Modification of Wettability of a Stainless-Steel Plate by Cathodic Plasma Polymerization of Trimethylsilane–Oxygen Mixtures

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SYNOPSIS

Wettability (by water) of a stainless-steel plate was modified by depositing an ultrathin layer of a plasma polymer of trimethylsilane (TMS) and an oxygen mixture. Plasma polymerization was carried out by cathodic glow discharge polymerization, in which a substrate stainless-steel plate was used as the cathode of the dc glow discharge. The plasma polymer of TMS (oxygen mol fraction = 0) is very hydrophobic, but the addition of oxygen in the monomer mixture increased the hydrophilicity of the plasma polymer. The value of cos θ (θ: advancing contact angle of water) linearly increased with the mol fraction of oxygen in the monomer mixture. Oxygen in the monomer mixture acts as (1) an ablating agent of a carbon-based plasma polymer and (2) a comonomer for a silicon-based plasma polymer. The atomic composition of a plasma polymer, which can be expressed as SiC_xO_y, changes (x decreases and y increases) as the mol fraction of oxygen increases. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The modification of surface characteristics of a metal by glow discharge plasma polymerization is generally carried out in a polarity alternating discharge [e.g., audio frequency (AF) and radio frequency (RF) regardless of the factor of whether or not the metal is placed on an electrode surface.[1,2] The deposition of a plasma polymer occurs predominantly on the cathode surface in a dc glow discharge.[3] Although this could be a distinctive advantage of dc plasma polymerization in the surface modification of a metal, the cathodic plasma polymerization, which utilizes a metallic substrate as the cathode of a dc glow discharge, has not been explored because of some difficulty associated with a dc glow discharge, e.g., sparking at low pressure and an oily product at elevated pressure.[4] In so far as plasma polymerization is concerned, a dc glow discharge has been nearly abandoned since the early investigations.[3,4]

The preferential deposition of plasma polymer onto the cathode surface in a dc glow discharge is a serious drawback in the treatment of dielectric materials such as polymers, glasses, and ceramics, in which a substrate is placed in between electrodes, because the cathode will be covered by a plasma polymer and the glow discharge will eventually extinguish. However, for the treatment of a metal surface, it provides an ideal situation in which the deposition of plasma polymer occurs nearly exclusively onto the substrate surface, which is the main product.

The plasma treatment of a metal surface often plays an important role in an adhesive joint[5] and in paint adhesion.[6] Furthermore, there seems to exist a general trend that the adhesion of a plasma polymer on a metal surface is highly dependent on the mode of plasma polymerization and that the adhesion follows a trend: (dc cathodic polymerization) > (AF magnetron glow discharge polymerization) ≫ (RF glow discharge polymerization).

In recent studies[7,8] dealing with the mechanisms of bubble formation from a single-hole orifice plate immersed in water, a necessity arose to change the contact angle of water on the orifice plate, which

has a laser-drilled hole with a precise size and geometry, without changing the orifice parameters. The cathodic polymerization is obviously an ideal candidate process to achieve such a task. In this article, data is presented that illustrate how the cathodic polymerization was performed and how the surface energy of the stainless-steel orifice plate was modified.

EXPERIMENTAL

The substrate used was a 314 stainless-steel plate (6 × 6 in.). Trimethylsilane (TMS) was purchased from Petrarch and used as received. The O_2 used was at least 99.9% pure.

The plasma treatment of the stainless-steel panel (6 × 6 in.) was carried in a glass bell jar-type reactor. The plasma was generated and maintained by an MDX-1K magnetron power supply. Two stainless-steel plates (10 × 10 × $\frac{1}{16}$ in.) used as anodes were 6 in. apart. The cathode, the stainless-steel sample, was placed in the midway between the two parallel anodes.

The stainless-steel panel was first cleaned thoroughly with organic solvent. Before the plasma polymer deposition, the panel was treated with an oxygen plasma as the final cleaning. The treatment conditions were an O_2 flow rate of 2 sccm, dc power of 10 W, pressure of 50 mTorr, and plasma treatment time of 2 min. After the oxygen plasma pretreatment, the TMS or TMS–oxygen mixture plasma was used for the polymer deposition. The total flow rate of the TMS–oxygen mixture was kept at 2 sccm. The other deposition conditions were 50 mTorr, 20 W, and 1 min.

The electron spectroscopy for chemical analysis (ESCA) was performed on a Perkin-Elmer 5300 ESCA system at Armco Research & Technology and deconvoluted with a proprietary software available in the VISION workstation. The water-contact angle of the plasma-polymerized TMS thin film was measured on a KERNCO goniometer Model G-1. Before the measurement, the plasma-polymerized TMS was first stored in the air for 2 h after the film deposition.

RESULTS AND DISCUSSION

Cathodic Plasma Polymerization in dc Glow Discharge

The plasma polymer coating used in this study was carried out in a dc discharge system with a metal substrate as the cathode. Sparking has been known to be one of inherent problems of dc glow discharge. It was observed in this study, however, that the sparking took place only at beginning of the plasma treatment. For the oxygen plasma pretreatment, severe sparking occurred only in the initial period (e.g., the first 30 s), which depended on the preexisting surface condition, and only occasional sparking took place in the remaining period of the treatment.

The extent of sparking is much less if the metal surface had been cleaned properly. A similar trend was found in the plasma polymer deposition, except that the period of sparking is much shorter, normally within 5 s, and there was no occasional aftersparking. Figure 1 shows typical discharge characteristics of TMS deposition, and each spike (voltage drop) represents a sparking. Besides the self-termination of the sparking, the film deposition is a self-healing process. The film damage caused by the early sparking is recovered by a later deposition. Thus, a plasma-polymerized thin film with adequate properties can be prepared by cathodic plasma polymerization.

Effect of Oxygen in TMS–O_2 Mixture on the Surface Characteristics

The influence of the oxygen content in the TMS/oxygen monomer on the water contact angle of plasma polymerized TMS (pp-TMS) thin film is shown Figure 2. The addition of oxygen in the monomer mixture decreases the contact angle of the plasma-polymerized film. The advancing contact angle of water decreases with increasing amount of oxygen in the monomer mixture. When no oxygen is added or the oxygen concentration in the monomer mixture is low, the film of pp-TMS is very hydrophobic. At a high oxygen concentration, the surface of pp-TMS becomes hydrophilic.

Figures 2 and 3 explain how the pp-TMS film was transformed from hydrophobic to hydrophilic. The C(1s) spectra (Fig. 3) evolved toward high binding energy states and the Si(2p) spectra (Fig. 4) also gradually shifted to high binding states as the amount of added oxygen increased.

The C — C state dominated the C(1s) spectra when no oxygen or a small amount of oxygen was added [Fig. 3(a) and (b)]. When the mol fraction of oxygen was higher than 0.4, the C — O state became the dominant peak accompanied by small amounts of the other binding states [Fig. 3(c)]. The C — C state disappeared when the mol fraction of oxygen was higher than 0.6 [Fig. 3(d)]. Further increases in the mol fraction of oxygen showed only marginal changes in the spectra [Fig. 3(e)].
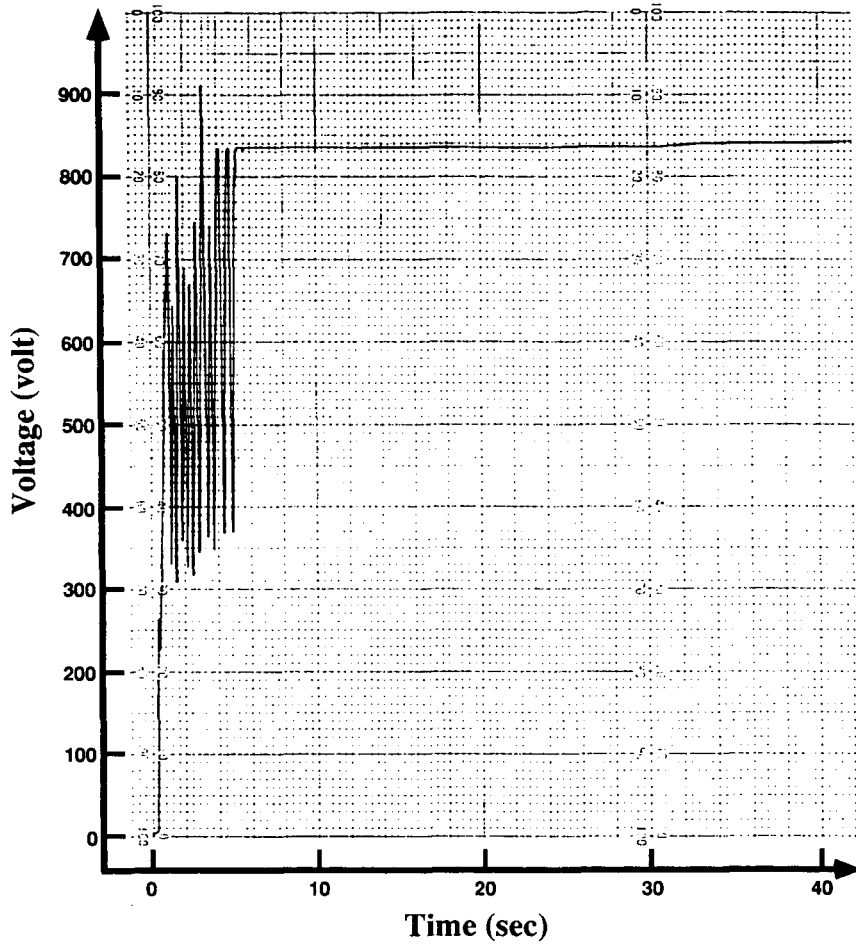
Figure 1   Typical discharge voltage–time relationships for the dc glow discharge of TMS (a steel plate as cathode).
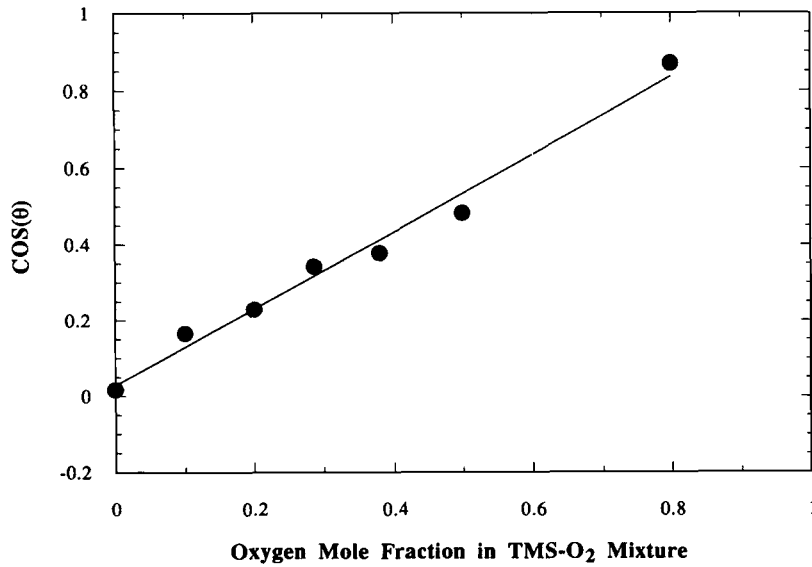

Oxygen Mole Fraction in TMS-O$_2$ Mixture

Figure 2   Water-contact angles of pp-TMS thin films as a function of the oxygen mol fraction in the TMS–oxygen monomer mixture. θ is the advancing contact angle of water. The flow rate of the TMS-O$_2$ mixtures were kept at 2 sccm and the other deposition conditions were 50 mTorr, 20 W, and 1 min.
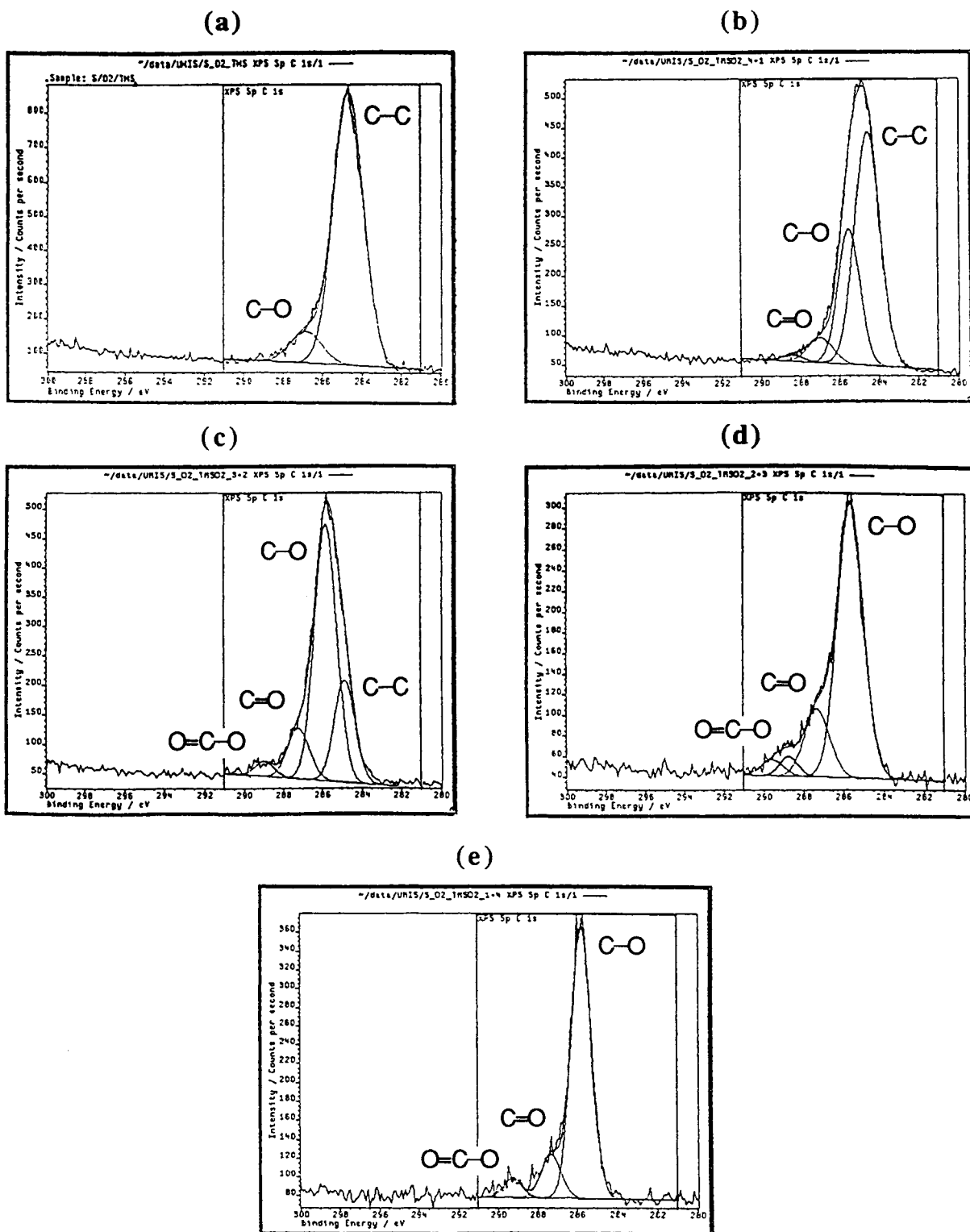
(a)

(b)

(c)

(d)

(e)

Figure 3 Evolution of C(1s) XPS spectra of pp-TMS deposited at an oxygen mol fraction of (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, and (e) 0.8 in the TMS–O₂ monomer mixture.
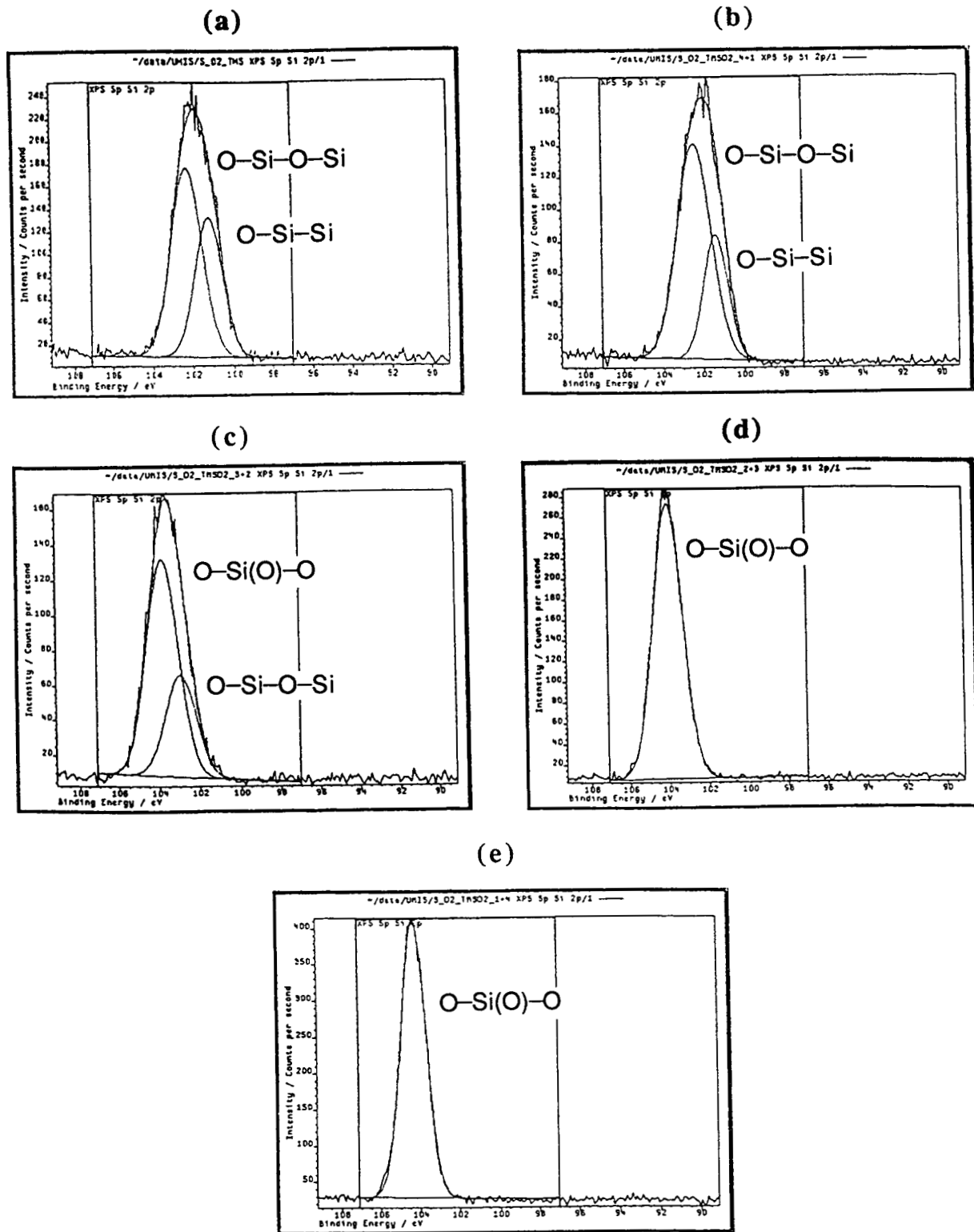
(a)

(b)

(c)

(d)

(e)

Figure 4   Evolution of Si(2p) XPS spectra of pp-TMS deposited at an oxygen mol fraction of (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, and (e) 0.8 in the TMS–O_2 monomer mixture.

As shown in Figure 4, the Si(2p) spectra were dominated by the O—Si—O—Si state with some O—Si—Si (or O—Si—C) at no oxygen or when a small amount of oxygen was added [Fig. 4(a) and (b)]. The O—Si—Si (or O—Si—C) state disappeared and the spectra were dominated by the O—Si(O)—O state when the mol fraction of oxygen was higher than 0.4 [Fig. 4(c)]. When the mol fraction of oxygen was higher than 0.6 [Fig. 4(d) and (e)], the O—Si(O)—O state became the only peak in the spectra.

Effect of Oxygen Content in the Monomer Mixture on the Atomic Composition of Plasma Polymers

The atomic composition of plasma polymers of the TMS-O_2 mixture can be expressed in terms of x and y in the general composition SiC_xO_y. Table I illuminates the influence of the mol fraction of oxygen in the monomer mixture on the chemical composition of the plasma polymers. The value of x remains above 3.0 up to the mol fraction of oxygen 0.4, but decreases sharply above 0.4. This is in accordance with the critical oxygen mol fraction where the C—C state disappeared. The value of y, on the other hand, increases abruptly when the mol fraction of oxygen increases above 0.2. This threshold mol fraction of oxygen is also in accordance with the critical mol fraction of oxygen where the O—Si—Si disappeared and O—Si(O)—O became dominant.

From Figures 3 and 4 and Table I, it appears that the addition of oxygen tends to remove carbon from silicon (in TMS) and plasma polymerization of silicon-based precursors and carbon-based precursors proceed simultaneously. The degree of oxidation of both components increases with the mol fraction of oxygen. At a low mol fraction range, the oxygen
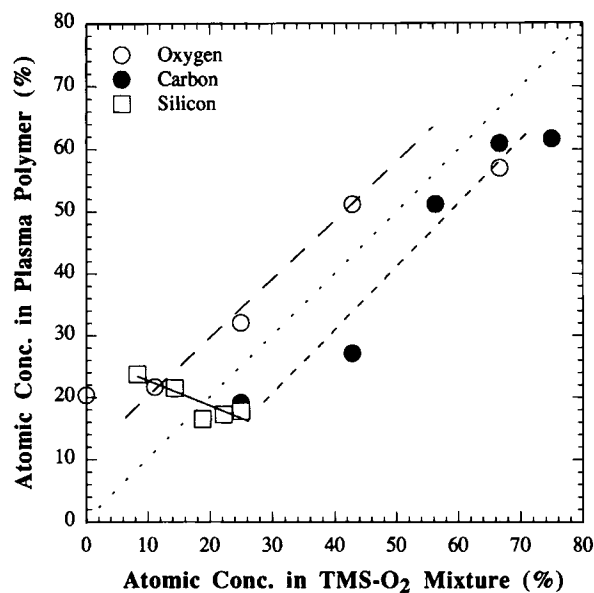

Figure 5   Elemental contents of pp-TMS as a function of the elemental concentrations of the TMS-O_2 monomer mixture.

seems to incorporate into the polymer film in terms of the partial oxidation of carbon and the siloxane linkage (and/or silanol). At a high mol fraction of oxygen (i.e., 0.4 or higher), it appears that the deposition of the carbon-based polymer was inhibited, whereas the silicon-based polymer becomes more of an inorganic nature.

To elucidate one interesting aspect of this TMS-O_2 mixture system, the chemical composition of the plasma-polymerized TMS was plotted as a function of the chemical composition of the monomer gases (Fig. 5). Figure 5 shows that the oxygen and carbon contents of the film increase with increasing concentration of the respective atoms in the monomer mixture. On the other hand, the silicon content in film decreases slowly with increasing silicon content in the monomer mixture.

The oxygen content in the plasma polymer shows a positive deviation at a low gas oxygen concentration and a negative deviation at a high gas oxygen concentration. The positive deviation of oxygen at a low oxygen content can be explained by the reaction of trapped free radicals with atmospheric oxygen after the surface is exposed to ambient air, which occurs more with carbon-based plasma polymers, which seems to agree with the other phenomena described above.

The adhesion of cathodic plasma polymers investigated in this study to the stainless-steel substrate was excellent, although no specific adhesion test has been performed. In the bubble formation

Table I   Influence of the Gas Oxygen Concentration on the Chemical Composition (SiC_xO_y) of pp-TMS Film Deposited in a dC Glow Discharge

Oxygen Mole Fraction	Atomic Ratio Si : C : O	x	y
0	1 : 3 : 0	3.46	1.14
0.2	1 : 3 : 2	3.52	1.25
0.4	1 : 3 : 5.33	3.09	1.94
0.6	1 : 3 : 12	1.26	2.37
0.8	1 : 3 : 32	0.81	2.40

study,[7,8] no sign of delamination was observed in contact with liquid water, which can be considered a severe adhesion test, and a plasma polymer layer had to be removed by sandpaper for the preparation of a different plasma polymer.

CONCLUSION

The surface energy of a metal surface can be modified by cathodic polymerization of a TMS and oxygen mixture. The plasma polymer of TMS with a mol fraction of oxygen of zero is hydrophobic. The addition of oxygen decreases the hydrophobicity and the surface becomes highly hydrophilic when the mol fraction of oxygen in the monomer mixture reaches roughly 0.8. Therefore, this monomer system can produce a surface with any desired contact angle of water by changing the mol fraction of oxygen.

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