of the plasma-deposited SiOx on PC substrates was conducted in this study. Figure 7 presents the UV–vis transmission spectra of the plasma-deposited SiOx coatings with different TMDSO–O_2 ratios. The resulting SiOx plasma coatings were colorless and had greater than 80% light transmission in the visible light region, as measured on the PC substrates. As a result, UV–vis transmission analysis evidently confirmed that the plasma-deposited SiOx coatings

TABLE I
Hardness Change in the Resulting SiOx Plasma Coatings with Different TMDSO–O_2 Ratios of the Gas Mixture Used in the Low-Temperature Plasma-Deposition Process

	TMDSO/O_2 ratio				
	Reference	1 : 3	1 : 6	1 : 10	1 : 10 (with interlayer)
PC substrate	6B<	H	4H	H	H

Plasma conditions: 1-sccm TMDSO; 3-, 6-, and 10-sccm O_2; 30 mTorr of pressure; and 40-W RF power input.

TABLE II
Dry Tape Test Results for the Plasma-Deposited SiOx Coatings on the PC Substrates

	TMDSO–O_2 ratio for the plasma deposition of SiO			
TMDSO–O_2 ratio	1 : 3	1 : 6	1 : 10	1 : 10 (with interlayer)
Tape test rating	4B	5B	5B	5B

Plasma conditions: 1-sccm TMDSO; 3-, 6-, and 10-sccm O_2; 30 mTorr of pressure; and 40-W RF power input.

had excellent transparency. In addition, the hardness of the plasma-deposited SiOx on the PC substrate improved above 1H from the pencil hardness method, as shown in Table I. Moreover, a 1 : 6 (TMDSO–O_2) ratio was found to further enhance the hardness to 4H; this corresponded to the highest intensity of the Si—O absorption peak observed from the FTIR–ATR spectra (as shown in Fig. 5). This indicates that the relevance between Si—O groups and the hardness of the resulting SiOx plasma coatings on plastic substrates.

To improve the adhesion of the SiOx plasma coatings on the PC substrates, an interfacial plasma thin layer from a pure TMDSO precursor was deposited onto the PC substrate before SiOx plasma coating deposition. Typical plasma conditions for such plasma interlayer deposition were 1-sccm TMDSO, 30 mTorr, 40 W, and 1 min. The dry-tape test results are summarized in Table II. The adhesion of the plasma-deposited SiOx coating on the PC substrates was excellent, with ratings of 4B to 5B according to the ASTM tape test method. Compared to the dry-tape test results, however, the wet-tape test results of the plasma-deposited SiOx coatings on PC

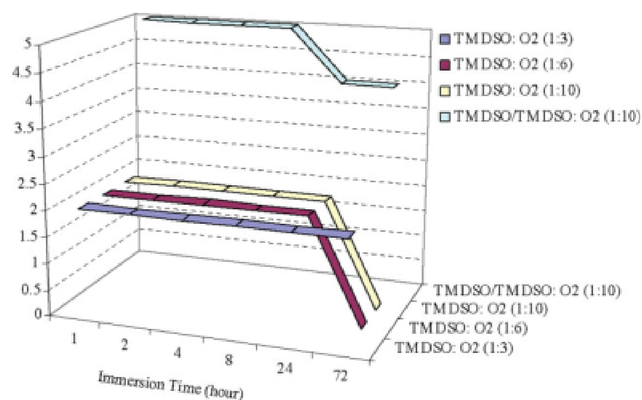

Figure 8 Change in the tape test ratings of the SiOx plasma coatings deposited on PC substrates from gas mixtures with different immersion times of the test specimens in boiling water. Plasma conditions: 1-sccm TMDSO, 30 mTorr of pressure, 40 W of RF power input, and 25-min deposition time. The coating thicknesses were in the range 0.66–0.79 μm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

substrates are much less admirable, as shown in Figure 8. As anticipated, with a thin interface layer, the SiOx plasma coatings prepared with TMDSO–O_2 with a ratio of 1 : 10 had excellent wet adhesion with a rating of 4B after 72 h of hot-water immersion. This result indicates that the adhesion on the plasma-deposited SiOx hard coatings on the PC substrates was significantly improved and well controlled by the simple introduction of an ultrathin plasma interlayer through plasma deposition with the same plasma reactor setup with the same precursor. The plasma polymer layer acted as an adhesion promoter that was applied on the surface because the interfacial plasma thin layer from the pure TMDSO precursor had excellent film cohesive integrity because of its three-dimensional network structures and insolubility by various solvents.[12]

CONCLUSIONS

SiOx protective coatings were successfully produced on PC substrates with a TMDSO precursor with oxygen addition through a low-temperature deposition process. The resulting SiOx plasma coatings were hard and transparent in the visible light region. It was demonstrated that uniform SiOx plasma coatings were obtained on relatively large PC substrates. Also, the resulting SiOx plasma coating uniformity was closely related to the uniformity of plasma glow or luminous gas phases, as recently reported. FTIR–ATR analysis results show that the plasma-deposited SiOx coatings had inorganic features. The inferior interface adhesion, which is a common problem in the deposition of hard coatings on plastic glasses, was significantly improved by the deposition of an ultrathin plasma polymer layer with the same TMDSO precursor with the same reactor setup as used for the deposition of the SiOx plasma coatings. Therefore, we concluded that low-temperature plasma deposition is a promising technique for the production of protective hard coatings on plastic materials, especially because of its simplicity and suitability to a large-scale substrate size for industrial needs.

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