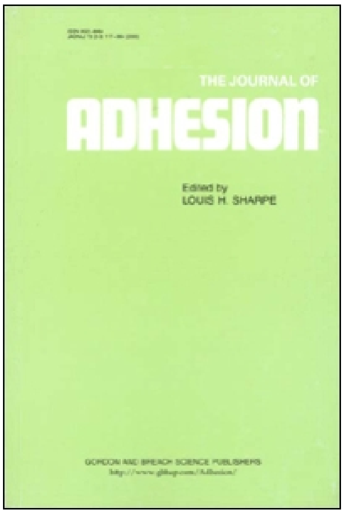

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Plasma and Silane Surface Modification of SiC/Si: Adhesion and Durability for the Epoxy-SiC System

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Plasma and Silane Surface Modification of SiC/Si: Adhesion and Durability for the Epoxy–SiC System

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Gaseous plasma pretreatments and surface derivatization using silane coupling agents (SCA) have been used to enhance the adhesive bonding of an epoxy to SiC-coated Si wafers (SiC/Si). The surface modification approaches included 1) an SCA treatment using 3-aminopropyltriethoxysilane (APS) or 3-glycidoxypropyltrimethoxysilane (GPS) and 2) an oxygen plasma pretreatment followed by a silane treatment. Durability was evaluated by immersing epoxy-coated SiC/Si samples in aqueous solutions at various pHs at 60°C for selected times. Adhesion durability for the epoxy-coated SiC/Si systems was qualitatively evaluated by visual inspection to identify debonding and quantitatively evaluated with a probe test to determine the critical strain energy release rate, G_c. Durability via either test approach varied as a function of surface treatment in this manner: oxygen plasma treatment plus silane modification > silane treated > no treatment. X-ray photoelectron spectroscopic characterization of surfaces was carried out following the surface treatments and after complete adhesion failure in the durability tests. The XPS results suggested that improved performance was due to plasma cleaning and modification of the substrate surface, promotion of silane surface interaction, and the formation of a thicker oxide layer.

Keywords: Bond durability; Derivatization; Epoxy–SiC/Si system; O_2 plasma surface modification; Silane coupling agent; Strain energy release rate; Surface analysis

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INTRODUCTION

Epoxy adhesives are widely used in the microelectronics industry as coating and encapsulant materials to provide environmental protection and thermomechanical protection for integrated circuit (IC) devices. Several requirements exist for a coating/encapsulant material, including high modulus of elasticity, high glass transition temperature (T_g), low thermal expansion, low moisture absorption, and good adhesion between the adherend and the polymeric material [1]. Epoxies have been used as packaging materials because of their excellent chemical and corrosion resistance, thermal insulation, electrical characteristics, physical properties, low shrinkage, excellent adhesion, and reasonable material cost [2]. The role of the coating/encapsulant is critical in electronic assemblies because the material serves as an insulator as well as a protective coating against adverse operating conditions [3]. Delamination (total loss of adhesion) between the substrate and epoxy is a major concern for yield loss and device reliability, especially in high humidity and elevated thermal conditions [4,5].

Surface pretreatment is important in most adhesion systems. To achieve optimum adhesion durability, it is often necessary to modify the native substrate surface. Silane coupling agents (SCAs) improve adhesion between inorganic oxides and polymer resins [6]. The coupling agent-contains both organic and inorganic functionalities, allowing it to act as a chemical bridge between two dissimilar materials.

Surface modification *via* plasma treatment is a nonsolution surface pretreatment method for improving adhesion [7]. Plasma treatments are commonly used in semiconductor processing and offer an attractive means to alter surface characteristics because they combine the features of safety, cleanliness, and cost effectiveness while enhancing adhesion performance. Plasma treatments that utilize nonpolymerizing gases are capable of removing carbon-containing surface contaminants in addition to physically and chemically altering the surface of the adherend.

In this study, silane derivatization and plasma surface-modification processes were investigated to improve adhesion of a model epoxy to silicon carbide–coated silicon wafers (SiC/Si). Silicon carbide is of interest because it is extremely stable, is capable of withstanding high heat, has low thermal expansion, exhibits resistance to acids and bases [8], and is commonly used in high-temperature, high-speed, high-power, and radiation applications. SCAs, 3-aminopropyltriethoxysilane (APS), and 3-glycidoxypropyltrimethoxysilane (GPS) were studied to improve adhesion durability. Oxygen plasma pretreatments prior to the deposition of either APS or GPS were investigated to further enhance adhesion performance. Surface modifications included silane treatment of SiC/Si with APS or GPS and O_2 plasma treatment of SiC/Si followed by silane treatment.

Adhesive bond performance was evaluated *via* immersion in aqueous solutions and a probe test. In the immersion test, specimens were immersed in aqueous solutions at 60°C. Performance was evaluated by noting blister formation and/or debonding as a function of time. The probe test was used to quantify adhesion *via* the determination of the critical strain energy release rate, G_c, as a function of immersion time. The principal goal of the immersion experiments was to study debonding at the interphase as a result of solution component migration/ingression through the epoxy coating.

EXPERIMENTAL

Substrate

Silicon wafers coated with SiC (SiC/Si) were obtained from the Hewlett-Packard Company (Corvallis, OR). The SiC layer was deposited by chemical vapor deposition (CVD). The thickness of the wafers was approximately 66 μm.

Adhesive

A model epoxy consisting of a bis-phenol F diglycidyl ether (Epon® 862) was used in all experiments and was obtained from the Shell Chemical Corporation (Houston, TX). The epoxy was cured with 4-methyl-2-phenylimidizole (Aldrich, St. Louis, MO). In addition, 1,4-butanediol (Aldrich, 99+% purity) was incorporated into the model epoxy to increase the solubility of the curing agent. The epoxy resin was stirred with 10 parts per hundred (phr) of 1,4-butanediol at 70°C for approximately 5 min to obtain a clear mixture. Then, 3 phr of 4-methyl-2-phenylimidizole were added, and the mixture was heated at 70°C for about 20 min. The adhesive was degassed at room temperature for 30 min, and then it was degassed in an ice water bath for 15 min followed by degassing in a hot water bath at 60°C for another 15 min. All of the degassing operations were carried out on a vacuum line. The epoxy was then deposited on a SiC/Si substrate either by spin casting or by sandwiching the sample between Teflon® plates. The epoxy was thermally cured at 130°C for 1 h in air. The T_g of the cured epoxy was approximately 110°C.

Silane Coupling Agents (SCAs)

SiC/Si wafers were chemically modified using one of the two SCAs (Aldrich, St. Louis, MO), APS, or GPS, with purities of 99% and 98%, respectively.

Plasma Reactor and Treatments

A custom-built 27.12-MHz radio frequency (RF) plasma reactor was used for all plasma treatments [9,10]. Oxygen plasma pretreatments were carried out at 50 W at a flow rate of 20 standard cubic centimeters per minute (sccm) for 2, 5, 15, or 30 min. After the plasma treatment, the samples were purged with O_2 gas for 10 min (no RF power). Plasma-treated samples were stored in a desiccator and were subsequently treated with SCAs or were bonded with adhesive within about 2 h. Plasma-treated sample surfaces were characterized with x-ray photoelectron spectroscopy (XPS) within about 2–4 h of the plasma treatment.

Silane Treatment

As-received and O_2 plasma–treated SiC/Si samples were immersed for 15 min in a solution consisting of 5 mL of 0.1 M HCl in 100 mL of 100% ethanol. The surface-modification reaction was initiated by adding a solution composed of 5 mL of 0.1 M HCl and 5 mL of SCA (APS or GPS) in 100 mL of 100% ethanol. Samples remained in this combined solution for 30 min. Samples were removed, rinsed in 100% ethanol, and allowed to dry in air at room temperature. The samples were then placed in an oven and heated in air for 30 min at 120°C.

Immersion Test Samples

SiC/Si substrates, 12 mm × 12 mm, were spun-cast with the model epoxy to form a film approximately 10–40 μm thick. Drops of epoxy were placed on the substrate, and the substrate was heated to approximately 80–100°C with a heat lamp. The temperature was measured by placing a thermometer or a thermocouple on the surface of the substrate. The sample was then spun at 2000 rpm for approximately 30 s. The specimen was then heated under a heat lamp for approximately 2 min to allow the epoxy to harden. The coated sample was subsequently heated in an oven at 130°C in air for 1 h to cure the epoxy adhesive. Samples prepared in this manner were used in the long-term immersion durability experiments.

Probe Test Samples

Samples were prepared by first placing a 75-µm-thick Teflon® template on the 20 mm × 20 mm SiC/Si specimens. The epoxy was then applied to the SiC/Si wafer. The epoxy/template/SiC/Si sample was sandwiched and clamped between two Teflon plates. The adhesive was cured in an oven at 130°C for 1 h.

Edge Protection Treatment

The purpose of coating the sample edges was to seal the edges of the film to promote fluid migration through the epoxy film into the interphase region. Coated samples were immersed for 30 min in a solution consisting of 5 mL of 0.1 M HCl and 5 mL of SCA in 100 mL of 100% ethanol. The specimens were subsequently rinsed with 100% ethanol, allowed to dry in air, and heated for 30 min at 120°C in air. Samples were edge treated with the same coupling agent that was used in the silane treatment. Samples that were not silane treated were edge protected using APS.

Immersion Test

Spin-coated specimens were immersed at 60°C in capped glass vials containing the formulated aqueous solutions. The solutions included water, a surfactant, organic and inorganic solutes, and organic solvents. The pHs of the formulated solutions were 4.2, 6.7, 7.7, and 8.2. The immersed samples were visually examined as a function of time, and debonding occurrences were recorded. The time to initial debond is the time at which the first pronounced appearance of blisters or film debonding from the surface, corners, or edges occurred. The time to complete debond is the time corresponding to 100% delamination of the adhesive film from the substrate. For the long-term immersion experiments, the samples were immersed in fresh solutions on a regular, at least weekly, basis.

Probe Test

Following immersion of the samples in the formulated solutions at 60°C for 0, 1, 7, 14, 21, or 28 days, the specimens were removed from the solution and blotted dry with a tissue to remove excess solution, and adhesion was evaluated with the probe test. Three probe-test measurements were performed for each sample. Probe tests were conducted before visual evidence of spontaneous debonding occurred due to exposure alone.

The probe apparatus [11] consisted of a Nikon UM-2 Measurescope microscope (Tokyo, Japan), a digital measuring stage, and a Karl Suss micromanipulator (Waterbury Center, VT) that allowed the user to manipulate the probe along the Cartesian axes. A tungsten probe with a tip radius of 10 μm was inserted at an edge of the adhesive film/substrate interphase to initiate film debonding. The debonded area was illuminated with light passing through a green filter with a wavelength of 414.5 nm. A digital camera was attached to the viewing lenses to photograph debonding events. All measurements were made at a probe angle of 25° relative to the plane of the substrate.

Debonding at the interphase produced a semi-ellipsoidal delamination as shown in Figure 1. Closed-form solutions for such delaminations are not yet available, so the critical strain energy release rate, G_c, was estimated using the solution that would result if a probe were used to delaminate a circular film satisfying plate assumptions [12]. The critical energy release rate for such a case is given by

$$G_c = \frac{2Eh^3}{3(1-\nu^2)}\left(\frac{w_0^2}{a^4}\right), \tag{1}$$

where a is the crack radius, w_0 is the maximum film deflection, E is the elastic modulus of the film, h is the film thickness, and ν is the Poisson's ratio.

Because Equation 1 is based on a semicircular crack and not a semi-elliptical crack, $a = \sqrt{r_1 \cdot r_2}$ was used to calculate the crack length a, where r_1 and r_2 are the delamination dimensions directly ahead and on the flanks of the probe, as shown in Figure 1. For the purposes of this article, the estimates of critical energy release rate are based on this approximation, and all values were determined at a probe

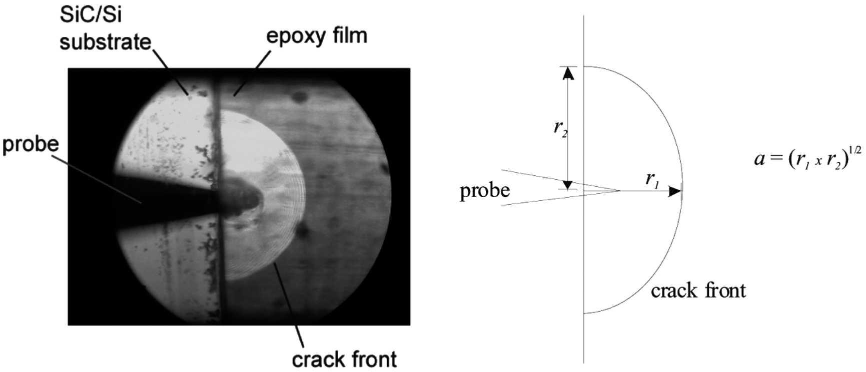


FIGURE 1 Photograph and schematic drawing of a debonding event.

penetration distance of 0.250 mm. The maximum deflection of the film, w_0, was determined by measuring the maximum vertical separation distance of the film from the substrate at the point of probe intrusion. The values used to calculate G_c were w_0, 116.6 μm E, 2.5 GPa [13]; v, 0.33 [14]; h, 75 μm.

X-ray Photoelectron Spectroscopy (XPS)

A PHI Perkin-Elmer (Eden Prairie, MN) model 5400 photoelectron spectrometer equipped with a Mg K_α x-ray source ($hv = 1253.6\,eV$) was used to characterize the surfaces. The x-ray source was operated at 300 W. All spectra were taken at a spot size of 1 mm × 3 mm and an electron take-off angle of 45°. Binding energy values were referenced to the C–C/C–H carbon 1 s peak at 285.0 eV [15]. Analyses of C 1 s, Si 2p, and N 1 s photopeaks were carried out by curve-fitting the peaks using a Gaussian function.

Chemical stoichiometry, chemical functionality (Si–C, SiO_2, Si–OR), and spectral features were used as a guide in curve-fitting the Si 2p photopeaks. The full-width-at-half-maximum (FWHM) for silicon-containing components was approximately 1.7 eV. The FWHM values for C and N were 1.8 eV and 2.0 eV, respectively. In some cases, the FWHM was varied by ±0.2 eV to obtain the best curve fit. All XPS spectra were obtained for edge-treated samples.

RESULTS AND DISCUSSION

Surface Characterization of Substrates and Adhesive Film

Carbon (45.8 at.%), oxygen (17.8 at.%), silicon (34.2 at.%), and fluorine (2.2 at.%) were detected *via* XPS on the as-received SiC/Si wafer. It is suspected that fluorine arises from wafer-cleaning processes. The C 1 s spectrum was resolved into four Gaussian peaks corresponding to 1) carbide carbon from SiC at 283.4 eV, 2) adventitious CH/CC carbon at 285.0 eV, 3) C–O carbon at 286.4 eV, and 4) C=O carbon at 288.9 eV. All carbon 1 s peak assignments were consistent with reported values for sputter deposited SiC [16] (C–Si at 283.1–283.6 eV, CH/CC at 285.0 eV, C–O at 286.5–286.7 eV, and C=O at 288.7–289.2 eV).

The Si 2p spectrum was resolved into two Gaussian peaks attributed to SiC (81%) at a binding energy of 100.4 eV and to SiO_2 (19%) at 102.4 eV. Both binding energies are consistent with reported values [16]. Although the binding energy for SiO_2 for silica is 103.3 eV, the binding energy for SiO_2 associated with SiC has been reported [16] in the range 102.4–102.8 eV. The presence of an oxidized surface is consistent with Rahaman's [17] proposed model of SiC powder involving an outer layer of adventitous hydrocarbon carbon and an intermediate layer of SiO_2 that overlays bulk SiC.

Assuming that the model [17] applies to the SiC/Si in this study, the thickness of the oxide layer can be estimated using the following relationship [18]:

$$\frac{SiC}{SiO_2} = \left(\frac{\rho_{Si,c}}{\rho_{Si,o}}\right)\left(\frac{\exp(-x/\lambda_c)}{1-\exp(-x/\lambda_o)}\right), \tag{2}$$

where SiC and SiO_2 are the areas of the respective Si 2p peaks, $\rho_{Si,c}$ and $\rho_{Si,o}$ are the atomic densities of Si in silicon carbide and in silicon dioxide, and λ_c and λ_o are the escape depths of the photoelectrons in carbide and dioxide. Using the molecular weight and density of 60 g/mol and 2.2 g/cm^3 for SiO_2, 40 g/mol and 3.2 g/cm^3 for amorphous SiC, $\rho_{(\mathrm{Si,c})}/\rho_{(\mathrm{Si},o)}\mathrm{x} = 2.18$, and $\lambda_o = 1.9\,\mathrm{nm}$, and $\lambda_c = 1.6\,\mathrm{nm}$ [19], the thickness of the air-oxidized SiO_2 layer was estimated to be $0.72 \pm 0.07\,\mathrm{nm}$.

The $\mathrm{Si_{SiC}/C_{SiC}}$ atom ratio was 1.1 ± 0.08, which is slightly higher than the theoretical $\mathrm{Si_{SiC}/C_{SiC}}$ ratio. Deviation from the theoretical $\mathrm{Si_{SiC}/C_{SiC}}$ ratio is dependent on the film-deposition process and deposition parameters [16].

Epoxy Adhesive

The model epoxy surface was composed of 81.5 at.% carbon and 18.5 at.% oxygen. Because no nitrogen was detected, it is apparent that nitrogen from the imidazole curing agent exists in the bulk epoxy and not at the film surface. The C 1 s peak could be fit to two components: C–H/C–C (61%) at 285.0 eV and C–O (epoxy group) (39%) at 286.6 eV.

Adhesion Durability for the Nonderivatized Samples

The performance of the model epoxy/SiC/Si bonded system was evaluated *via* the immersion test at 60°C. The immersion test results summarized in Figure 2 revealed that adhesive durability was quite poor for the epoxy/nonderivatized SiC/Si system. Samples without edge protection showed initial failure within 3–8 days, whereas initial failure occurred in up to 20 days for samples with edge protection. Specimens without edge protection completely debonded within 2–5 days of the observed initial debond. Edge-protected samples did not fail completely until 12–15 days after the initial debond.

Sample durability was also evaluated using the probe test for specimens that had been immersed at 60°C in pH 6.7 and pH 8.2 solutions and in deionized (DI) water at pH 6.3. The results are summarized in Figure 3. The G_c for the bonded system measured on a dry specimen

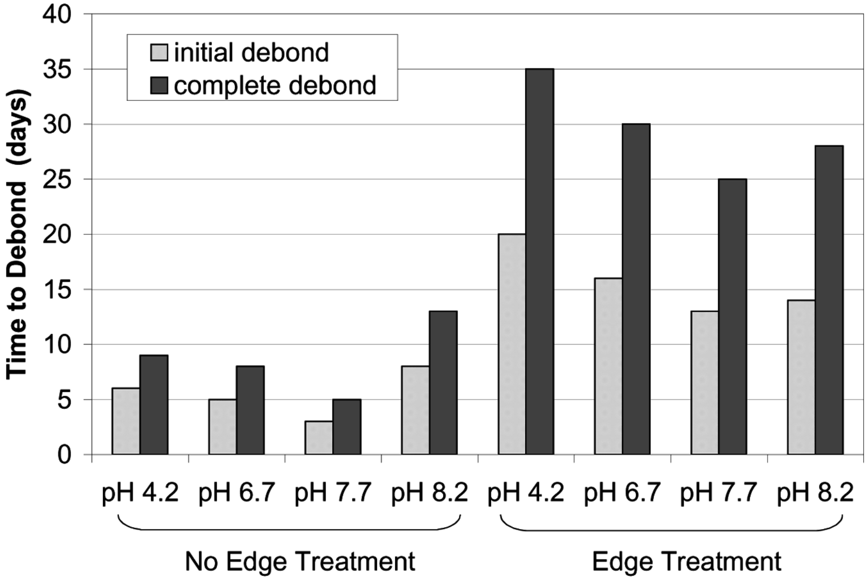


FIGURE 2 Adhesion durability data for epoxy/nonderivatized SiC/Si samples tested in various aqueous solutions at 60°C.

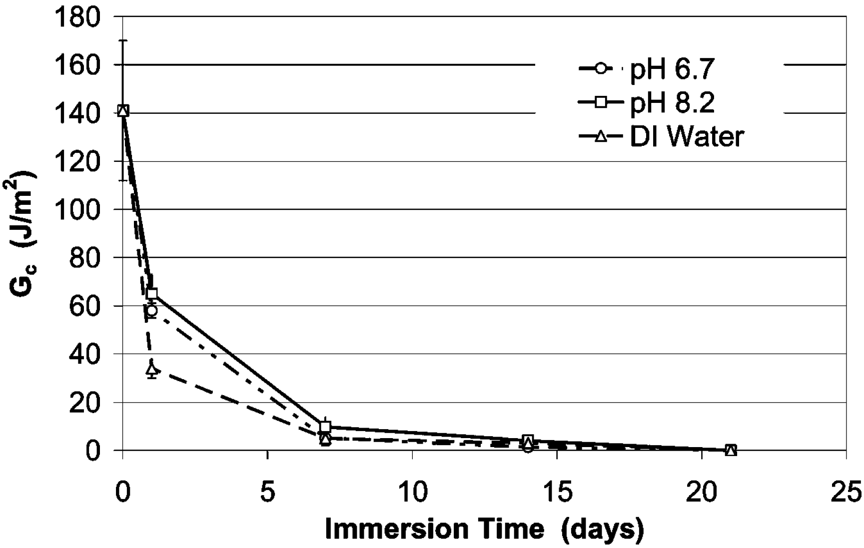


FIGURE 3 Critical strain energy release rate G_c as a function of time for epoxy/nonderivatized SiC/Si specimens tested in pH 6.7 and pH 8.2 formulated solutions and DI (pH 6.3).

(no immersion) was $\sim 141\,\mathrm{J/m^2}$. After 24 h of immersion in the solutions, G_c decreased to 30–60 $\mathrm{J/m^2}$ and changed to 2–5 $\mathrm{J/m^2}$ following 14 days of immersion. After 21 days of immersion, all samples failed either by debonding of the epoxy film at the sample edges (which prevented probe testing of the samples) or by complete delamination. The results are similar to the performance trend noted in the immersion tests.

The failure mode for completely debonded samples in the immersion tests was determined using XPS. The absolute percentages for carbon and silicon species are presented in Table 1. A significant finding is that SiO_2 is detected on the epoxy failure surface at all pHs, and yet the respective carbon and oxygen concentrations on the epoxy failed sides were comparable with those for the adhesive control. This result indicates that failure occurred at the SiO_2/epoxy interphase in all formulated solutions. The amount of SiC on the substrate failure surfaces generally decreased relative to the control as the pH of the formulated solutions increased from 4.2 to 7.7, but the SiC content was higher for failure surfaces obtained from tests at pH 8.2. At the same time the percent SiO_2 increased as pH increased from 4.2 to 7.7 but is low for samples tested in pH 8.2. Thus, the surface analysis results indicated that failure occurred in the epoxy–SiO_2:SiC region. Failure in the interphase region could be explained by the fact that an oxide layer is hydrolyzed by water. In addition, secondary bonds between the epoxy and siliceous substrates can be degraded by water [19–21]; even in the absence of stress [20]. The very low G_c values (Figure 2) are undoubtedly related to degradation of the epoxy–substrate bonds upon immersion in the formulated solutions.

TABLE 1 Absolute Percentages for C 1s and Si 2p Curve-Fit Species for Control and Failed Epoxy/SiC/Si Specimens at Different pH Solutions

Surface	pH	% C–Si	% CH/CC	% C–O	% Si–C	% $Si–O_2$
Adhesive control		<0.1	49.5	31.9	<0.1	<0.1
Adhesive failed side	4.2	<0.1	48.2	29.9	<0.1	1.8
	6.7	<0.1	46.5	27.3	<0.1	3.3
	7.7	<0.1	53.3	31.2	<0.1	5.2
	8.2	<0.1	46.5	27.3	<0.1	0.8
Substrate control		32.7	7.8	3.6	27.5	6.7
Substrate failed side	4.2	25.7	14.2	4.9	26.2	7.2
	6.7	15.7	20.8	6.3	18.6	10.4
	7.7	14.2	22.2	6.9	17.2	9.6
	8.2	28.5	10.9	4.0	29.6	4.4

TABLE 2 XPS Elemental Composition (Atom %) for As-Received, As-Received/APS-, and AS-Received/GPS-treated SiC/Si

Sample	% C	% O	% Si	%N	% F
As-received	45.8	17.8	34.2	<0.2	2.2
As-received/APS	49.3	22.5	25.9	1.3	1.0
As-received/GPS	47.1	15.5	35.6	<0.2	1.8

XPS Analysis of Treated Surfaces

Silane Treatment

XPS analysis results for APS- and GPS-derivatized substrates are given in Table 2. The presence of nitrogen is an indication that APS interacted with the surface. The C 1s spectrum also indicated the presence of APS. Compared with the as-received substrate, the curve-fit C 1s spectrum for as-received/APS shows an increase in the C–H/C–C peak intensity relative to the C–Si peak.

In the curve-fit Si 2p spectrum, two peaks were resolved at 100.4 eV and 102.4 eV and were assigned to Si–C (~72%) and Si–O_x (~28%), respectively. A slight increase in peak intensity for the SiO_x photopeak was observed compared with the respective peaks for the as-received samples. The FWHM was 12.5% greater than the FWHM for the as-received specimens. The increase in peak intensity and broadening of the peak are attributed to Si–O–Si species. Others [22] have reported a binding energy in the range 102.3 eV–102.7 eV for Si–O–Si species. The SiO_x composite peak was composed of SiO_2 and Si–O–Si components.

For the GPS surface-modified substrate (Table 2), the atom percentages on a GPS-treated surface were essentially equivalent (within 2%) to the composition for the as-received surface. However, in the C 1s spectrum for a GPS derivatized surface, the intensities for the CH/CC and CO peaks relative to C–Si were greater compared with the relative intensities for as-received SiC/Si.

Oxygen Plasma Activation and Silane Treatment

Oxygen Plasma Pretreatment

Substrates were pretreated in an O_2 plasma for 2, 5, 15, and 30 min. XPS analysis results (Table 3) show a decrease in carbon, an increase in oxygen, relatively no change in silicon content, and removal of fluorine relative to the results for the as-received SiC/Si samples. The increase in oxygen suggests the formation of a thicker oxide layer attributed to SiO_2 on the silicon carbide surface. An increase in treatment time resulted in an increase in the Si–O_2 to Si–C (SiO_2/SiC)

TABLE 3 Elemental Analysis (Atom %) for O_2 Plasma–Treated SiC/Si at Various Treatment Times and O_2 Plasma–Treated GPS- and APS-Derivatized SiC/Si Samples

Sample	C%	O%	Si%	%N	F%
As-received	45.8	17.8	34.2	<0.2	3.2
2 min O_2 plasma	20.8	49.6	29.7	<0.2	<0.1
5 min O_2 plasma	19.2	50.6	30.2	<0.2	<0.1
15 min O_2 plasma	18.6	51.4	30.1	<0.2	<0.1
30 min O_2 plasma	16.5	53.6	29.9	<0.2	<0.1
2 min O_2 plasma/APS	36.7	38.0	21.7	3.6	<0.1
5 min O_2 plasma/APS	35.7	39.2	21.3	3.7	<0.1
15 min O_2 plasma/APS	38.1	38.1	20.5	3.4	<0.1
30 min O_2 plasma/APS	34.9	39.6	22.0	3.5	<0.1
2 min O_2 plasma/GPS	29.2	43.8	27.1	<0.1	<0.1
5 min O_2 plasma/GPS	28.7	44.8	26.5	<0.1	<0.1
15 min O_2 plasma/GPS	30.2	43.8	26.0	<0.1	<0.1
30 min O_2 plasma/GPS	26.1	47.2	26.7	<0.1	<0.1

ratio from 0.23 for as-received SiC/Si to ratios in the range 1.2 (2 min) to 1.9 (30 min) for the O_2 plasma–treated samples. The oxide (SiO_2) thicknesses are shown in Figure 4, and it is noted that the thickness increased as treatment time increased.

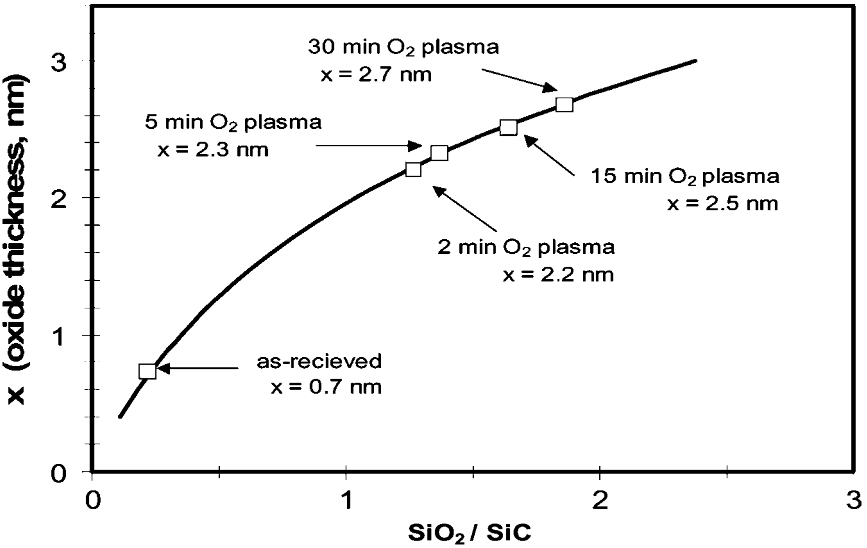
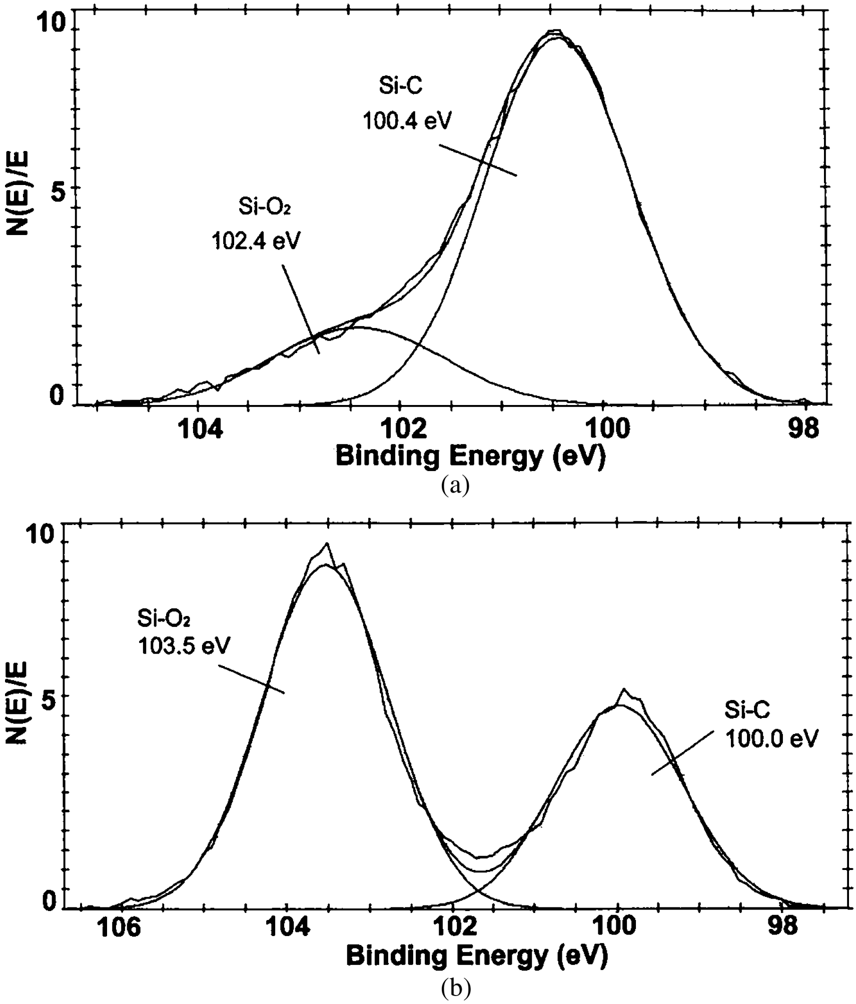


FIGURE 4 Oxide thickness as a function of the SiO_2/SiC ratio.

The Si 2p spectrum for O_2 plasma–treated SiC/Si in Figure 5 is compared with the spectrum for an as-received SiC/Si sample. An increase in the binding energy for Si$-O_2$ from 102.4 eV to 103.3–103.7 eV and a decrease in the binding energy for Si$-$C from 100.4 eV to 99.7 eV–100.0 eV occur as a result of SiC oxidation in the plasma. The binding energy for plasma-formed SiO_2 is consistent with literature values [23] for Si$-O_2$ on silica and Si$-O_2$ on silicon.



(a)

(b)

FIGURE 5 Si 2p for (a) as-received SiC/Si and (b) a typical O_2 plasma–treated surface (15 min O_2 plasma).

Silane Treatment

Following an O_2 plasma pretreatment, samples were further modifed with either APS or GPS. The atom percentages for a typical O_2 plasma–treated surface (as-prepared) and for a typical O_2 plasma/SCA surface are summarized in Table 3. The XPS results show an increase in carbon and nitrogen and a decrease in silicon and oxygen for O_2 plasma/APS modified samples relative to surfaces treated with only an O_2 plasma. From curve fitting, the C$-$H/C$-$C to C$-$Si ratios for the as-prepared and the O_2-plasma/APS surfaces were 0.9 and 4.2, respectively. Compared with the silane-treated samples without plasma pretreatment (as-received/silane), O_2 plasma/APS-treated samples yielded a two- to three fold increase in silane on the surface. The extent of surface modification for APS is indicated by the increase in the nitrogen percent, from 1.3% for the nonplasma/APS sample to 3–4% for the O_2 plasma/APS sample.

For O_2 plasma treated–GPS modified surfaces, an increase in carbon and a decrease in oxygen and silicon percentages were noted relative to surfaces that had only been O_2 plasma treated. The C$-$H/C$-$C and C$-$O photopeaks for the various plasma pretreatment times showed an increase in C$-$H/C$-$C from $\sim$8% to $\sim$15% and an increase in C$-$O from $\sim$1% to 4–5%. XPS data indicated that the extent of GPS interaction with the O_2 plasma–modified samples was greater than for the nonplasma/GPS samples by up to a factor of two to three, as suggested by the absolute concentration of C$-$O attributed to GPS, and 1.4% and $\sim$3–4% for nonplasma/GPS and O_2 plasma/GPS samples, respectively.

Adhesion Durability—Silane Modification

Immersion Studies

Durability tests for epoxy-coated, surface-treated SiC/Si samples immersed in pH 4.2, 6.7, 7.7, and 8.2 formulated solutions showed that the various surface treatments enhanced adhesion. For nonderivatized SiC/Si samples, initial debonding occurred in less than 20 days. GPS- or APS-treated as-received samples showed initial debonding after about 90 days of immersion. Samples having a 2-min O_2 plasma pretreatment followed by derivatization with SCAs showed initial debonding at approximately 200 days for the GPS- and 350 days for the APS-treated samples, respectively.

The time to initial debond results are shown in Figure 6 for O_2 plasma-treated GPS- and APS-modified SiC/Si samples as a function of plasma treatment time. For both the GPS and APS modified samples, respectively, the 2- and 5-min O_2 plasma treatments yielded

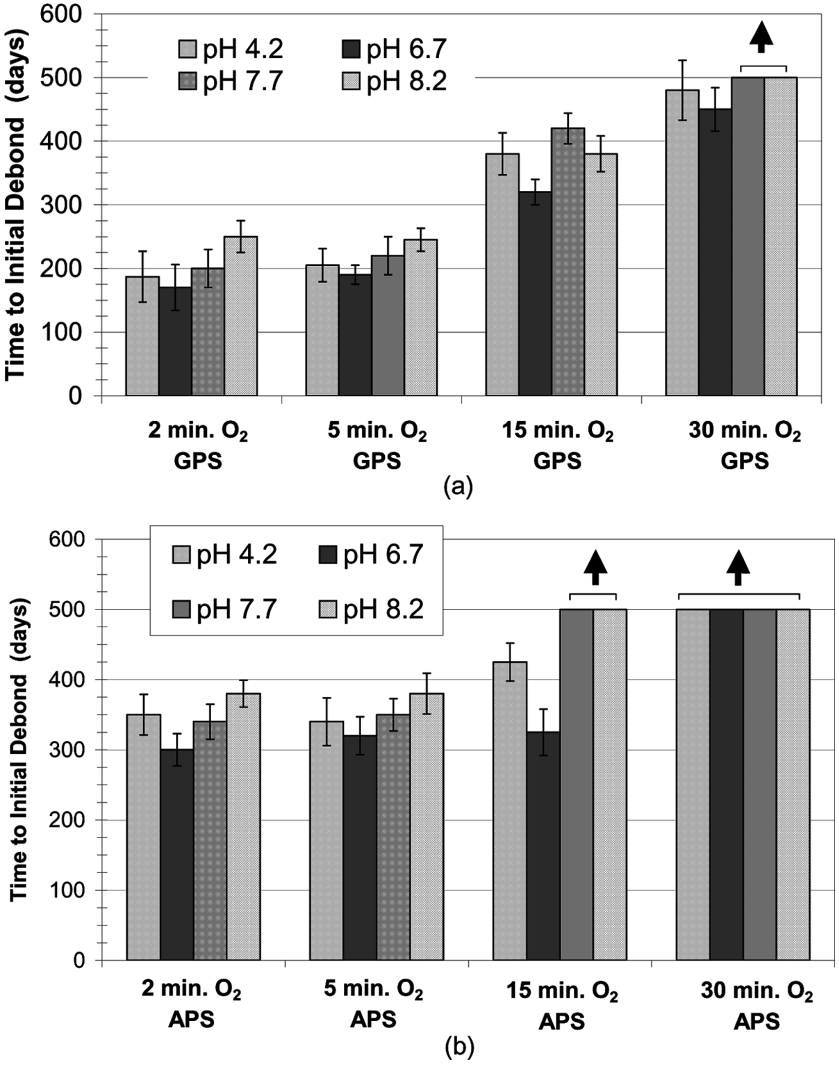


FIGURE 6 Adhesion durability: time to initial debond data for plasma/SCA samples tested in formulated solutions at 60°C for (a) GPS with various O_2 plasma pretreatment times and (b) APS with various O_2 plasma pretreatment times. Arrows indicate that samples did not reach initial failure in 500 days.

about the same durability as indicated by equivalent times to initial debond. Samples pretreated for 15 and 30 min in an O_2 plasma and modified with SCAs exhibited increased durability relative to that for derivatized samples that had been treated in an O_2 plasma for shorter times. Generally, the APS-treated samples exhibited better durability than the GPS-treated samples. For a 15-min O_2 plasma treatment, GPS samples immersed in the four different pH solutions all exhibited initial failure at approximately 350–400 days. APS samples tested in pH 4.2 and 6.7 formulated solutions failed in about 350–450 days and samples immersed in pH 7.7 and 8.2 formulated solutions did not show failure for immersion tests lasting up to 500 days. Some 30-min O_2 plasma/GPS samples showed failure at about 450 days for tests in pH 4.2 and 6.7 solutions, whereas specimens tested at pH 7.7 and 8.2 had no initial failure following immersion for up to 500 days. Samples having a 30-min O_2 plasma/APS modification treatment exhibited no sign of initial failure following 500 days of immersion in any of the four formulated solutions. Because the immersion tests ended at 500 days, the debond lifetimes for all of the epoxy/O_2 plasma/SiC/Si samples are unknown. It is apparent that an oxygen plasma treatment for 30 min followed by derivatization of the treated SiC/Si surface with SCAs enhances epoxy/SiC/Si bond durability.

The improvement in adhesion in the epoxy/O_2 plasma/SiC/Si system may occur because of 1) the cleaning effect of the oxygen plasma [24] and 2) the generation of a plasma-formed oxide. Oxygen plasmas are capable of effectively removing organic contamination from inorganic surfaces, and as plasma time increased, a thicker oxide layer developed to include oxygen-containing functionalities.

Strengthening of the epoxy–SiC interface against degradation for the surface treated specimens was also observed in the debonding behavior of the epoxy film when immersed in aqueous solutions at 60°C. For the as-received, unmodified samples (no SCA or plasma), debonding occurred primarily as lifting of the edges and corners as a result of the ingression of the aqueous solution. Some debonding was apparent as small blisters originated at the edges of the film, then growing in size and population inward toward the center of the film. Such debonding behavior suggests that the ingression of aqueous solution occurred primarily at the interphase between the adhesive film and substrate.

For the surface-modified specimens, initial debonding at the edge of the film was not observed. Instead, debonding occurred *via* random blister formation. Typically, the blisters grew in size with time and eventually coalesced. This type of blistering/debonding indicates that the mechanism of failure occurred primarily *via* aqueous solution diffusion through the bulk of the epoxy film.

The time to complete debonding was also affected by the surface treatment. For the as-received nonderivatized specimens, complete delamination of the epoxy film occurred within 12–15 days after the first appearance of an initial debond. For surface-treated samples, complete delamination did not occur before four months after the initial debond. For nonplasma/SCA samples, complete debonding of the film occurred approximately 2 months after the initial debond. Complete debonding for some plasma/SCA samples occurred at about 4 months; however, many of the plasma/SCA samples surpassed four months. Because the immersion test concluded after about 17 months, the time to complete failure is not known for some plasma/SCA samples.

Probe Test Studies

Probe tests were conducted to evaluate changes in the critical strain energy release rate, G_c, for as-received, as-received/GPS, as-received/APS, 30 min O_2 plasma/GPS, and 30 min O_2 plasma/APS samples as a function of immersion time in pH 6.7 and pH 8.2 formulated solutions and in DI water (pH 6.3). G_c values decreased with increasing immersion time. G_c appeared to reach a limiting value following immersion for about 20–28 days. The trend in durability performance as indicated by the values of G_c was O_2 plasma/APS > O_2 plasma/GPS > as-received/APS ≈ as-received/GPS.

Figure 7 summarizes results from the probe tests for nonderivatized and derivatized specimens not immersed in solutions and following 28 days of immersion in formulated solutions at pH 6.7 and pH 8.2 and in DI water (pH 6.3). Following 28 days of immersion, the G_c values for unmodified as-received samples were not measurable because the samples debonded during the immersion tests. For as-received samples that had been modified with APS and GPS, the G_c values were in the range $\sim$100 to 225 J/m^2. Enhanced adhesion was obtained for the 30 min O_2 plasma/GPS specimens; G_c values for samples immersed in the aqueous solutions were approximately 225 to 325 J/m^2. Similarly, for 30 min O_2 plasma/APS specimens, G_c values for samples immersed in the aqueous solutions were in the range 325 to 400 J/m^2. The adhesion trend in these probe tests is similar to that for the immersion tests with the exception of the difference in adhesion durability for as-received/GPS and as-received/APS. In the immersion study, the as-received/APS surface-treated samples exhibited better adhesion. In the probe tests the samples prepared with the two treatments exhibited equivalent adhesion performance.

Sample surfaces modified with an O_2 plasma and derivatized with APS exhibited better adhesion than that for O_2 plasma/GPS samples. It is reasonable that improved adhesion for plasma/APS samples may be due to a combination of factors including the polarity of the

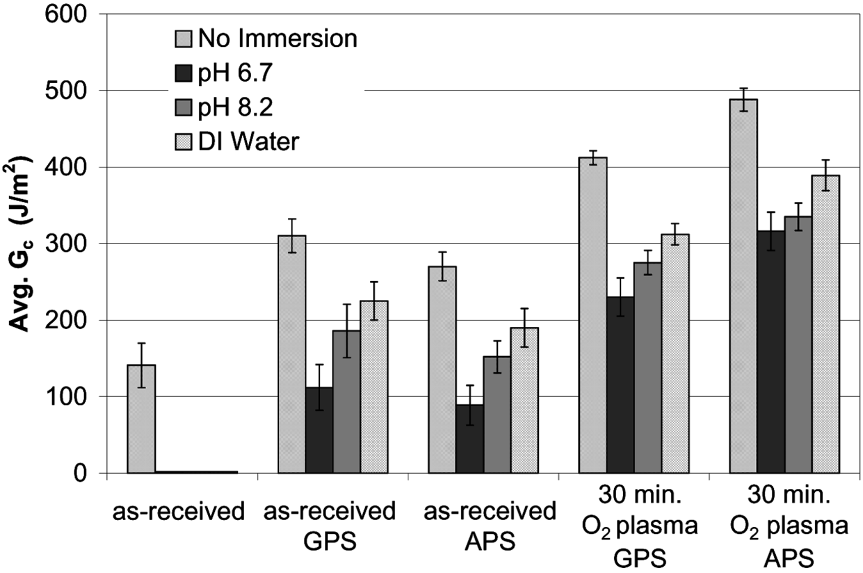


FIGURE 7 Average critical strain energy release rates, G_c, for as-received and surface-treated samples following 28 days of immersion in formulated solutions at pH 6.7 and pH 8.2 and in DI water. Values are an average of three runs per sample.

APS silane. The reported critical surface tensions for APS and GPS on glass at 20°C are 35.0 N/m and 44.6 N/m respectively [25]. Although the difference in surface tensions may be small between APS and GPS, the nature of APS provides a more water-resistant interphase region, thus inhibiting hydrolysis and aqueous solution ingression. In addition, XPS surface analysis suggested that greater surface derivatization was achieved with APS than GPS.

Determination of Failure Mode for the Surface-Modified Systems

Surfaces of failed specimens from the immersion tests were characterized *via* XPS to determine the failure mode. Detailed XPS analysis showed that all samples, regardless of surface preparation, failed within the adhesive–SCA interphase region. To illustrate the manner of determining the failure mode, XPS analysis for 5 min O_2 plasma/APS APS and 5 min O_2 plasma/GPS samples are discussed.

The atom compositions for the failed surfaces for 5 min O_2 plasma/APS tested in pH 6.7 solution and for the as-prepared surfaces are shown in Table 4. The compositions for the failed SiC surface and for the as-prepared surface (plasma and silane treated) were equivalent:

TABLE 4 Elemental Surface Composition for As-Prepared (before Bonding) and Debonded Surfaces for 5 min O_2 Plasma/APS (the Sample was Tested in pH 6.7 Solution)

	Surface composition			
Sample	C%	O%	Si%	N%
As-prepared SiC surface	35.7	39.2	21.3	3.7
Failed SiC side	37.3	40.4	20.1	2.2
Model epoxy coating	81.6	18.4	<0.1	<0.1
Failed epoxy side	79.7	17.7	<0.1	2.6

~36% C, ~40% O, and ~20% Si. Except for the slight decrease in nitrogen content from 3.7% (as-prepared SiC) to 2.2%, the surface chemistry for the two surfaces was similar. For the failed epoxy side, the carbon and oxygen contents were also equivalent (within 2%) to the as-prepared epoxy coating.

The C 1 s and Si 2p spectral regions for the as-prepared APS-treated SiC surface and as-prepared epoxy surfaces were compared with the failed substrate and failed adhesive surfaces. The C 1 s and Si 2p spectra in Figure 8 for the as-prepared and failed SiC/Si surfaces are similar. Both C 1 s spectra show a prominent C–H/C–C photopeak at 285.0 eV, a C–Si peak at 282.8 eV, and a very slight shoulder due to C–O at 286.5 eV. The Si 2p spectra of both surfaces show a dominant photopeak at 102.4 eV, which is assigned to the composite peak consisting of SiO_2 and Si–O–Si, and a less prominent photopeak at 99.5 eV attributed to silicon in SiC. The C 1 s spectra for the surface of the failed epoxy side and the as-prepared epoxy are equivalent, showing a C–H/C–C photopeak at 285.0 eV and a C–O photopeak at 286.5–286.7 eV, which are characteristic of the epoxy adhesive. The shape and relative intensities of the C–H/C–C and C–O photopeaks for the failed and as-prepared epoxy surfaces are equivalent. No silicon was detected on the failed epoxy surface, which indicates that no silane was on the epoxy film. The XPS results indicate that failure occurred at the epoxy adhesive–SCA interphase.

As a representative of the failed GPS-treated samples, the XPS data for failure analysis for a 5 min O_2 plasma/GPS sample tested in pH 8.2 solution are presented in Table 5. For the failed SiC surface, the carbon content increased slightly from 28.7% to 33.7%, oxygen was relatively unchanged at about 45%, and silicon decreased from 26.5% to 21.0%. For the failed epoxy side, C, O, and Si were detected. The relative percentages of carbon and oxygen for the failed surface are equivalent within 1% of the values for the as-prepared surface.

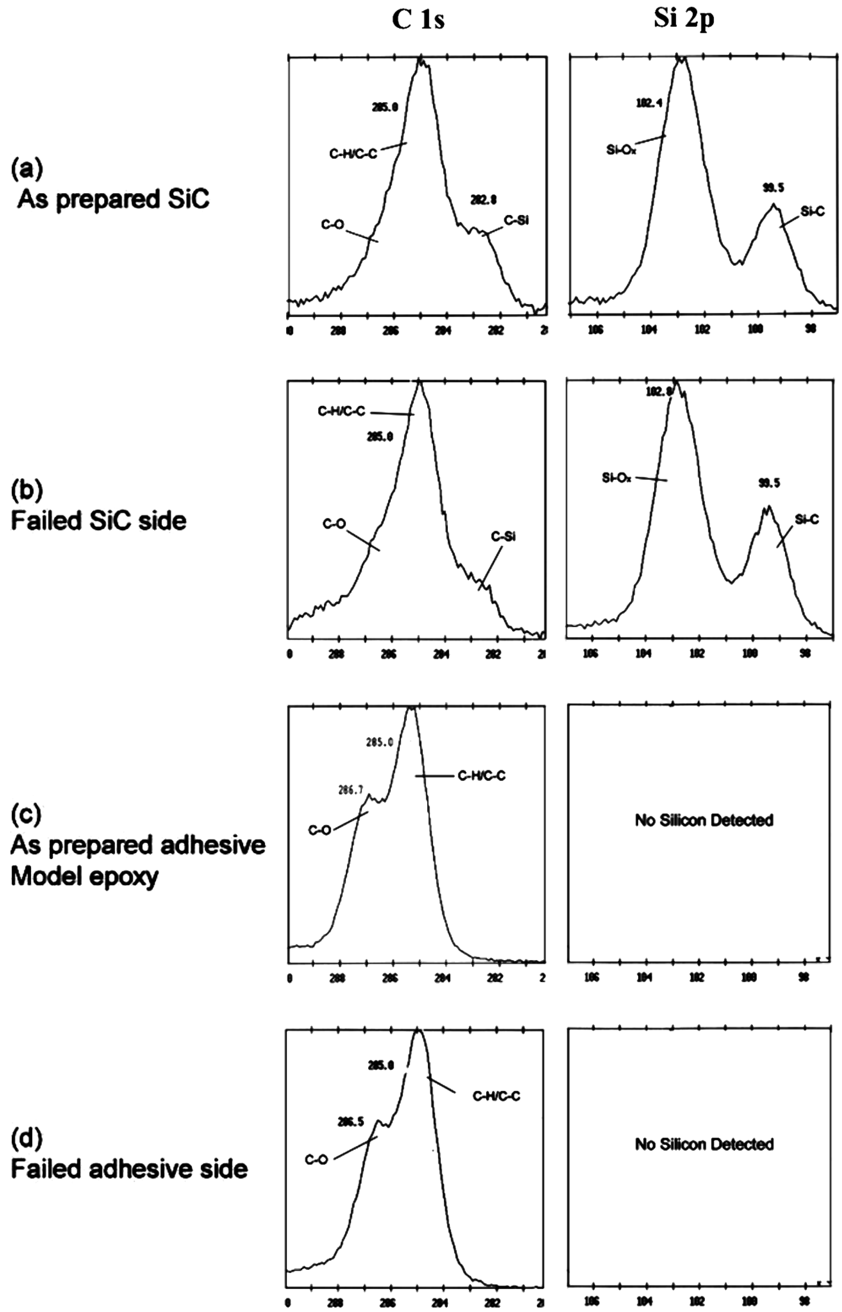

C 1s
Si 2p
(a)
As prepared SiC
285.0
C-H/C-C
C-O
282.8
C-Si
102.4
Si-Ox
99.5
Si-C
(b)
Failed SiC side
C-H/C-C
285.0
C-O
C-Si
102.8
Si-Ox
99.5
Si-C
(c)
As prepared adhesive
Model epoxy
285.0
286.7
C-H/C-C
C-O
No Silicon Detected
(d)
Failed adhesive side
285.0
286.5
C-H/C-C
C-O
No Silicon Detected
288
286
284
282
106
104
102
100
98

TABLE 5 Elemental Surface Composition for As-Prepared (before Bonding) and Debonded Surfaces for 5 min O_2 Plasma/GPS (the Sample was Tested in pH 8.2 Solution)

	Surface composition			
Sample	C%	O%	Si%	N%
As-prepared SiC surface	28.7	44.8	26.5	<0.1
Failed SiC side	33.7	45.3	21.0	<0.1
Model epoxy coating	81.6	18.4	<0.1	<0.1
Failed epoxy side	80.4	18.8	0.81	<0.1

The low concentration of silicon (0.81%) on the failed adhesive side suggests the presence of silane.

Although individual spectra are not shown for the GPS-modified sample, the failed SiC surface shows slightly broader C–H/C–C and C–O photopeaks at 285.0 eV and 286.5 eV, respectively, compared with the as-prepared surface, suggesting that a small amount of epoxy was present on the substrate. The Si 2p peaks were equivalent to the respective photopeaks for the as-prepared sample, indicating that the silane and oxide layers were present on the failed surface and suggesting failure at the epoxy/silane interphase. On the epoxy-failed side and as-prepared epoxy surface, the C–H/C–C and C–O photopeaks were similar and equivalent. The Si 2p spectrum revealed a photopeak at 102.5 eV indicative of Si–O–Si and SiO_2. The overall analysis of the failed surfaces indicated that failure occurred predominantly at the GPS-epoxy adhesive interphase.

In summary, all samples exhibited failure primarily at the silane–epoxy interphase. Although siloxane bonds may be reversibly hydrolyzed by water [26], the vulnerability of the silane/epoxy interphase may be due to 1) inefficient bonding between the silane/epoxy interface and/or 2) stresses across the silane/epoxy interphase due to epoxy shrinkage during curing and/or changes in the properties of the epoxy as a result of absorption of solution components.

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FIGURE 8 C 1 s and Si 2p XPS spectral regions of failed surfaces for 5 min O_2 plasma/APS sample tested pH 6.7 solution compared with as-prepared surfaces: (a) as-prepared, 5 min O_2 plasma/APS wafer surface, (b) failed SiC wafer side surface, (c) as-prepared model epoxy coating, and (d) failed epoxy side surface. In all figures the ordinate is **N(E)/N** and the abscissa is **Binding Energy (eV)**. The binding energy range for C 1s is 290.0–280.0 eV and that for Si 2p is 107.0–90.0 eV.

SUMMARY AND CONCLUSIONS

The effectiveness of silane treatments (APS or GPS) and an oxygen plasma pretreatment followed by a silane treatment of SiC/Si to improve adhesion was investigated. Adhesion durability in aqueous solutions at 60°C was evaluated qualitatively using an immersion test and quantitatively by determining the strain energy release rate G_c via a probe test. As-received samples (without modification) resulted in initial failure in 20 days, whereas silane-treated samples yielded initial failure at approximately 100 days. The immersion studies showed that oxygen plasma/silane–treated SiC/Si samples exhibited no sign of initial failure even at the end of the 500-day immersion test. An increase in O_2 plasma treatment time yielded an increase in adhesion durability. The probe test results confirmed that O_2 plasma/silane–treated samples exhibited significantly improved adhesion performance compared with samples without plasma treatment. The results from the probe test and the immersion tests exhibited the same trend in adhesion as influenced by immersion in formulated solutions. Although the O_2 plasma–treated SiC/Si surface is not completely converted to SiO_2, the results indicate that even some conversion of SiC to SiO_2 improves the adhesive system durability.

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