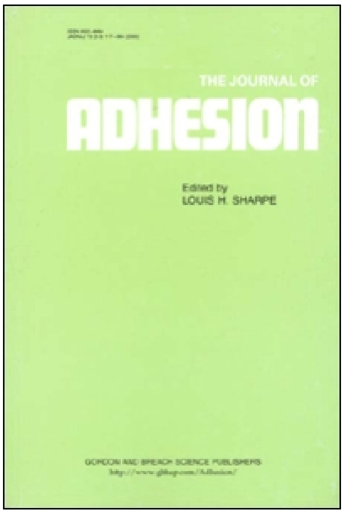

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Plasma Polymer Films as Adhesion Promoting Primers for Aluminum Substrates. Part I: Characterization of Films and Film/Substrate Interfaces

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Plasma Polymer Films as Adhesion Promoting Primers for Aluminum Substrates. Part I: Characterization of Films and Film/Substrate Interfaces

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Plasma-polymerized hexamethyldisiloxane (HMDSO) films (~800 Å in thickness) were deposited onto aluminum substrates (6111-T4 alloy) in radio frequency (RF) and microwave (MW) powered reactors to be used as primers for structural adhesive bonding. Processing variables such as substrate pre-treatment, carrier gas, and film post-treatment were adjusted to produce films that had different structures and properties. The plasma polymerized films were characterized by reflection-absorption infrared spectroscopy (RAIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and ellipsometry. Films deposited using argon as the carrier gas were siloxane-like. When siloxane-like films were post-treated with an oxygen plasma, a silica-like surface layer was produced. Silica-like films were deposited using oxygen as the carrier gas. Plasma polymerized silica-like films were formed of spheroidal particles deposited next to each other and impinging upon one another. These spheres were thought to be islands formed by the growth of stable nuclei. Etching aluminum substrates in argon and argon/hydrogen plasmas before deposition of the primer removed adsorbed water from the surface, possibly creating a more stable oxide surface to which the silica-like primer could bond. The effect of etching silica-like films in an Ar plasma was to promote the condensation of adjacent silanol groups to form Si—O—Si bonds but with little change in the film thickness or the concentration of isolated silanol groups.

Keywords: Plasma-polymerized films; plasma etching; hexamethyldisiloxane; silica-like films; reflection-absorption infrared spectroscopy; X-ray photoelectron spectroscopy; scanning electron microscopy; ellipsometry

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I. INTRODUCTION

Plasma etching and plasma polymerization are attractive processes for surface engineering. One reason for this is the degree of process control that is possible. Plasmas can be used to etch or clean substrates and even to introduce functional groups onto the surface of a substrate before deposition of a film. During plasma polymerization, processing variables can be manipulated to give films with a wide range of compositions. Post-deposition plasma etching can be used to modify the surface properties of a plasma-polymerized film while retaining the bulk properties. Plasma etching and plasma polymerization can be carried out in the same vacuum system or on the same production line, thus increasing efficiency and minimizing contamination between the cleaning and film deposition steps. However, some of the most important reasons for our interest in plasma processes for surface engineering are related to environmental considerations. Plasma etching and plasma polymerization are dry, gas-phase processes that are carried out in vacuum at pressures (0.5 to 1.0 Torr) that are easily obtained in commercial operations and they do not result in the production of liquid wastes such as chromates which are expensive to dispose of properly.

Plasma-polymerized films show promise as protective coatings for metals and polymers [1, 2]. Specifically, plasma-polymerized films of silicon-containing monomers have been shown to be pinhole free, chemically resistant, and highly adherent [3–5]. Organic plasma polymers deposited from hexamethyldisiloxane have been shown to provide carbon steel with corrosion resistance to salt water environments comparable with that provided by conventional polytetrafluoroethylene films [1]. Wear-resistant silicon oxide films have been deposited from silane and oxygen onto brass and steel. The coated substrates performed well in Taber wear tests whereas brass and steel substrates that were not coated exhibited severe abrasion when tested in a similar manner [2].

Several investigators have considered the effect of plasma etching of metal substrates on the formation of plasma-polymerized films on the substrates and on the adhesion and corrosion resistance of the films. Exposing silicon wafers to an argon/hydrogen plasma was shown to promote the growth of smooth sputtered titanium films. The argon/

hydrogen plasma removed carbon from the wafer surface. Ion bombardment did not play a large role in the pre-treatment process [6]. Brande *et al.* [7] investigated the effect of plasma pre-treatment of steel substrates on the growth mechanisms of plasma-deposited amorphous carbon films. Films grown on steel treated with an argon/hydrogen plasma formed by a layer-by-layer growth mode, whereas films grown on untreated steel formed a discontinuous layer of islands. Once again, the argon/hydrogen pre-treatment was thought to remove hydrocarbon contamination completely from the steel substrate and promote continuous film growth. Long pre-treatment times were found to remove oxygen completely from the steel surface and allow the formation of some iron carbide during deposition of amorphous carbon films. Complete removal of the oxide layer was not necessary to obtain layer-by-layer film growth. Amorphous carbon films deposited onto plasma-etched steel were found to form a protective barrier against the oxidation of the steel.

The goal of this research is to develop a plasma treatment process consisting of plasma etching or cleaning followed by the deposition of a plasma-polymerized primer film for structural adhesive bonding of aluminum. Argon and argon/hydrogen plasmas were used to etch aluminum substrates before plasma polymerization. Plasma-polymerized primers were deposited using hexamethyldisiloxane (HMDSO) as the monomer and argon or oxygen as a carrier gas. In some cases, the plasma-polymerized films were post-treated with either an oxygen or an argon plasma. The primers were characterized using X-ray photoelectron spectroscopy (XPS), reflection-absorption infrared spectroscopy (RAIR), ellipsometry, and scanning electron microscopy (SEM). In this paper, we will discuss the characterization of the plasma-polymerized films. In the subsequent paper, we will present the results of mechanical tests conducted to evaluate the plasma-polymerized films as primers for adhesive bonding of aluminum.

II. EXPERIMENTAL

A. Substrate Preparation

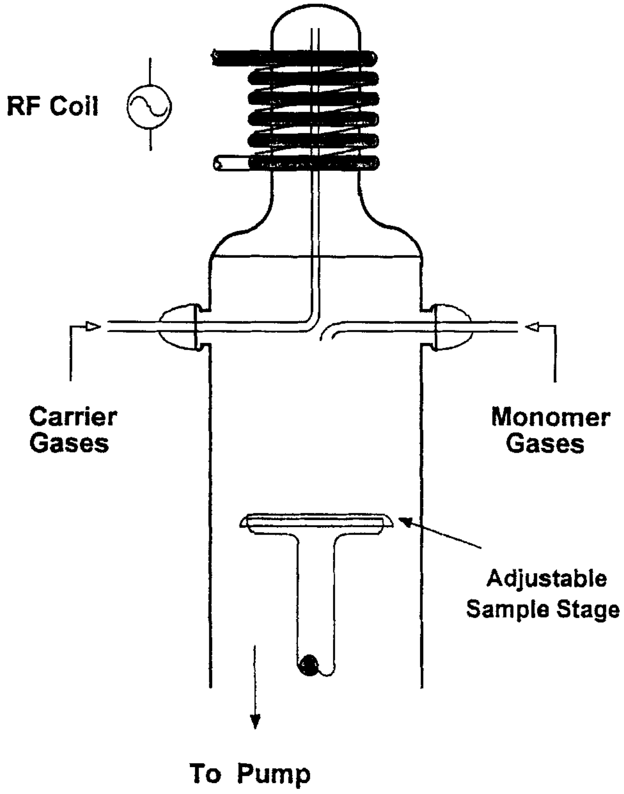
Aluminum substrates (6111-T4 alloy) having a thickness of 2.0 mm, were degreased by wiping with Kimwipes soaked in acetone and then cleaned ultrasonically in acetone for 15 minutes. The aluminum coupons were rinsed a final time with fresh acetone and blown dry with nitrogen.

Since aluminum substrates with a mirror finish were needed for RAIR and ellipsometry, some coupons were mechanically polished. First, abrasive grinding was done with 600 and 1000 grit silicon carbide paper. The coupons were then polished with aluminum oxide slurries of decreasing particle size (14.5 and 3.0 μm). A slurry of 3.0 μm magnesium oxide particles was used for the final polishing step. The coupons were rinsed in distilled deionized water between polishing steps.

Some coupons were etched at 80°C in a solution of 18.4 g of chromium trioxide and 86.4 ml of sulfuric acid in 500 g of distilled deionized water. An aluminum coupon, which had been cleaned with acetone, was placed in the acid solution for 15 minutes. It was then removed, rinsed with distilled deionized water for up to 15 minutes and blown dry with nitrogen.

B. Plasma Etching and Plasma Polymerization

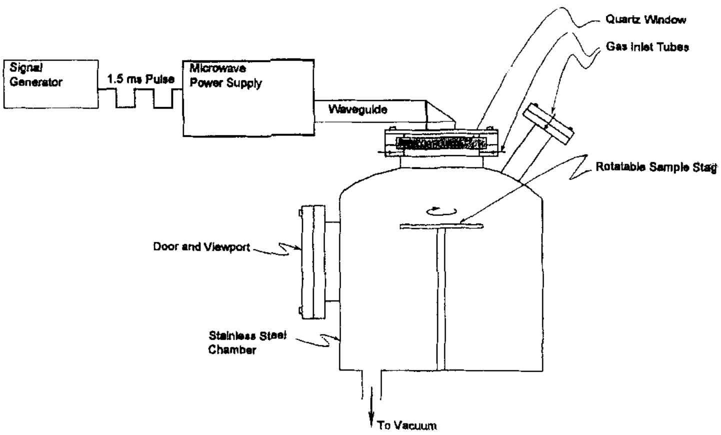
Plasma etching and plasma polymerization were carried out in an inductively-coupled radio-frequency (RF) reactor and in a microwave (MW) reactor (see Fig. 1). The operation of the RF reactor has been discussed in detail elsewhere [8]. Etching gases and carrier gases were introduced into the reactor at a point above the RF coil. Monomer was introduced below the coil. Samples were placed on a stage located downstream from the monomer insertion port and the active plasma. All substrates prepared in the RF reactor were pre-treated in an Ar plasma before deposition of plasma-polymerized films. Several different types of films were considered. Plasma-polymerized siloxane-like films were deposited using HMDSO as the monomer and Ar as the carrier gas. In some investigations, siloxane-like films were post-treated with an oxygen plasma to form films that had siloxane-like bulk properties but silica-like surface properties. Silica-like films were deposited using HMDSO as the monomer and oxygen as the carrier gas. Table I lists the processing parameters used in the operation of the RF reactor.



(A)

FIGURE 1 Schematic drawings of the (A) – RF and (B) – MW reactors.

The MW reactor was also operated in a downstream configuration (see Fig. 1). Carrier or etching gases were introduced into the reactor from ports just below the quartz window. Monomer was introduced from a port just above the sample stage, which could be rotated at several revolutions per minute. Argon and argon/hydrogen plasmas were used to etch the surfaces of aluminum substrates before deposition of plasma-polymerized films. In a few cases, argon plasmas were also used to etch the surfaces of plasma-polymerized films. Silica-like films were deposited in the MW reactor using oxygen as a carrier gas. However, a small amount of argon was needed to ignite the



(B)

FIGURE 1 (Continued).

TABLE I Processing parameters used for plasma etching and plasma polymerization in the RF and MW reactors

Reactor	*Process*	*Gas Flow Rates(sccm)*	*Pressure (Torr)*	*Power (Watts)*	*Time (Min.)*
RF	Ar Etch	Ar: 20	1	20	10
RF	Siloxane Deposition	Ar:150 HMDSO: 0.5	1	20	10
RE	O_2 Etch	O_2 : 25	0.5	100	10
RF	Silica-like Deposition	O_2 : 20 HMDSO: 0.5	0.5	50	10
MW	Ar Etch	Ar: 20	0.5	200	10
MW	Silica-like Deposition	Ar :5 O_2: 45 HMDSO: 0.2	0.5	200	10
MW	Ar + H_2 Etch	Ar: 5 H_2: 20	0.5	200	10

plasma. Reactor parameters used for etching and deposition in the MW reactor are also summarized in Table I.

C. Characterization

The approximate thickness of plasma-polymerized films deposited on polished aluminum substrates was determined using a Rudolph

Research 436 ellipsometer. Values of the parameters Δ and Ψ were measured before and after film deposition. A computer program developed by McCrackin [9] was used to calculate the thickness and refractive index of the films from the observed values of Δ and Ψ.

Infrared spectra were obtained using a Perkin-Elmer 1800 Fourier-transform infrared spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) detector. RAIR spectra were obtained at an angle of incidence equal to 78° using an external reflection accessory from Harrick Scientific. Each RAIR spectrum was an average of at least 128 scans; 256 scans were averaged for films less than 50 Å in thickness. The RAIR spectra reported here are actually difference spectra obtained by subtracting spectra of polished aluminum substrates from spectra of polished aluminum substrates coated with plasma-polymerized films. Spectra were taken from 4000 cm^{-1} to 450 cm^{-1} at a resolution of 4 cm^{-1}.

XPS spectra of aluminum substrates and plasma-polymerized films deposited on aluminum substrates were obtained using a Physical Electronics 5300 X-ray photoelectron spectrometer. Mg $K\alpha$ radiation at a power of 300 Watts was used to excite the spectra. Most spectra were obtained at a take-off angle of 45°. The take-off angle was defined as the angle between the sample surface and the optical axis of the analyzer. Some spectra were also obtained at take-off angles of 15° and 75°, resulting in smaller or larger sampling depths, respectively, than for a take-off angle of 45°. High-resolution (multiplex) spectra were corrected for charging by referencing the C(1s) peak for saturated hydrocarbons to a binding energy of 284.6 eV. Curve fitting was accomplished using software provided by Perkin-Elmer.

SEM micrographs of the plasma polymer surfaces were obtained on a Cambridge scanning electron microscope at a magnification of 25,000. The electron acceleration voltage was 25 kV.

III. RESULTS AND DISCUSSION

A. IR Characterization of Plasma Polymerized Films

The transmission infrared spectrum of HMDSO monomer is shown in Figure 2. A very strong band near 1058 cm^{-1} was assigned to the

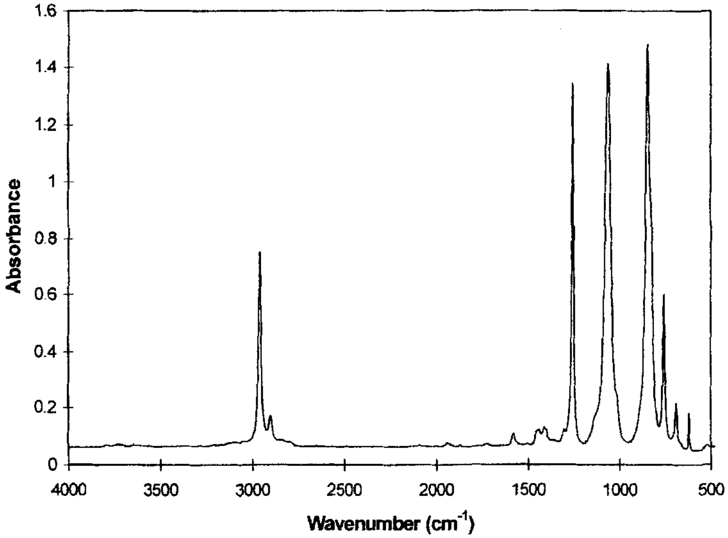


FIGURE 2 Transmission IR spectrum of the monomer HMDSO.

Si—O—Si asymmetric stretching vibration while the weak band near 522 cm^{-1} was attributed to the symmetric Si—O—Si stretching mode. Peaks due to methyl asymmetric and symmetric stretching were observed near 2959 and 2901 cm^{-1}, respectively. Bands due to asymmetric and symmetric stretching of Si—C groups were seen near 688 and 620 cm^{-1}, respectively. The position of bands due to methyl rocking, near 844 and 756 cm^{-1}, was characteristic of three methyl groups bonded to each silicon atom [10–12].

RAIR spectra of four different plasma-polymerized films deposited onto polished aluminum substrates are shown in Figure 3. The spectrum of a siloxane-like film deposited in the RF reactor using Ar as a carrier gas is shown in Figure 3(A). The intense band near 1065 cm^{-1} was assigned to the Si—O—Si asymmetric stretching vibration of a siloxane-like polymer while the band at 1259 cm^{-1} was assigned to deformation of Si—CH_3 groups. Bands near 847 and 805 cm^{-1} were assigned to a combination of Si—C stretching and methyl rocking for two methyl groups bonded to each Si [10, 11]. Since the monomer contained Si atoms with three methyl substituents, these peaks indicated that Si—C bonds were broken in the plasma. Peaks

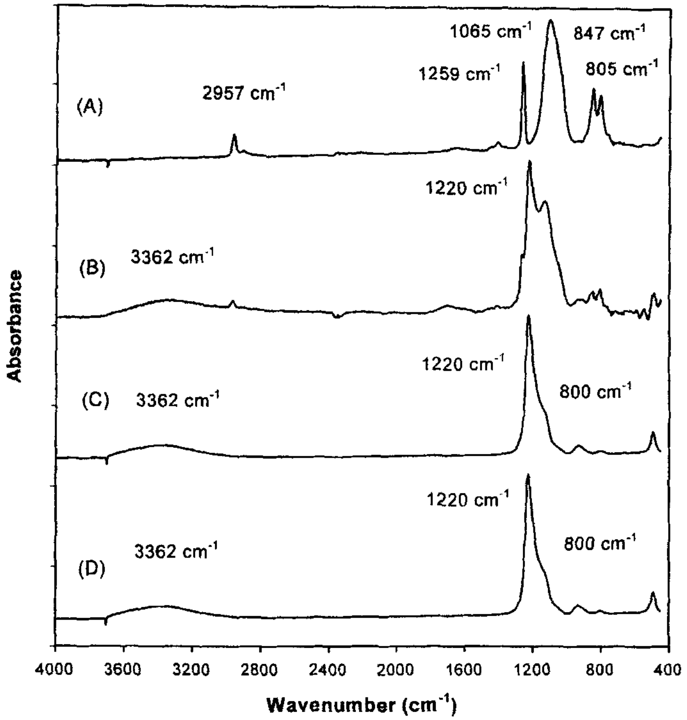


FIGURE 3 RAIR spectra of plasma-polymerized HMDSO films deposited on polished aluminum substrates: (A) – HMDSO deposited with Ar as a carrier gas in the RF reactor, (B) – HMDSO deposited with Ar as carrier gas and then etched in an O_2 plasma in the RF reactor, (C) – HMDSO deposited with O_2 as carrier gas in the RF reactor, and (D) – HMDSO deposited with O_2 as carrier in the MW reactor.

due to CH stretching in CH_3 groups were observed near 2957 and 2872 cm^{-1} while bands due to CH stretching in CH_2 groups were seen at 2902 and 2855 cm^{-1}. Bands related to asymmetric and symmetric deformation of CH_3 groups were seen at 1408 and 1378 cm^{-1}, respectively. Weak bands due to the stretching of Si—H bands and the deformation of Si—CH_2—Si groups were observed at 2120 and 1356 cm^{-1}, respectively, [11, 12]. Since Si—H and CH_2 groups were not present in the monomer, it was concluded that Si—C and C—H bonds were broken in the plasma, and that Si—H and Si—CH_2—Si groups were formed.

Etching a siloxane-like film in an O_2 plasma resulted in significant changes in the RAIR spectrum of the film (see Fig. 3(B)). Bands near 2955, 2902, 1259, and 844 cm^{-1}, which were assigned to carbon-containing functional groups, were greatly reduced in intensity. The peak related to Si—O—Si stretching in siloxane compounds was seen near 1088 cm^{-1}. A new, strong peak was observed near 1220 cm^{-1} and assigned to the longitudinal optical (LO) phonon mode of Si—O—Si linkages in silica-like structures. Bands due to silanol (SiOH) groups were observed near 3650, 3362, and 936 cm^{-1} [13]. The band near 3650 cm^{-1} was assigned to the OH stretching mode in silanol groups in which the hydrogen atom was hydrogen bonded to an oxygen atom in a siloxane (Si—O—Si) linkage, while the band near 3362 cm^{-1} was attributed to OH stretching in silanol groups where the hydrogen atom was hydrogen bonded to the oxygen atom of an adjacent silanol group. The band near 936 cm^{-1} was assigned to the Si—O stretching mode of the latter type of silanol groups. It was concluded that carbon-containing functional groups were preferentially etched, resulting in the formation of a silica-like layer at the surface of the siloxane-like film.

The RAIR spectra of plasma-polymerized HMDSO films deposited using O_2 as the carrier gas in the RF reactor and in the MW reactor are shown in Figures 3(C) and 3(D), respectively. These spectra were very similar. The band due to the LO phonon mode of Si—O—Si groups was seen at 1220 cm^{-1}. Bands due to Si—OH groups, as in the spectrum of the etched film, were observed at 3360 and 938 cm^{-1}. Bands due to CH_3, CH_2, or siloxane structures were not observed. When comparing the RAIR spectra of all four plasma polymerized films, the progression from siloxane-like films to silica-like films was easily discernible.

B. XPS Characterization of Plasma-polymerized Films

The XPS survey spectra of the same four plasma-polymerized HMDSO films are shown in Figure 4. In the spectrum of the siloxane-like film (see Fig. 4(A)), peaks due to carbon, oxygen and silicon were observed near 284.6, 533.7 and 101.5 eV, respectively [14, 15]. The relatively low value of the Si(2p) binding energy indicated

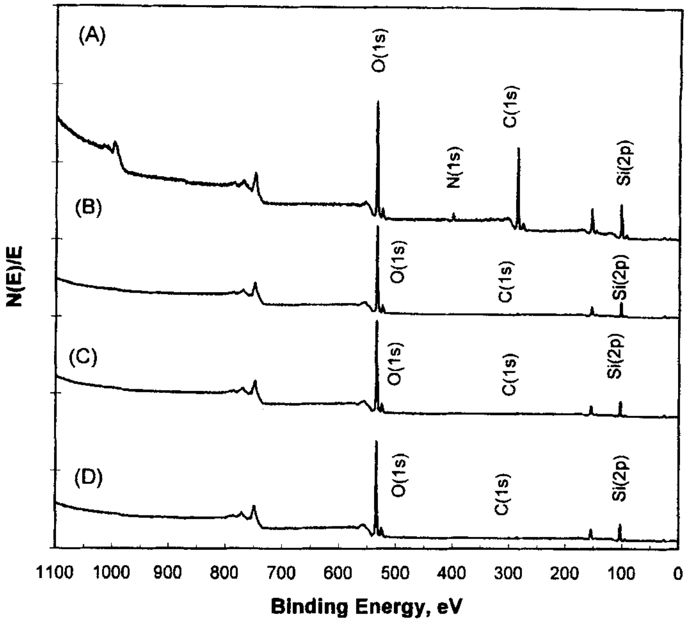


FIGURE 4 XPS survey spectra of plasma-polymerized HMDSO films deposited on aluminum substrates: (A) – HMDSO deposited with Ar as a carrier gas in the RF reactor, (B) – HMDSO deposited with Ar as carrier gas and then etched in an O_2 plasma in the RF reactor, (C) – HMDSO deposited with O_2 as carrier gas in the RF reactor, and (D) – HMDSO deposited with O_2 as carrier in the MW reactor.

that silicon was not highly oxidized and that the film was mostly siloxane-like. The surface consisted of 60.5% carbon, 17.0% oxygen and 22.5% silicon.

XPS survey spectra of the siloxane-like film that was post-treated in an O_2 plasma and of silica-like films deposited in the RF and MW reactors were very similar (see Figs. 4(B)–(D)). The intensity of the C(1s) peak near 284.6 eV was greatly reduced and the intensity of the oxygen peak was much stronger when compared with the corresponding peaks in the spectrum of the untreated siloxane-like film. The relatively high value of the Si(2p) binding energy, approximately 103.0 eV, indicated that silicon was extensively oxidized and that the surfaces of the films were silica-like [14]. No component characteristic of siloxanes was seen in the Si(2p) spectrum obtained from the siloxane primer that was etched in an O_2 plasma. The surface compositions of the siloxane-like film that was post-treated in an O_2

plasma and the silica-like films deposited in the RF and MW reactors were very similar.

C. Characterization of Plasma Pre-treatments and Thin Silica-like Films

Etching aluminum substrates in Ar or Ar/H_2 plasmas before deposition of plasma-polymerized primer films affects the strength of lap joints prepared from the substrates (see following paper). Therefore, RAIR was used to determine the effect that plasma etching of polished aluminum substrates had on the molecular structure of the interface between plasma-polymerized films and the substrates. In these investigations, silica-like films having a thickness of approximately 40 Å were deposited using HMDSO as the monomer, oxygen as the carrier gas, and a deposition time of thirty (30) seconds. Two important results were obtained. One was that there were more methyl groups near the interface than in the bulk of the films. The other was that plasma etching removed adsorbed water from the surface of the substrates.

RAIR spectra obtained from silica-like films deposited in the MW reactor for thirty seconds onto polished aluminum substrates that were not etched or were etched in an Ar or Ar/H_2 plasma for ten minutes before deposition of the films are shown in Figure 5. Bands due to vibrations of Si—O—Si groups were observed near 1220, 800, and 490 cm^{-1} while bands due to vibrations of silanol groups were seen near 3650, 3340, and 935 cm^{-1}. All three spectra shown in Figure 5 contained a peak near 1275 cm^{-1} that was assigned to Si—CH_3 deformations. Since this band was not observed in spectra of thicker films deposited using similar reactor parameters but longer deposition times, it was concluded that thin films were less oxidized and contained more methyl groups than did thick films.

A weak band was observed near 1625 cm^{-1} in the spectrum of the silica-like film that was deposited onto an aluminum substrate that was polished but not plasma etched (see Fig. 5). This band, which was assigned to vibrations of molecular water [10, 11], was not observed in the spectra of silica-like films that were deposited onto polished aluminum substrates that were etched in Ar or Ar/H_2 plasmas before

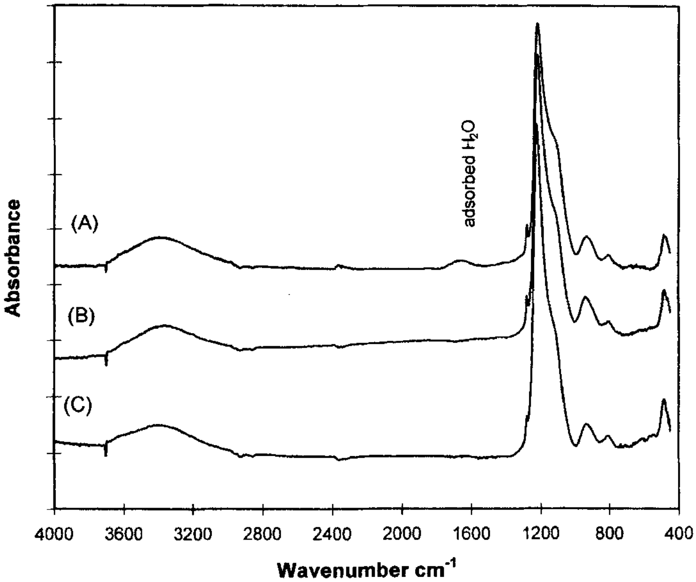


FIGURE 5 RAIR spectra of silica-like films deposited in the MW reactor for 30 seconds onto polished aluminum that was (A) – not etched in an Ar plasma, (B) – etched with an Ar plasma for 10 minutes, and (C) – etched with an Ar/H_2 plasma for 10 minutes.

deposition of the films. It was concluded that plasma etching before deposition removed adsorbed water from the surface of the polished aluminum substrates. No differences were observed between the spectra of films deposited onto polished aluminum substrates that were etched in Ar or Ar/H_2 plasmas before deposition.

D. Etching of Silica-like Films in Ar Plasmas

The effect of etching silica-like plasma-polymerized films in an Ar plasma was also investigated. RAIR spectra of a plasma-polymerized silica-like film deposited onto a polished aluminum substrate in the MW reactor and a similar silica-like film that had been etched with an Ar plasma after deposition are shown in Figure 6. A decrease in the intensity of the band near 3360 cm^{-1} due to SiO—H stretching and the band near 940 cm^{-1} due to non-bridging Si—O bonds was observed after etching. These observations are consistent with the assignment of the band near 3360 cm^{-1} to silanol groups *that are*

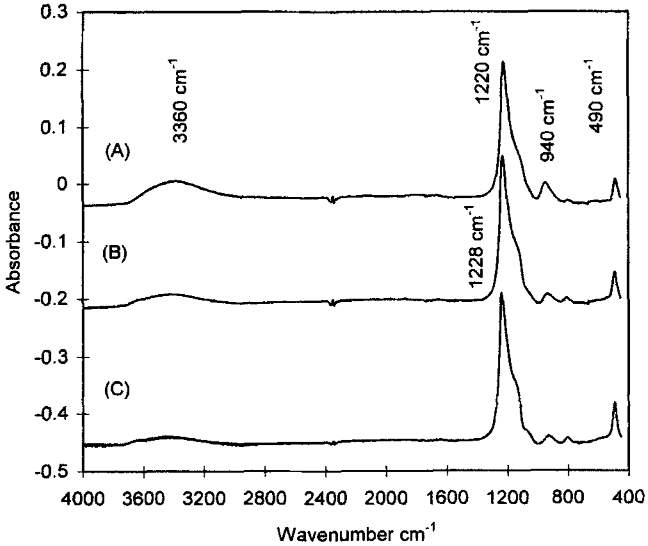


FIGURE 6 The RAIR spectra of a silica-like film deposited in the MW reactor onto polished aluminum that was etched in an Ar plasma: (A) – without post-deposition etching in an Ar plasma, (B) – after post-deposition etching in an Ar plasma, and (C) – after post-deposition etching in an Ar plasma and aging in air for 10 weeks. The film thickness was 958 Å.

hydrogen bonded to adjacent silanol groups and with the condensation of adjacent silanol groups to form Si—O—Si linkages during plasma etching. Additional support for the condensation of adjacent silanol groups was provided by the shift of the LO phonon mode of Si—O—Si groups from 1220 cm^{-1} before etching to 1228 cm^{-1} after etching. By comparison, the band near 3650 cm^{-1} did not change much in intensity, indicating that isolated silanol groups were not significantly affected by plasma etching.

Ellipsometry was used to measure the thickness of a silica-like film before and after etching in an Ar plasma. No significant change in the film thickness was observed. The main effect of etching in an Ar plasma was to promote the condensation of adjacent silanol groups to form Si—O—Si bonds. Other investigators studying the deposition of silicon oxide films from tetraethoxysilane (TEOS) and oxygen plasmas have examined the effect of ion bombardment on film composition [16]. Ion bombardment, which was produced by biasing the substrate, was found to induce condensation reactions in films containing a large number of Si—OH groups. This resulted in silicon oxide films that were somewhat more dense and harder than films that did not receive the ion bombardment treatment.

The effect of aging silica-like films that had been etched in an Ar plasma was also investigated (see Fig. 6(C)). After aging in air for 10 weeks, the Si—O—Si LO phonon mode shifted to even higher frequencies, from 1228 cm^{-1} to 1237 cm^{-1}. Thus, the condensation of silanol groups continued even after etching in an Ar plasma.

E. The Effect of Annealing Silica-like Films

The effect of annealing the plasma-polymerized silica-like films was investigated with RAIR and ellipsometry. RAIR spectra of a 735 Å film deposited onto polished aluminum before and after annealing at 180°C for 30 minutes are shown in Figure 7. This temperature and time were chosen to mimic the curing cycle of the automotive adhesive used for the stressed durability testing that is discussed in the following paper. After annealing, the peak assigned to the longitudinal optical phonon mode of Si—O—Si structures shifted from 1225 cm^{-1} to 1230 cm^{-1}. Peaks near 3360 and 930 cm^{-1}, which were related to silanol groups, decreased in intensity after annealing. As discussed above, this decrease in the concentration of silanol groups in the film was probably due to the thermally activated [16] condensation of adjacent silanol groups to form Si—O—Si linkages and release water. The increase in Si—O—Si bonds was observed in the shift of the LO phonon mode to higher wavenumbers. Annealing removed defects in the form of silanol groups from the silicon oxide films and formed more Si—O—Si bonds. However, annealing had little effect on the film thickness. The thickness of the as-deposited film was 735 Å while the thickness of the film after annealing was 720 Å.

Other investigators have used infrared spectroscopy to determine the effect of annealing on nonstoichiometric SiO_2 films deposited onto silicon wafers by chemical vapor deposition (CVD) [17]. When these films were annealed at 1000°C for 30 minutes in a nitrogen atmosphere, a shift toward higher frequencies of up to 25 cm^{-1} in the Si—O—Si asymmetric stretching band was observed. This shift was attributed to the formation of regions of stoichiometric silicon

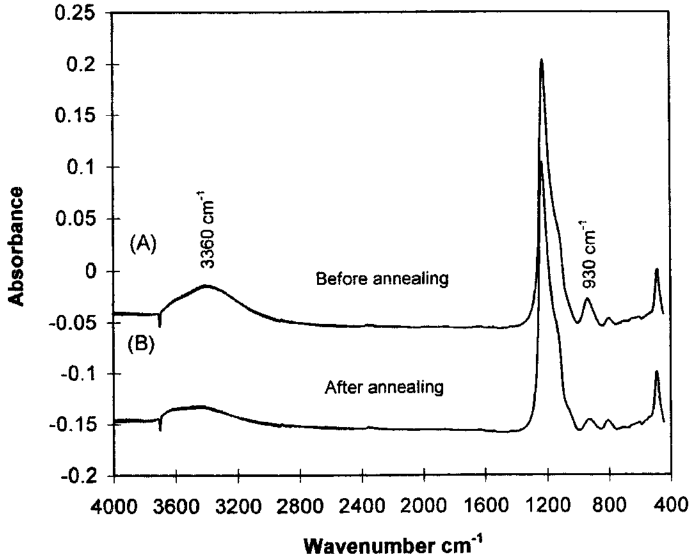


FIGURE 7 RAIR spectra of a film deposited in the MW reactor onto a polished aluminum substrate (A) – before and (B) – after annealing at 180°C for 30 minutes. The thickness of the film was 735 Å.

dioxide and of silicon. However, no bands due to silanol groups were observed in the spectra of the films before annealing, so the condensation reaction was not expected. This phase separation was not expected in our experiments because of the relatively low annealing temperature used.

F. Characterization of the Surface Morphology of Silica-like Films

Scanning electron microscopy was used to characterize the morphology and growth of plasma-polymerized films as a function of deposition time and plasma etching of the substrate. Figure 8 shows an SEM micrograph of acid-etched aluminum. Smooth, crater-like etch pits in the aluminum substrate were visible. Micrographs of silica-like films deposited for 15 and 30 minutes onto an acid-etched aluminum substrate that was also etched in an Ar plasma are shown in Figure 9. The surface of the substrate, including the etch pits, was covered with spherical particles deposited next to each other and

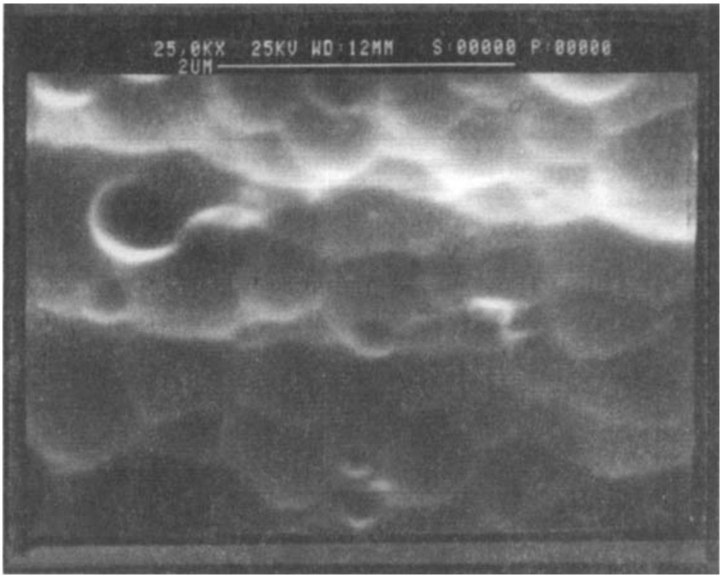


FIGURE 8 SEM micrograph of acid-etched aluminum.

impinging upon one another. The size of the particles increased with deposition time. However, for each deposition, the particle size was fairly homogeneous. The particles were approximately 0.08 μm and 0.2 μm in diameter after deposition for 15 and 30 minutes, respectively. These results are similar to those reported by other researchers [18]. Radeva also found that the size of spherical particles in plasma-polymerized HMDSO films increased with increasing deposition time.

The spheres were thought to be formed by adsorption and the three-dimensional growth of stable nuclei, not by powder particles from gas phase polymerization becoming incorporated in the film. The chemistry of powder produced in the gas phase has been shown to be different from that of films deposited downstream from the plasma [19]. Nucleation sites were observed to follow the ridges on the acid-etched aluminum surface. Physical ledges or bumps on the substrate surface formed favorable nucleation sites, thus promoting the growth of spherical particles along physical features of the aluminum substrate [20].

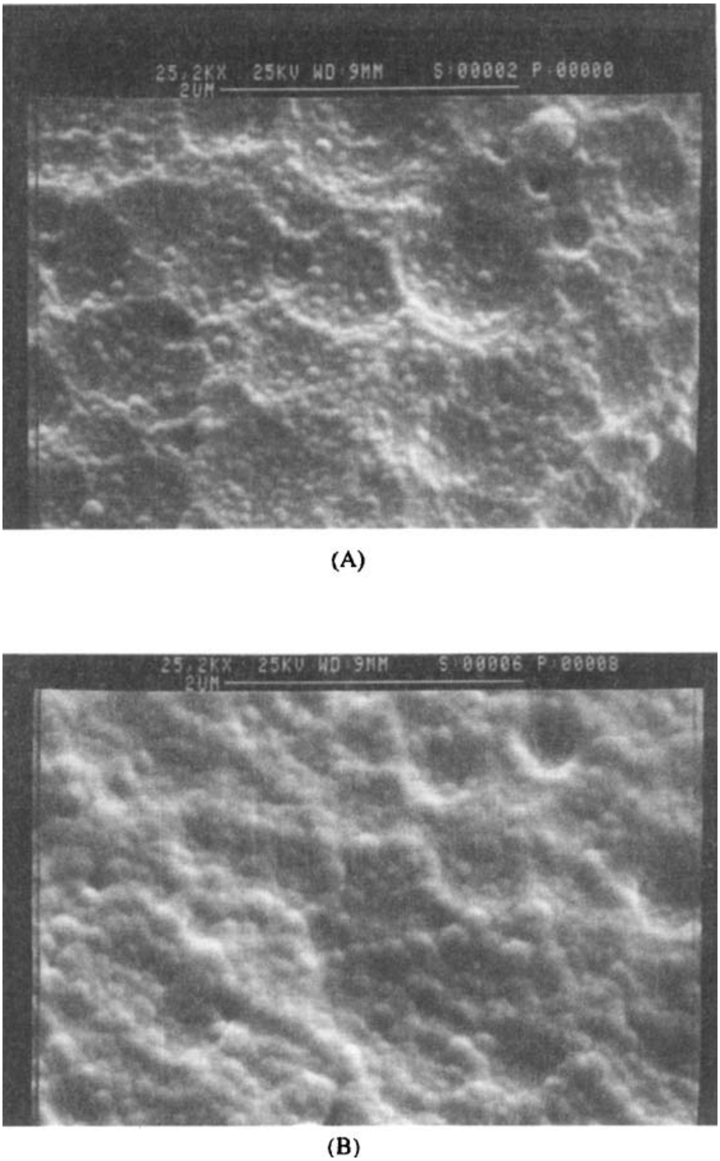


FIGURE 9 SEM micrographs of silica-like films deposited in the MW reactor for (A) – 15 and (B) – 30 minutes onto acid-etched aluminum that was etched in an Ar plasma before deposition of the film.

IV. CONCLUSIONS

- Plasma-polymerized HMDSO films deposited using argon as a carrier gas were siloxane-like. When siloxane-like films were etched with an oxygen plasma, a silica-like layer was produced on the surface. Silica-like films were deposited using oxygen as a carrier gas.
- Films deposited in the first 30 seconds of plasma deposition were less oxidized than films deposited for 10 minutes.
- Argon and argon/hydrogen plasmas removed adsorbed water from the surface of aluminum before the deposition of plasma-polymerized films, possibly creating a more stable oxide surface to which the silica-like primer could bond.
- The effect of etching silica-like films in an Ar plasma was to promote the condensation of adjacent silanol groups to form Si—O—Si bonds. There was little change in the film thickness. Similarly, there was little change in the concentration of isolated silanol groups.
- The effect of annealing silica-like films was to remove defects, in the form of silanol groups, from the silicon oxide structure of the film and to form more Si—O—Si bonds.
- SEM revealed that plasma-polymerized silica-like films were formed of spheroidally-shaped particles deposited next to each other and impinging upon one another. These spheroids were thought to be islands formed by the growth of stable nuclei, not the result of powder particles from gas phase polymerization becoming incorporated in the film.

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