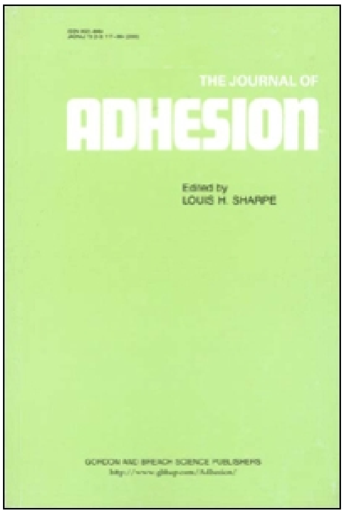

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Molecular structure of interfaces formed with plasma-polymerized silica-like primer films: Part I. Characterization of the primer/metal interface using infrared spectroscopy in SITU

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MOLECULAR STRUCTURE OF INTERFACES FORMED WITH PLASMA-POLYMERIZED SILICA-LIKE PRIMER FILMS: PART I. CHARACTERIZATION OF THE PRIMER/METAL INTERFACE USING INFRARED SPECTROSCOPY IN SITU

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Reflection-absorption infrared (RAIR) spectroscopy was performed in situ on plasma polymerized silica-like films that were deposited onto metal substrates. Relatively thick films (~8.0 nm) had infrared spectra that were typical of bulk amorphous silicon dioxide (a-SiO$_2$). When thinner films were analyzed (~0.6 nm), other infrared bands emerged that were due to the formation of silicon suboxide at the interface. Infrared bands due to oxidation of the substrate during deposition were also observed. It was determined that during the initial stages of plasma deposition, metal atoms from the substrate migrated to the metal-oxide surface. This resulted in preferential oxidation of metal atoms with the formation of silicon suboxide at the film/metal interface. In addition, interfacial suboxide formation was shown to have a dependence upon the diffusivity of the metal substrate atoms through the surface oxide of the metal. As a result, more interfacial suboxide was observed to form for depositions on titanium substrates in comparison with depositions on aluminum substrates.

Keywords: Plasma-polymerized films; Interfacial analysis; Suboxide; a-SiO$_2$ defects; In situ reflection-absorption infrared spectroscopy; Aluminum; Titanium

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INTRODUCTION

In recent years, plasma processing of materials as an adhesive bonding pretreatment has been shown to be a suitable alternative to aqueous-based pretreatments. In particular, amorphous silica-like (a-SiO_2) films, plasma polymerized from oxygen and hexamethyldisiloxane (HMDSO), have found use as successful alternatives for pretreating aluminum adherends. Epoxy adhesive joints fabricated from aluminum adherends that were pretreated with plasma-polymerized a-SiO_2 films were found to be very strong and durable when compared with adhesive joints that were prepared with conventional pretreatments [1, 2]. Durability testing showed that the interface between the plasma polymerized primer film and the aluminum substrate was very strong and environmentally stable [1–3]. The goal of this work is to characterize the molecular structure at the film/metal interface. A fundamental understanding of this interface would be beneficial, for instance, when applying these primer films to other metal or nonmetal substrates. By investigating depositions on aluminum and titanium substrates, the known properties of the substrate could be used to help understand how the molecular structure at the film/metal interface is formed during plasma polymerization.

There are several spectroscopic techniques that can be used to investigate buried interfaces. For instance, X-ray photoelectron spectroscopy (XPS) can be used to examine buried interfaces, provided that the overlayer is thin enough so that photoelectrons from the interface can escape for analysis (ca. < 5 nm). In addition, an ion beam can be used to sputter away surface material slowly and bring the interface into the detection range. However, damage to the molecular structure at the interface by the ion beam can limit the analysis to nothing more than an elemental composition of the interface. Other ion beam-related techniques suffer from the same difficulty to various degrees. One alternative to these methods is to use reflection-absorption infrared (RAIR) spectroscopy to investigate films that range in thickness from tens of nanometers to a few molecular layers. As the thickness of the film is decreased, the intensities of features in the spectra due to the bulk film are reduced while the spectral features characteristic of the interface increase. This technique has been applied here for investigating the film/substrate interface for plasma-polymerized films on metal substrates. In addition, this technique has been used for investigating the polymer/metal interface formed between metal substrates and adhesives [4].

The investigation of the interface for plasma-polymerized films on metal substrates introduces an interesting challenge. As thinner films are analyzed, the effects of surface contaminants from atmospheric exposure become an erroneous part of the spectral interpretation. Therefore, film preparation and analysis must be carried out in a contaminant-free environment. By applying the RAIR technique to a substrate while it is processed in the vacuum chamber of the plasma reactor, thin films can be deposited and analyzed in situ without environmental exposure and contamination. By analyzing a series of films with decreasing thickness, the spectral features due to the film/metal interface will emerge as the absorptions due to the bulk overlayer are reduced. Additionally, the RAIR experiment has an enhanced surface sensitivity, making it particularly well suited for analyzing ultrathin films.

Grundmeier and Stratmann constructed a capacitively coupled plasma reactor that was connected to an infrared spectrometer for studying plasma-polymerized (HMDSO) and hexamethyldisilazane on steel substrates [5]. By carrying out their studies in situ, they were able to analyze monolayer films and identify interfacial molecular structures without atmospheric contamination or hydration.

In Part I of this work, a specially built plasma reactor that enables films to be deposited and analyzed in situ with RAIR was utilized. With this analysis technique, the molecular structures at the film/metal interface for plasma-polymerized a-SiO_2 films on various metal substrates were characterized. Analysis of the film/metal interface using XPS in situ and durability testing of the film/metal interface will be reported in Parts II and III of this work, respectively.

EXPERIMENTAL

The in situ RAIR sample preparation and analysis system that was used consisted of a custom built 13.56 MHz inductively coupled RF-powered plasma reactor, which was interfaced directly to a Nicolet Magna^{TM} 760 Fourier transform infrared (FTIR) spectrometer. A diagram of the reactor is shown in Figure 1. The plasma reactor was constructed using a six-inch (15.2 cm) diameter stainless steel chamber with several ports for the plasma applicator, a mirror-mount sample holder, monomer inlets, vacuum, and the incident and reflected infrared beams. The plasma applicator was constructed by wrapping a copper induction coil around the exterior of a glass envelope. In order to prevent stray RF radiation, both the induction coil and glass envelope were contained inside an aluminum cylinder. The RF power generator output was connected to the copper induction coil using an automatic matching network designed for inductively coupled loads.

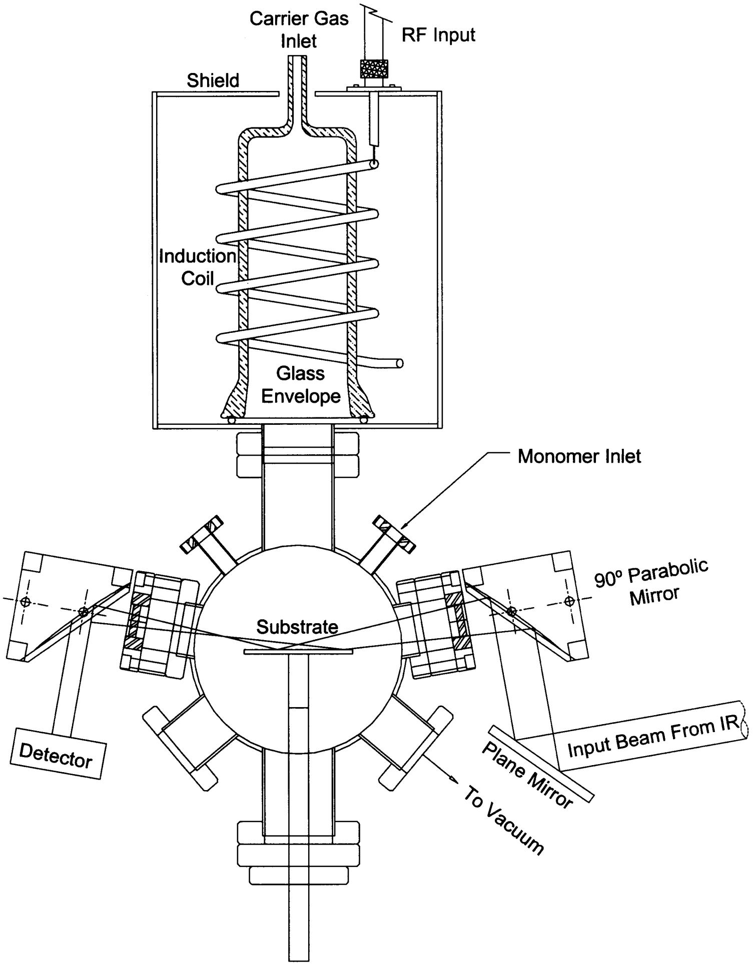

FIGURE 1 Diagram of the in situ plasma reactor interfaced to the infrared spectrometer.

An auxiliary beam from the infrared spectrometer was focused onto a substrate in the sample holder to have an incident angle of 80° between the beam and the normal axis of the substrate. Flat and off-axis parabolic mirrors were used to orient and focus the incident beam onto the sample, respectively. The incident and reflected infrared beams were passed through the vacuum chamber using zinc selenide (ZnSe) windows. Stainless steel shutters that could be opened and closed were constructed to protect the windows during plasma etching and deposition. An off-axis elliptical mirror was used to focus the output beam onto a liquid-nitrogen-cooled mercury cadmium telluride (MCT-A) detector, obtained from Nicolet. The infrared beam paths to and from the reactor chamber were purged with dry nitrogen gas. All spectra were obtained by averaging multiple scans at a resolution of 4 cm^{-1}.

Aluminum and titanium substrates (14 mm × 14 mm) were cut from 2024-T3 and Ti-6Al-4V sheet (ca. 2 mm thick), respectively. Samples were rough polished with 600-grit silicon carbide polishing paper and water. The rough polished samples were then polished to a mirror finish by using 6 μm and then 1 μm diamond polishing compounds. After diamond polishing, the samples were rinsed in reagent-grade toluene several times and then blown dry with a stream of nitrogen gas.

A substrate was mounted on the mirror-mount sample holder in the vacuum chamber of the plasma reactor. The substrate was plasma etched for 5 min at 100 W RF power using 50 standard cm^3/min (SCCM) of oxygen and 100 mTorr pressure. After plasma etching, the RF power was turned off and the background infrared spectrum was collected at 50 SCCM oxygen flow and 100 mTorr pressure. A plasma-polymerized a-SiO_2 film was then deposited from HMDSO with oxygen as a coreactant. Films were deposited for various deposition times at 50 Watts RF power using 50 SCCM oxygen and 0.3 SCCM HMDSO at a pressure of 100 mTorr After a few minutes of purging with oxygen at 100 mTorr, the sample infrared spectrum was obtained under 50 SCCM oxygen flow and 100 mTorr pressure.

Optical properties of the substrates and films were obtained ex situ using ellipsometry in order to determine film thickness. Immediately after deposition, the films were analyzed using a variable angle spectroscopic ellipsometer (VASE™) from J. A. Woollam Co. Δ and Ψ values were collected at 10 nm intervals in the spectral range 300−1200 nm and from 65° to 80° angle of incidence at 5° intervals. A computer program, WVASE™, was used to calculate the thickness of the films by performing a least squares fitting of the measured Δ and Ψ values to a model that used optical constants for SiO_2 [6].

RESULTS AND DISCUSSION

Aluminum Substrates

Using ellipsometry, the thickness of a film deposited for 4 min on aluminum was determined to be 2.5 nm, corresponding to a deposition rate of ca. 0.6 nm/min. At this deposition rate, a 30-s deposition resulted in an a-SiO_2 film that was approximately one monolayer in thickness, i.e., ~0.3 nm [7]. Films that were deposited for durations shorter than 30 s had less than one monolayer of Si-O-Si with patchy or incomplete surface coverage.

The RAIR spectrum of an a-SiO_2 film that was deposited onto an aluminum substrate for 4 min is shown in Figure 2. The Si-O-Si infrared absorption bands for this film were very similar to those of thermally grown a-SiO_2 [8, 9]. The film deposited for 4 min had infrared bands that were identical to those of much thicker films, also plasma polymerized from oxygen and HMDSO [1, 9]. The sharp feature at 3740 cm^{-1} in the spectrum shown in Figure 2 was due to O-H stretching of isolated silanol groups on the surface of the film [10–12]. Hydroxyl groups that were hydrogen bonded gave rise to the O-H stretching band around 3500 cm^{-1}. The broadness of the O-H band at 3500 cm^{-1} resulted from the geometrical distribution of various hydrogen-bonding arrangements for hydroxyl groups within the a-SiO_2 network [13]. The band at 3500 cm^{-1} also had a slight shoulder near 3650 cm^{-1} due to O-H stretching of surface silanol groups that were not isolated on the surface of the film but interacted with other silanol groups adjacent to them [13]. Another peak, also related to hydroxyl groups, was detected near 940 cm^{-1}. This peak was due Si-O stretching of nonbridging siloxane groups, as in Si-OH [7, 13].

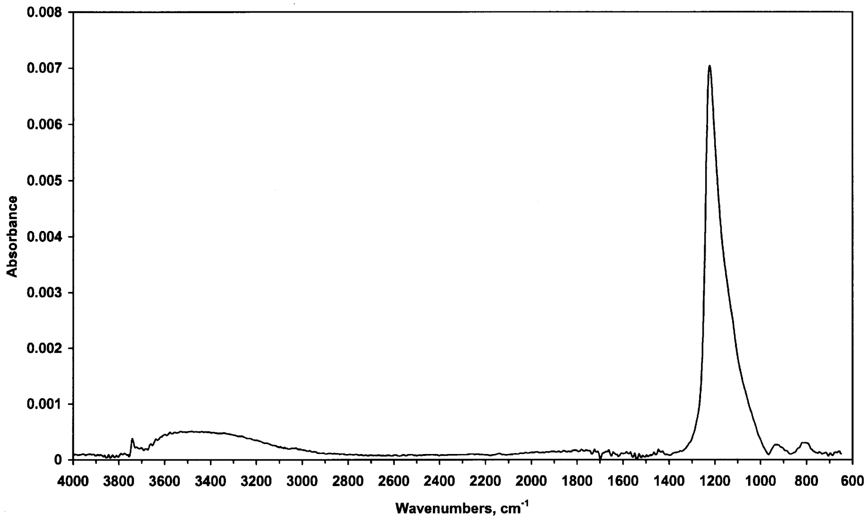

FIGURE 2 In situ RAIR spectrum of a plasma-polymerized a-SiO_2 film deposited onto an aluminum substrate for 4 min. The film was deposited with 50 Watts RF power at 100 mTorr using 50 SCCM oxygen and 0.3 SCCM HMDSO.

The strong peak near 1230 cm^{-1} and the small peak near 820 cm^{-1} were assigned to the longitudinal optical (LO) vibration modes for asymmetric stretching and bending of the bridging oxygen atoms between adjacent silicon atoms (Si-O-Si), respectively [8, 9]. Since the standing electric field in RAIR was perpendicular to the surface of the film, it strongly coupled with LO vibration modes. The transverse optical (TO) vibration modes for Si-O-Si groups were suppressed since electric fields cannot exist parallel or adjacent to the surface of the metal substrate [14].

Figure 3 shows the infrared spectra for films that were deposited onto aluminum substrates for a range of deposition times. Figures 4 and 5 show the enlarged 2000 cm^{-1} to 600 cm^{-1} and 4000 cm^{-1} to 2000 cm^{-1} regions of Figure 3, respectively. Reducing the deposition time reduced the film thickness and resulted in an overall decrease in the intensity of all infrared absorption bands due to the bulk. For films that were deposited for less than 1 min in duration, the Si-O-Si stretching band at 1230 cm^{-1} decreased in intensity and a new band appeared near 1090 cm^{-1}. This new band near 1090 cm^{-1} was attributed to a different molecular structure within the a-SiO_2 film,

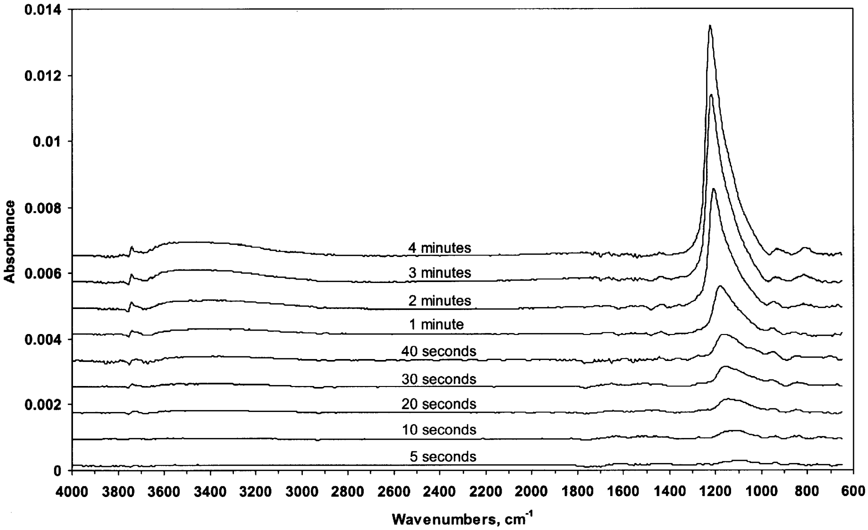

FIGURE 3 In situ RAIR spectra of plasma-polymerized a-SiO_2 films deposited onto aluminum substrates. The films were deposited for the indicated times with 50 Watts RF power at 100 mTorr using 50 SCCM oxygen and 0.3 SCCM HMDSO.

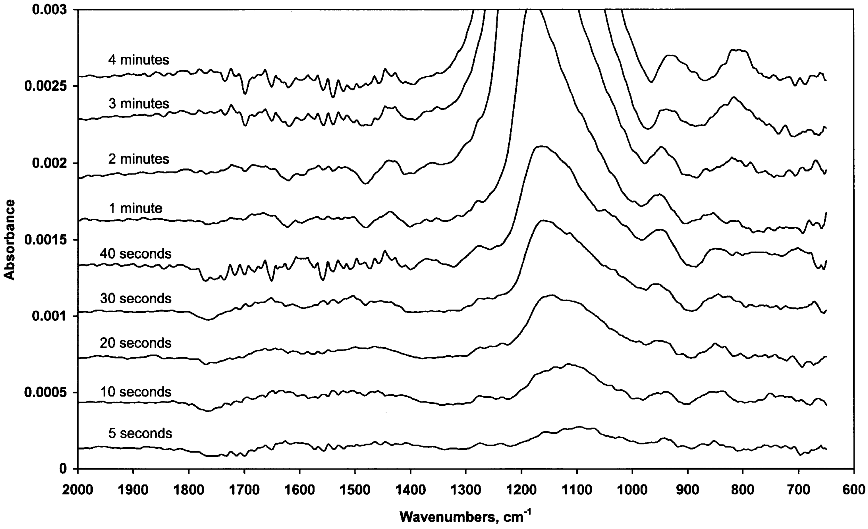

FIGURE 4 In situ RAIR spectra of plasma-polymerized a-SiO_2 films deposited onto aluminum substrates. Expanded view of the 2000 cm^{-1} to 600 cm^{-1} region of Figure 3.

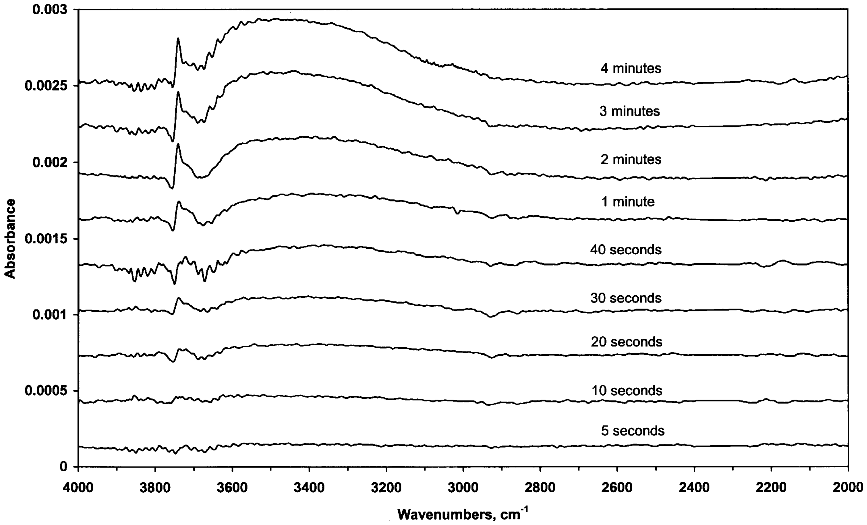

FIGURE 5 In situ RAIR spectra of plasma-polymerized a-SiO_2 films deposited onto aluminum substrates. Expanded view of the 4000 cm^{-1} to 2000 cm^{-1} region of Figure 3.

and since the band appeared to intensify with decreasing film thickness, this species was located at the film/metal interface.

The band at 1090 cm^{-1} was due to Si-O-Si groups that had adjacent defects within the a-SiO_2 network at the film/metal interface. These adjacent defects were nonbridging network defects that had a lack of coordinating oxygen atoms about the silicon atoms. Silicon atoms that have fewer than four coordinating oxygen atoms are known as suboxides [15]. Amorphous silicon dioxide that has been synthesized with suboxide defects has a Si-O-Si asymmetric stretching band with a lower frequency than that of defect-free a-SiO_2. The decrease in stretching frequency of a Si-O-Si group occurs due to the lack of charge withdrawal from the bridging oxygen atoms coordinated with the silicon atoms. Several authors have shown that the Si-O-Si asymmetric stretching band has a linear decrease in frequency with the stoichiometry, x, of SiO_x [15–19].

It has also been shown that the position of the Si-O-Si asymmetric stretching band is related to the interbond angle of Si-O-Si groups in thermally grown a-SiO_2 that have residual strain in the oxide [20]. However, Koller et al. have indicated that relatively thin a-SiO_2 films ($<$ 250 nm) produced with low-temperature plasma deposition ($< 100^\circ C$) are essentially strain free [21]. This would be especially true for this work, since these films were deposited at essentially room temperature, and the low wavenumber peak at 1090 cm^{-1} appeared for films that were only a few nanometers thick.

Figure 4 shows that the band due to Si-O-Si bending at 820 cm^{-1} reduced in intensity with decreasing film thickness and disappeared for depositions less than 1 min in duration. A new band appeared near 860 cm^{-1} due to the LO vibration mode of Al-O [22, 23] and indicated that oxidation of the aluminum substrate occurred during the deposition process.

Figure 4 also shows that a weak band near 1290 cm^{-1} appeared for depositions on aluminum shorter than 1 min, and was due the stretching mode of Si-C groups [8]. The presence of this band indicated that some of the organic groups of the monomer were either unoxidized or that some of the oxidized carbon from the monomer re-reacted with the film during deposition to form Si-C groups. Since the band at 1290 cm^{-1} appeared to increase in intensity with decreasing film thickness, the Si-C groups were located at the film/metal interface. In addition, this band may have been obscured for spectra of longer depositions by the high wavenumber base of the Si-O-Si LO band near 1230 cm^{-1}.

Figure 4 shows that the Si-O nonbridging band, initially near 940 cm^{-1}, for 4- and 3-min depositions, shifted to 955 cm^{-1} for depositions under 3 min. This band, due to nonbridging Si-O groups such as Si-OH, should have corresponded with the intensity of the SiO-H stretching bands at 3740 cm^{-1} and near 3500 cm^{-1}. However, Figure 5 shows that, although the intensity of the SiO-H band near 3500 cm^{-1} decreased in intensity with decreasing film thickness, the correlating Si-O band near 940 cm^{-1} did not. Instead, when no bands due to SiO-H near 3740 cm^{-1} and 3500 cm^{-1} were observed for the 5- and 10-s depositions, the nonbridging Si-O band, having shifted to 955 cm^{-1}, was still present.

One explanation for the increase in stretching frequency of the Si-O nonbridging band from 940 cm^{-1} to 960 cm^{-1}, with the absence of SiO-H bands at 3740 cm^{-1} and 3500 cm^{-1}, is dehydrogenation of SiOH groups, resulting in a Si-O ion. Removal of the terminating hydrogen atom from a SiOH group would slightly increase the stretching frequency of the Si-O bond and at the same time result in the disappearance of the bands due to O-H stretching. Another possible structure that would explain the above observations is a peroxy bridge (SiO-OSi). Electron spin resonance (ESR) studies have shown that peroxy bridges commonly form as defects within a-SiO_2 [22–25]. Although few infrared data exist for this species, the infrared Si-O stretching band for this particular network defect would be found at a higher frequency than that for Si-OH [26].

Suboxides in a-SiO_2 have been readily synthesized by plasma-polymerizing mixtures of SiH_4 and oxygen that were lean with respect to oxygen. In a study by Lucovsky et al., plasma-polymerized films of SiO_xH_y were prepared from $SiH_4/O_2/H_2$ mixtures and then analyzed using infrared spectroscopy [15]. Their work showed that, with decreasing oxygen content, the TO vibration mode of the Si-O-Si asymmetric stretching band shifted from 1030 cm^{-1} to 980 cm^{-1}. This decrease in Si-O-Si stretching frequency resulted from the incorporation of Si-H groups into the Si-O-Si network, thereby reducing the number of coordinating oxygen atoms with silicon atoms. For this work, no evidence of Si-H was observed due to the absence of a peak resulting from Si-H stretching in the 2250–2100 cm^{-1} regions of the infrared spectra (see Figure 5). Thus, it was unlikely that silicon suboxide at the film/metal interface occurred due to the formation of Si-H groups. Silicon suboxide due to the formation of Si-C at the film/metal interface may have occurred, since a weak band near 1290 cm^{-1}, due to Si-C stretching, was observed. However, since Si-C has a relatively high infrared activity, i.e., small amounts of Si-C give rise to large absorptions, and the relatively weak intensity of the band at 1290 cm^{-1} did not correlate well with the relatively strong suboxide band near 1090 cm^{-1}, the formation of a Si-C suboxide at the film/metal interface may have contributed to only part of the overall suboxide concentration.

The suboxide at the film/metal interface more likely occurred due to the formation of Si-Si bonds or by the formation of oxygen vacancy defects within the a-SiO_2 network [15, 27]. The formation of these species within the a-SiO_2 network would result in suboxides of silicon and decrease the stretching frequency of adjacent Si-O-Si groups to 1090 cm^{-1}. Shallenberger observed Si-Si bonding in the bulk of plasma-polymerized a-SiO_2 films that contained suboxide defects [27]. They indicated that a material having a microstructural mixture of Si-Si and a-SiO_2 would be thermodynamically more favorable than a high density of suboxide dispersed in an a-SiO_2 network. In addition, Lucovsky et al. have observed the formation of Si-Si bonds in the bulk of plasma deposited films [15].

Although a-SiO_2 can be plasma polymerized to contain bulk suboxide defects, this study has shown that they have formed preferentially at the film/metal interface. Silicon suboxide formation at the a-SiO_2/metal interface was also observed by Brendel and Hezel [22]. They used infrared spectroscopy to study a-SiO_2 films that had thin films of aluminum deposited onto an a-SiO_2 surface. Their results indicated that silicon suboxides formed along with aluminum oxide at the a-SiO_2/aluminum interface during thermal annealing. It was shown that a reduction reaction occurred, which depleted the oxygen from the adjacent a-SiO_2 layer in order to oxidize the aluminum at the a-SiO_2/aluminum interface. In a similar study by Bauer et al., the same reduction/oxidation phenomenon was observed to occur at the a-SiO_2/aluminum interface when studied by XPS [28]. They observed an increase in the intensity of the Al^{+3} oxide peak and a reduction in the intensity of the metallic Al^0 peak, which indicated that the oxidation of the aluminum layer occurred at the a-SiO_2 interface. The oxidation of the aluminum proceeded by reducing a-SiO_2, which left a-SiO_x ($x < 2$) and excess Si at the interface. The reduction reaction was driven by the free energy of formation for the aluminum oxide, which is strong enough to reduce a-SiO_2 [29, 30].

Undoubtedly, the very same oxidation and reduction reactions have occurred at the plasma-polymerized a-SiO_2/aluminum interface, even though aluminum oxide was already present before deposition. However, in order for this work, the plasma promoted oxidation of the substrates to occur during deposition of the a-SiO_2 films. As monomer molecules were initially deposited onto the substrate, they competed for oxidation with metal substrate atoms, and full oxidation of the adjacent silicon atoms did not occur. This was supported by the observation of the Al-O stretching peak at 860 cm^{-1}, which indicated that aluminum oxide formed during deposition. Further deposition of a-SiO_2 inhibited the defect layer from fully oxidizing or increasing in thickness.

TITANIUM SUBSTRATES

Because the substrate has a significant effect on the plasma-polymerized film, titanium substrates were also used. Titanium was selected because its naturally passivated oxide surface is different in many ways compared with aluminum substrates [31, 32]. For instance, the activation energy for titanium atom diffusion in titanium oxide is an order of magnitude less than that for diffusion of aluminum atoms in alumina [33]. In addition, the application of plasma-polymerized primer films as an alternative to aqueous pretreatments for promoting durable adhesive bonding of titanium adherends is of great interest.

Ellipsometry results indicated that the deposition rate was approximately 0.6 nm/min, the same as it was for depositions on aluminum. Figure 6 shows the RAIR spectra of a-SiO_2 films deposited on titanium substrates for various deposition times. Overall, the

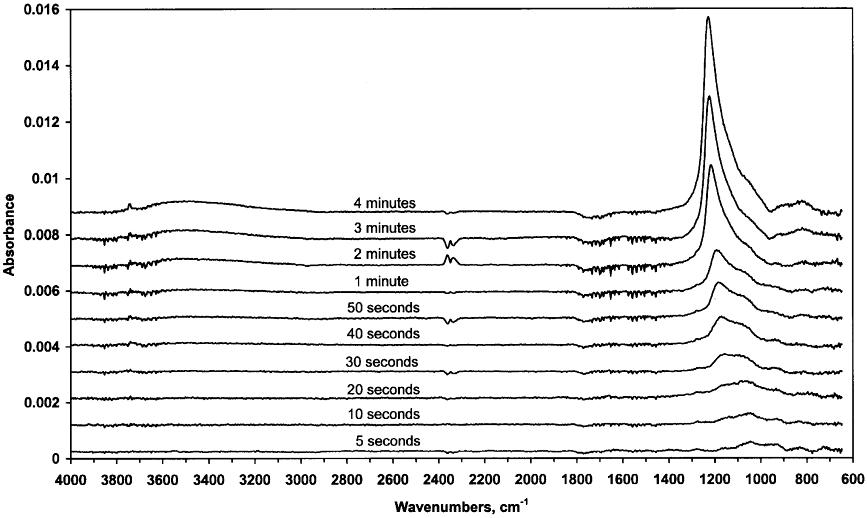

FIGURE 6 In situ RAIR spectra of plasma-polymerized a-SiO_2 films deposited onto titanium substrates. The films were deposited for the indicated times with 50 Watts RF power at 100 mTorr using 50 SCCM oxygen and 0.3 SCCM HMDSO.

spectra looked similar to those obtained for equivalent depositions on aluminum substrates in Figure 3. However, the weak band at 3500 cm^{-1} indicated that depositions on titanium had comparatively fewer hydroxyl groups than the depositions on aluminum. In addition, the sharp band due to O-H stretching of isolated silanol groups at 3740 cm^{-1} was barely observed, unlike similar depositions on aluminum. Figures 7 and 8 show the enlarged 2000 cm^{-1} to 600 cm^{-1} and 4000 cm^{-1} to 2000 cm^{-1} regions of Figure 6, respectively. Figure 7 shows that both bands at 810 cm^{-1} and 945 cm^{-1}, which were observed for the shortest depositions on aluminum, were not very intense or well resolved, especially for short deposition times. However, the lack of intensity of the Si-O (nonbridging) band at 940 cm^{-1} was expected since the weak O-H band at 3500 cm^{-1} indicated there were few hydroxyl groups in the films. The spectra in Figure 7 also showed a weak feature near 1290 cm^{-1} due to Si-C for short depositions on titanium substrates, similar to the depositions on aluminum substrates. Most of the spectra in Figure 7 show a small peak at 930 cm^{-1}, especially for depositions less than 50 s in duration. The peak at 930 cm^{-1} has been assigned to the LO vibration mode of Ti-O bonds [34]. This peak indicated that, similar to the depositions on

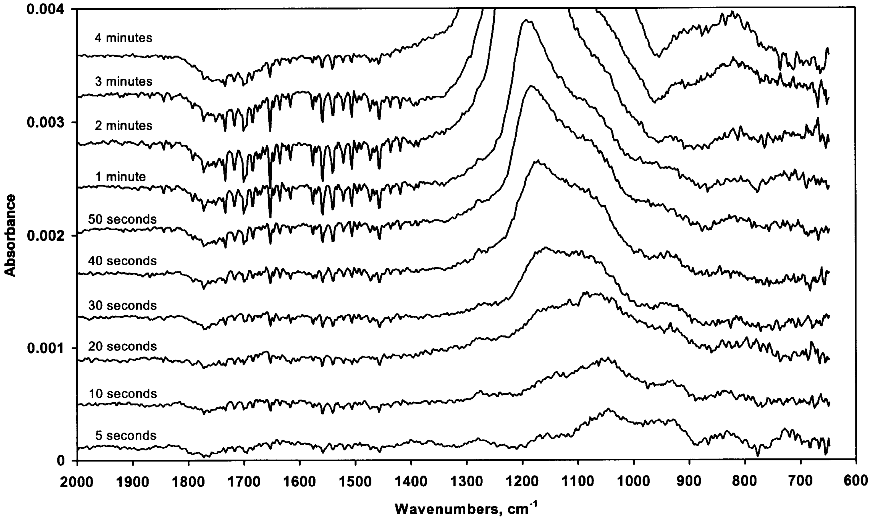

FIGURE 7 In situ RAIR spectra of plasma-polymerized a-SiO_2 films deposited onto titanium substrates. Expanded view of the 2000 cm^{-1} to 600 cm^{-1} region of Figure 6.

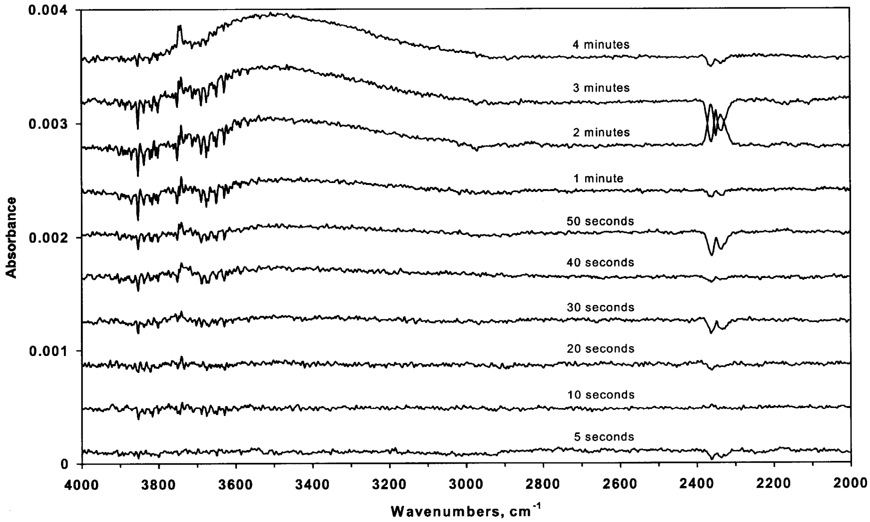

FIGURE 8 In situ RAIR spectra of plasma-polymerized a-SiO_2 films deposited onto titanium substrates. Expanded view of the 4000 cm^{-1} to 2000 cm^{-1} region of Figure 6.

aluminum, oxidation of the titanium substrates occurred during plasma deposition.

Overall, the most pronounced difference between depositions on aluminum and titanium substrates was that more suboxide was present (in the case of titanium) at the film/metal interface due to the much more intense band near 1090 cm^{-1}. The evolution of the suboxide formed at the film/metal interface was determined by plotting the curve-fit peak intensity of the band at 1090 cm^{-1} versus the film thickness for depositions on aluminum and titanium. Figure 9 shows that the intensity of the band at 1090 cm^{-1} due to the suboxide species initially increased with increasing film thickness and then leveled out at a maximum intensity for thicker films. This maximum intensity was substrate dependent, and was more intense for depositions on titanium substrates than for aluminum. Due to the difference in the maximum intensities of the suboxide bands, relatively thick films (e.g., > 0.6 nm) deposited on titanium substrates had approximately twice as much suboxide at the interface when compared with films deposited on aluminum substrates. When considering these results, the suboxide layer at the film/metal interface may have been located within a region of the same thickness on either substrate but with different suboxide densities, or the suboxide layers had similar densities on

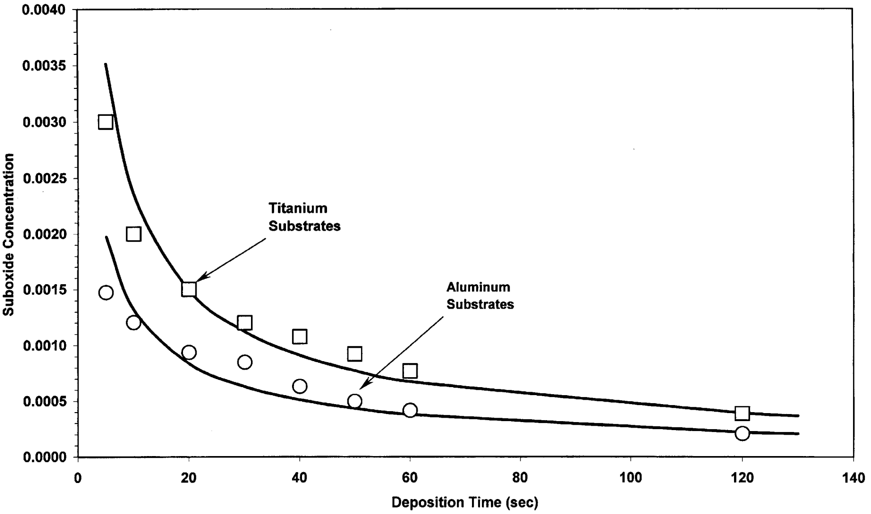

FIGURE 9 Plot showing the concentration of the suboxide species formed at the film/metal interface as a function of deposition time for plasma-polymerized films deposited onto aluminum and titanium substrates. The fitted lines were generated with Equation (1).

both substrates but different in thickness. In addition, unoxidized titanium atoms may have formed more suboxide than aluminum due to their higher valence.

By curve fitting the suboxide peak in the Si-O-Si stretching band and normalizing its absorbance to film thickness, the general concentration profile of suboxide can be plotted with deposition time [8]. Figure 9 shows the concentration of the suboxide band plotted for films of increasing thickness that were deposited on titanium and aluminum substrates. When assuming that the infrared adsorption coefficient for the suboxide species is substrate independent, approximately twice the concentration of suboxide was formed for depositions on titanium substrates compared with those on aluminum substrates. It is proposed here that the interfacial suboxide was formed due to the diffusion of metal atoms from the substrate to the film/metal interface and correspondingly the concentration profile should follow the diffusion-controlled oxidation rate equation for aluminum and titanium [35–39],

$$d = K \ln(t + 1), \qquad (1)$$

where d is the metal-oxide thickness, t is time, and K is a constant. Aluminum and titanium are typical metals that form thin passive oxide films (e.g., less than 100 nm) at low temperatures according to Equation (1), which is based on the theory that the rate-limiting step for logarithmic oxide growth is the electric field-assisted diffusion of atomic species across the oxide layer [36, 37]. By normalizing Equation (1) to the total film thickness of the plasma-polymerized films, the two solid-lined curves in Figure 9 were generated using $K = 0.98$ for depositions on titanium substrates and $K = 0.55$ for depositions on aluminum substrates. The experimental data followed the proposed model fairly well in support of the proposed mechanisms for interfacial suboxide formation.

The diffusivity of metal ions within the oxides of aluminum and titanium varied greatly and was responsible for the different amounts of suboxide formed on them. The activation energy values (E_a) for diffusion of aluminum and titanium ions in their respective oxides, Al_2O_3 and TiO_2, are 5.3 eV and 0.41 eV respectively [33]. Low activation energies for ion transport in oxides have been attributed to a high concentration of oxide defects and is a characteristic property of TiO_2, and to a much lesser degree Al_2O_3 [40, 41]. With regard to the current theory of passive oxide film formation, the application of the electrically charged plasma sheath assisted metal ion transport to the metal-oxide surface during deposition [36, 37]. Since diffusion of the titanium atoms to the a-SiO_2/titanium interface occurred with greater ease than for aluminum atoms diffusing to the a-SiO_2/aluminum-oxide interface, more suboxide was observed to occur at the a-SiO_2/titanium-oxide interface than at the a-SiO_2/aluminum-oxide interface.

CONCLUSIONS

In situ RAIR spectroscopy was a highly sensitive and very effective technique for analyzing thin films of plasma-deposited a-SiO_2 without atmospheric hydration or contamination. Thick films on aluminum and titanium showed infrared spectra characteristic of bulklike a-SiO_2. As the thickness of the films on aluminum and titanium substrates was reduced, bands due to the bulk film reduced in intensity, and a new band at 1090 cm^{-1} appeared due to the LO vibration mode of Si-O-Si groups having adjacent silicon suboxide defects within the a-SiO_2 network.

The formation of the interfacial suboxide at the film/metal interface was due to a plasma-assisted reduction/oxidation reaction of the initial monolayers of plasma-deposited film. Infrared bands due to Al-O and Ti-O stretching were detected at the a-SiO_2/metal interface for thin a-SiO_2 films deposited in situ. This indicated that metal atoms diffused to the oxide surface during plasma deposition and oxidized by reducing a-SiO_2 into silicon suboxide. This was assisted by the charged plasma sheath, which formed at the surfaces exposed to the plasma [42]. Since metal atoms diffused more readily through the titanium oxide than through aluminum oxide, more suboxide was formed at the a-SiO_2/titanium-oxide interface in comparison with the a-SiO_2/aluminum-oxide interface. Although some unoxidized Si-C was detected at the a-SiO_2/metal interface, the results of this work indicated that most of the suboxide species formed were not due to Si-C but to either oxidized Si-Si groups or oxygen vacancies within the a-SiO_2 network.

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