Effect of Silane Functional Group on Adhesion of Selected Epoxies for Microelectronic Packaging

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Abstract

This paper describes experiments designed to evaluate the effect of various silane surface treatments on the thin-film adhesion of epoxies filled with spherical silicon oxide. Fracture mechanics-based methods evaluated adhesion of both filled and unfilled epoxies to silicon oxide. SEM was used to examine fracture surfaces and evaluate fracture mechanisms. Two different epoxies were tested, including one with four components and multiple intermediate cure reactions. It was found that the only silanes that augmented adhesion of the epoxies to silicon oxide were those with functional groups identical to those of the epoxies which take part in the final curing reaction. However, when these silanes were used to coat filler, adhesion of filled epoxies to silicon oxide wafers remained the same or was slightly reduced. In all cases, fracture occurred at or near the epoxy-wafer interface, suggesting that deformation within the epoxy layer was limited. Only one set of specimens, in which the silane was improperly prepared, resulted in augmented epoxy-wafer adhesion facilitated by filler-matrix delamination. In other words, filled epoxy-wafer adhesion increases with decreasing efficacy of silane adhesion promoter treatment.

Keywords

aliphatic, bisphenol-f, delamination, epoxy, filler, silanes, silica

Introduction

For decades, researchers have investigated the mechanical properties of particulate-reinforced, epoxy composites, including those in which the spherical silicon oxide filler has been treated with a silane adhesion promoter [1]-[3]. More recently, these materials have been employed in microelectronics to mechanically stabilize solder balls in flip-chip packages [4]. A wealth of experimental data and models exist for bulk composites. However, there is sharp disagreement as to what degree of reinforcement-matrix adhesion and corresponding filler surface treatment are most desirable. In addition, there is little direct evidence of the degree to which bulk properties and observations can be applied to composite thin films, such as those used in microelectronic packaging. The desired properties appear to be strongly dependent on load geometry and intended application. For example, fracture-resistant interfaces transfer loads well; however, less resistant interfaces toughen a film by allowing energy dissipation through subsurface debonding above and below the crack plane.
Consensus as to the ideal degree of reinforcement-matrix adhesion has not been reached due in part to a variety of incompatible metrics. Adhesion energy G, Young's modulus, stress intensity factor K, and yield stress σ_{ys} have all been used as criteria to evaluate the performance of these composites [5]-[10]. Even when adhesion energy is isolated, references can be found in support of both increasing [7], [11], [12] and decreasing [14] filler-matrix adhesion in order to maximize composite adhesion.

Two major mechanisms have been found to operate in particulate-reinforced epoxy composites: crack blunting and crack pinning [6]-[14]. In each case, stability of crack growth and analysis of SEM micrographs indicate the mechanism. Crack blunting occurs when filler-matrix adhesion is weaker than matrix cohesion. It can often be identified by stick-slip fracture behavior. In this case, the crack front partially follows the contour of the filler surfaces, resulting in a significantly greater surface area and resulting adhesion energy [5], [8], [9], [13]. SEM micrographs of these surfaces feature intact filler particles with clean surfaces and often river markings in the surrounding matrix. Crack blunting is often observed in composites with low yield strengths (<100 MPa), particularly those prepared by treating the filler with a release agent [6], [8], [9], [13].

In contrast, crack pinning occurs when filler-matrix adhesion is sufficiently high to resist delamination. Instead, the debond propagates through the matrix. Therefore, composites with yield strengths above 100 MPa often experience crack pinning. Crack pinning is characterized by stable crack growth [13], [14]. SEM micrographs often feature “tails” that extend behind filler particles [10], [15]. In specimens in which a silane adhesion promoter has been used to treat the filler surfaces, microcracks indicative of shear yielding in the matrix have also been observed [10], [16].

The primary goal of the current study is to determine the effect of various silicon oxide filler surface treatments on adhesion of epoxy composite films to silicon oxide. Two epoxies were chosen as representative of the chemistries used in microelectronic packaging. Identical tests were performed on each epoxy, although different silanes were used to complement epoxy chemistry. SEM was used to examine fracture surfaces and verify the fracture mechanism.

Materials and Methods

Two epoxy systems were selected as representative of a broad family of epoxy underfills currently in use in microelectronic packaging. Various silane treatments were also employed to vary the degree of filler-epoxy adhesion. Each of these materials are described in detail before the experimental procedure is outlined.

A. *Aliphatic Epoxy Underfill System*

The aliphatic underfill consists of four components. In addition to a resin and curing agent, two additional components are required to transform the anhydride curing agent into an alkoxide ion capable of attacking one of the carbon atoms of the resin’s epoxy groups [17]. These two additional components are referred to as accelerators because they take part in intermediate curing reactions. This series of reactions is described in greater detail elsewhere [17].

The resin molecule; 3,4-epoxycyclohexylmethyl-3,4 epoxycyclohexanecarboxylate; methylhexahydrophthalic anhydride curing agent and n,n-dimethylbenzyl amine accelerating agent were obtained from Vantico Inc., East Lansing, MI. The second accelerating agent, ethylene glycol, was obtained from Aldrich of Milwaukee, WI.

This epoxy was prepared by mixing 100 parts (by weight) resin with 100 parts curing agent and 5 parts each of both accelerating agents. The cure cycle of three hours at 125°C followed by one hour at 200°C was performed in atmosphere.

B. *Bisphenol-F-based Epoxy Underfill System*

The bisphenol-f-based epoxy is a simple two-component system. The resin is diglycidyl ether of bisphenol-f and epichlorohydrin, and the curing agent is 2-ethyl-4-methyl-1H-imidazole. The series of curing reactions is described in greater detail elsewhere [18], [19]. The resin was obtained from Resolution Performance Products, Houston, TX, and the curing agent was from Air Products & Chemicals, Allentown, PA. The resin was mixed with 4 pph (parts per hundred, by weight) curing agent, and the cure cycle of four hours at 60°C followed by two hours at 150°C was performed in atmosphere.

C. *Selection of Silanes*

Adhesion promoters or coupling agents are short ($2 \leq n \leq 18$), linear, organic molecules with reactive functional groups at each of their two ends. Ideally each end is able to bond to a different material, increasing adhesion of two layers that might otherwise easily delaminate. What characterizes silanes is a distinct a trichloro- or trialkoxy-group that bonds with an oxide or similar substrate during deposition. At the other end of the molecule is typically an amine, vinyl, methacrylate, chloro, mercapto, or other functionality [20]. Typically, silanes are selected for use based on this functional group and its potential reactivity with layers that are to be deposited onto the oxide substrate [3], [21].

For the present study, silanes were selected which mimic the functional groups of each epoxy that take part in the curing reactions. The four silanes selected for use with the aliphatic epoxy are (1) 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECS); (2) 2-

trimethylsilylethanol (TMSE); (3) γ-aminopropyltriethoxysilane (APS); and (4) ethyltrimethoxysilane (ES). ES was included as a control silane treatment because it is not expected to react with the epoxy. Table I lists the chemical formulas and describes which epoxy component each silane represents. No silane was readily available to mimic the curing agent.

The silanes selected for the bisphenol-f epoxy are (1) 3-glycidoxypropyltrimethoxysilane (GPS), (2) γ-aminopropyltriethoxysilane (APS), and (3) ethyltrimethoxysilane (ES). In this case as well, ES was included as a control silane. Table II lists the chemical formulas of these silanes and describes their relationship to the epoxy components.

Solutions of the silanes were prepared by dissolving one part silane in 100 parts deionized water and diluting with ~900 parts methanol to produce a 0.1wt% solution. A few drops of propylamine were added as a catalyst to solutions of silanes not containing an amine group [22].

D. *Specimen Preparation*

The two specimen configurations employed are illustrated in Figure 1. First, adhesion energy of the interface between silicon oxide, selected silanes, and epoxy was quantified using the native oxide of silicon wafers to model the spherical filler surface. No filler was included in these initial “layered” specimens. A second set of “composite” specimens was created by coating spherical silicon oxide filler (3 μm average size) with a silane and mixing the filler with epoxy to create a composite comprising 40wt% filler. The filler was obtained from Inabata America Corp., New York, NY. These particles were coated with silanes by mixing approximately 10g silicon oxide particles with 15mL of silane solution and drying the mixture at 50°C. The particles were then rinsed in acetone to remove excess silane and dried again at 50°C.

Silicon wafers with native oxide (e.g. 10-15Å) were used as substrates for both specimen configurations. The wafers were cleaned in 9:1 H_2SO_4:H_2O_2 at 120°C for 20 minutes before being rinsed with deionized water and dried in a spin rinse dryer. Solutions of various silanes were then deposited on the wafers designated for the “layered” specimen geometry by spin coating within a few hours of mixing the solutions. Wafers were not rinsed or cured on a hot plate following silane deposition. For the “composite” specimens, wafers were not treated with silane.

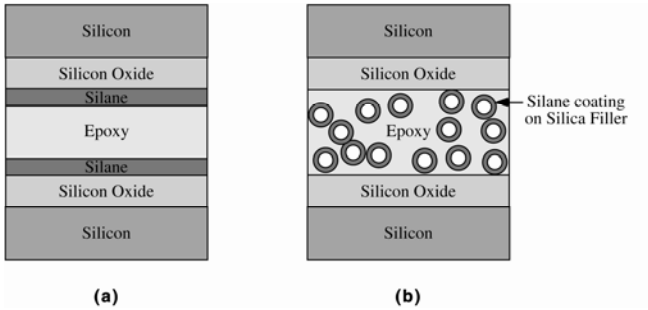

Figure 1. Two specimen geometries used to test epoxy adhesion energy. (a) “Layered” geometry in which the native oxide of the wafer was used to approximate adhesion of epoxy to silica filler. No filler was used in this sample geometry. (b) “Composite” geometry in which silica filler was coated with silane. Silanes were not used to treat wafers in these specimens.

Table I
Silanes used in this research to study the effect functional group on aliphatic epoxy adhesion.

Name	Abbr.	Formula	Feature
2-(3,4-Epoxycyclohexyl)-ethyltrimethoxysilane	ECS	$OC_6H_3(CH_2)_2Si(OCH_3)_3$	Functional group mimics epoxy groups on resin.
2-Trimethylsilylethanol	TMSE	$OH(CH_2)_2Si(OCH_3)_3$	Hydroxyl (OH) functional group mimics ethylene glycol accelerating agent.
γ-Aminopropyltriethoxysilane	APS	$NH_2(CH_2)_3Si(OC_2H_5)_3$	Amine functional group mimics N,N-dimethylbenzyl amine accelerating agent.
Ethyltrimethoxysilane	ES	$CH_3CH_2Si(OCH_3)_3$	Non-reactive CH_3 end group. “Control” silane treatment.

Table II
Silanes used to study effect of functional group on bisphenol-f epoxy adhesion.

Name	Abbr.	Formula	Feature
3-Glycidoxypropyltrimethoxysilane	GPS	$OCH_2CHCH_2O(CH_2)_3Si(OCH_3)_3$	Functional group mimics epoxy groups on resin molecule.
γ-Aminopropyltriethoxysilane	APS	$NH_2(CH_2)_3Si(OC_2H_5)_3$	Amine functionality mimics curing agent.
Ethyltrimethoxysilane	ES	$CH_3CH_2Si(OCH_3)_3$	Non-reactive CH_3 end group. “Control” silane treatment.

Each wafer was cleaved to create a 40 mm x 40 mm substrate and two 40 mm x 15 mm rectangles. A thin layer of gold was sputtered as a 10 mm strip along the edge of the square substrate. This layer later served as a weak region during testing to bifurcate the crack at the epoxy-wafer interface. Two ends of the substrate were covered with 75 μm Kapton (polyimide) tape to act as a spacer. The substrate and rectangles were placed face to face and held in place with more tape. These structures were then placed on a hot plate at 90°C, while epoxy or filled epoxy composite was dispensed onto the outer ledges using a syringe. Capillary action drew the material through the 15-mm region to fill the entire gap. The specimens were then cured according to the schedule listed above for each epoxy.

The bonded squares were diced into 40mm x 5 mm x 2 mm bend specimens, and tabs were glued to the ends of each specimen containing the gold layer. Specimens were tested in a custom-built micromechanical test rig with a servomotor actuator and custom computer control. Critical adhesion energies were measured using the double-cantilever beam (DCB) specimen geometry. In this configuration, strain energy release rate, *G*, is a function of critical load, P_c, at the start of debonding and the length of the debond, *a*, immediately prior to debond extension. *G* is given by [23], [24]:

$$G_c = \frac{12P_c^2a^2}{Eb^2h^3}\left(1-0.64\frac{h}{a}\right)^2, \quad (1)$$

where *E* is the biaxial modulus, b is the specimen width, and *h* is the half-height. Debond lengths were measured in-situ using both optical microscopy and beam compliance relationships. DCB tests were completed with a constant crosshead speed of 2 μm/s, which resulted in a crack velocity of ~20 μm/s. This test involves normal (mode I) loading only, as indicated by the phase angle of ~0°.

A Hitachi 2500 SEM with a LaB_6 filament was used to analyze the fracture surfaces of the composite specimens. All micrographs were captured digitally with the detector in secondary electron mode. An accelerating voltage of 15 kV was used throughout.

Results and Discussion

A. Aliphatic Epoxy System

Adhesion energies for the aliphatic epoxy are plotted in Figure 2. Figure 2a presents the values obtained from the layered test structures containing no filler. It is immediately apparent that ECS is the only silane to augment adhesion of this epoxy to silicon oxide. This result is reasonable, since this is the only silane tested that mimics either the resin or curing agent, which take part in the final curing reaction. The other two silanes, TMSE and APS, slightly degraded adhesion of epoxy to silicon oxide. Unlike ECS, these silanes mimic accelerating agents, which only take part in intermediate reactions. The present results suggest that TMSE and APS only bonded to epoxy components during intermediate curing reactions, if at all, and are not tightly bound to the crosslinked epoxy network. The layered specimen results agree with Plueddemann’s [21] suggestion that for high interfacial adhesion energy, silanes should be selected to mimic epoxy cure chemistry.

Figure 2b presents adhesion energies for composite specimens in which these same silanes were used to coat silicon oxide filler. (Note that wafers were not coated in these specimens.) The opposite trend is now evident: the silanes that proved least effective as adhesion promoters are now most effective as toughening agents, resulting in the highest composite-wafer adhesion energies. These results are consistent with more recent investigations of bulk epoxy composite specimens with silane-coated filler [13]. The data suggest that filler-epoxy delamination, or crack blunting, may be the principal deformation mechanism in the aliphatic composite. Subsurface debonding above and below the plane of the crack may have contributed to energy dissipation. Examination of fracture surfaces with SEM would reveal the mechanism. Thus far, the mechanical data indicate crack blunting. However, previous studies of similar composites prepared with silanes predict crack pinning.

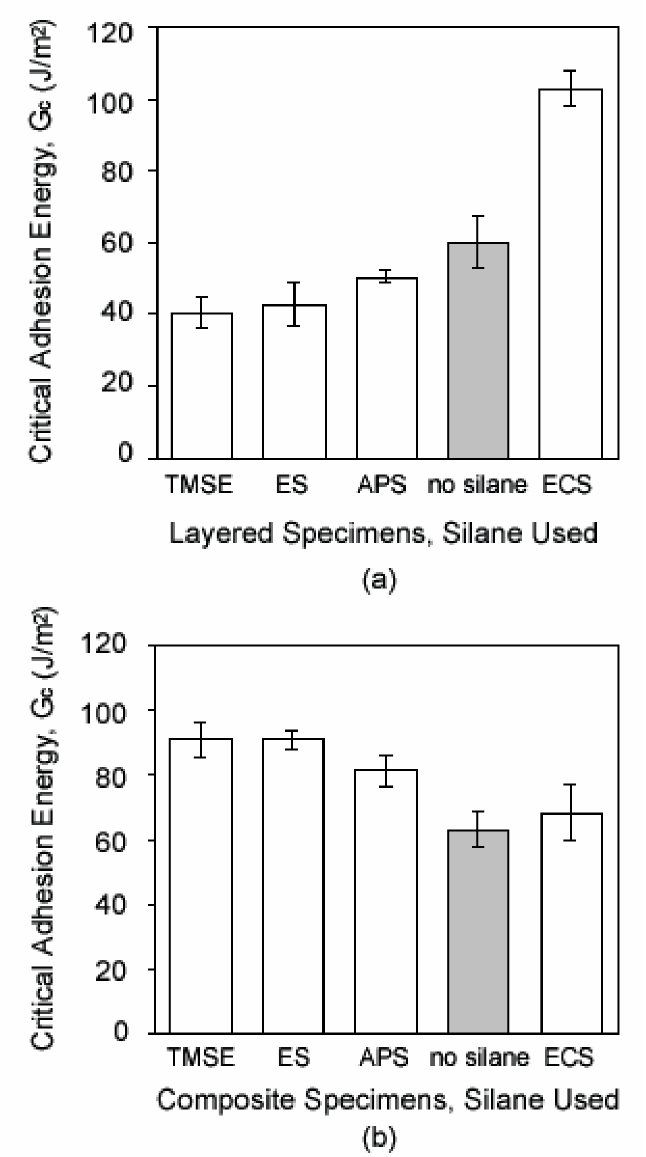

Figure 2. Adhesion energies in aliphatic epoxy system. (a) Simple layered structures in which wafer oxide models filler. (b) Composite structures with 40wt% silane-coated filler.

SEM micrographs for fracture surfaces of selected composite specimens are included in Figure 3. Figure 3a and b present mating fracture surfaces of a specimen prepared with TMSE, characteristic of specimens with the highest adhesion energies. Figure 3c and d consists of fracture surfaces of a specimen prepared with ECS, which are representative of specimens with the lowest adhesion energies. These micrographs do not clearly indicate either of the two deformation mechanisms described above.

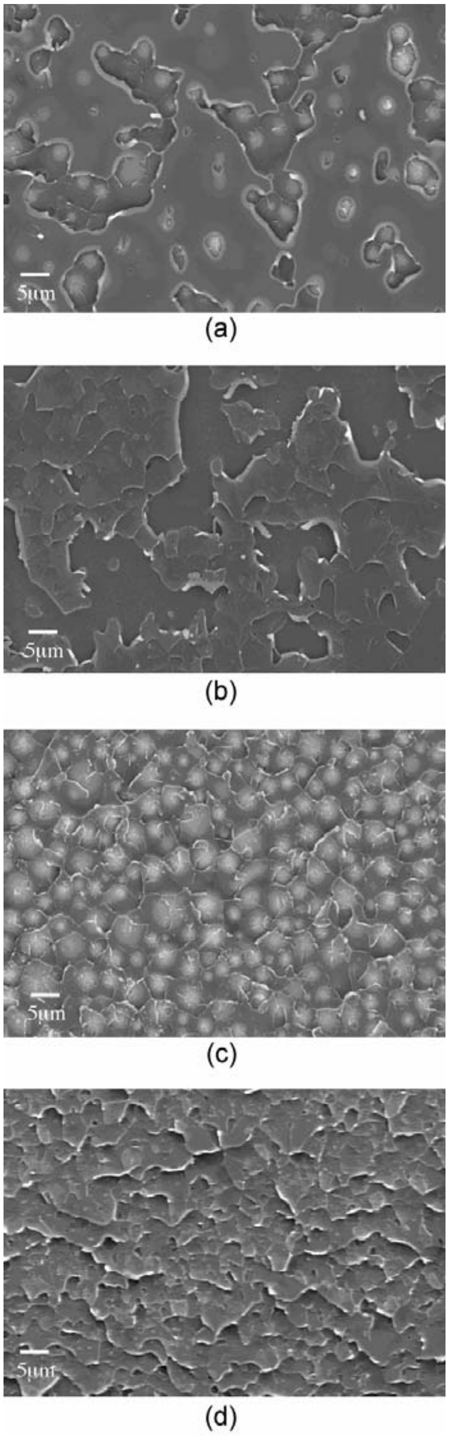

Figure 3. SEM fractography of aliphatic composites. (a) Polymer side and (b) Wafer side of specimen with highest adhesion energy, which exhibits both interfacial and cohesive failure. (c) Polymer side and (d) wafer side of specimen with lowest adhesion energy, which shows only cohesive failure within the epoxy. The direction of crack propagation is from the top of this page to the bottom.

The trend indicated by the mechanical data, that of lower filler-epoxy adhesion resulting in higher composite-wafer adhesion energy, suggests some degree of filler-epoxy delamination, or crack blunting [13], [14]. However, the clean filler surfaces indicative of crack blunting are not evident. The micrographs more closely resemble those previously published for crack pinning. The features directly above the filler surfaces in Figure 3a and c are most likely microcracks in the epoxy. A small amount of debonding at the epoxy-filler interfaces may have occurred, but not enough to force the crack tip to blunt and follow the contour of the filler surfaces.

It may be the case that failure occurs too close to the interface between the composite and wafer to be comparable to bulk deformation mechanisms. Most of the fracture in these specimens is cohesive, through the epoxy, but very close to the filler surfaces. The specimens with the highest adhesion energies also exhibit some adhesive failure between the composite and wafer, as indicated by flat areas in Figure 3a. This combination of cohesive and adhesive failure suggests that the variation in adhesion energies can be attributed to the surface energy contribution associated with fracture paths of differing length. In the toughest specimens, the fracture path alternates between (1) a plane defined by the settling of filler and (2) the epoxy-wafer interface. This proposed fracture path is illustrated in Figure 4. In specimens with lower adhesion energies, the path is restricted to the settling plane. Although the fracture surfaces of specimens with the lowest adhesion energies (Figure 3c and d) may appear rougher, AFM verifies that the path in Figure 3a and b is longer. As determined by tapping mode AFM (Digital Instruments MultiMode SPM with type D piezoelectric scanner), the height range of the specimens in Figure 3a and b is 2.8 µm, while the range in 3c and d is only 1.7 µm.

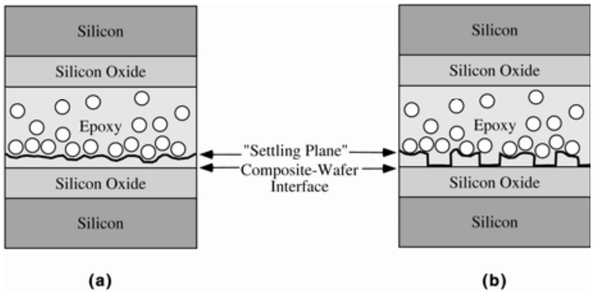

Figure 4. Schematic representation of the two fracture planes of aliphatic specimens. (a) Schematic of weakest specimens (Figure 3b) in which the crack follows the plane defined by settling of filler. (b) Schematic of the toughest specimens (Figure 3a) in which the crack alternates between the composite-wafer interface and the plane defined by settling of filler.

It is clear from these results that treatment of filler with silanes does not significantly augment adhesion of filled aliphatic epoxy to silicon oxide. However, based on the results presented in Figure 2a, it is likely that treatment of wafers with silanes would.

A. Bisphenol-F Epoxy System

Adhesion energy results for the bisphenol-f-based system are plotted in Figure 5. Figure 5a presents the values obtained from the layered test structure containing no filler. Unlike the aliphatic epoxy system discussed, none of the silanes tested with the bisphenol-f system degraded adhesion between silicon oxide and epoxy. Both APS and GPS were found to augment adhesion energy, presumably because they formed covalent bonds with the cured epoxy. ES had no effect on epoxy-wafer adhesion, even though the contact angle of specimen wafers was observed to change dramatically upon deposition of the silane.

Figure 5b is a plot of adhesion energy of the composite specimens. It is apparent that coating the filler had no effect on toughness of the composite samples. (Note that wafers were not coated in these specimens.) These results indicate that filler-epoxy delamination is not a significant mechanism in the bisphenol-f system. In other words, the adhesion energy of the untreated filler-epoxy interface is inherently high enough to resist delamination in composite structures. When this is true, improvement of the filler-epoxy interface has little effect on composite-wafer adhesion.

SEM analysis supports the above interpretation of the adhesion energy data. Figures 6a and b represent typical fracture surfaces, which indicate simple adhesive failure between the composite epoxy films and the wafer. A few specimens exhibited a small amount of deformation through the composite layer, which resulted in a few areas in which the entire thickness of composite was transferred to the "wafer side" fracture surface. Figure 6c includes some of these areas. It is to be noted that in all specimens most of the fracture was interfacial between the epoxy and wafer.

In the case of the bisphenol-f-based epoxy, treating filler surfaces with silanes had no effect on the mechanical properties of the composite. Since nearly all delamination occurred at the composite-wafer interface, neither crack blunting nor crack pinning can be interpreted to be the principal deformation mechanism. It is likely that if a release agent, rather than a silane adhesion promoter, was used as a filler surface treatment, delamination at epoxy-filler interfaces, debond propagation through the composite layer, and features indicative of crack blunting would have been observed [6], [8], [9], [13].

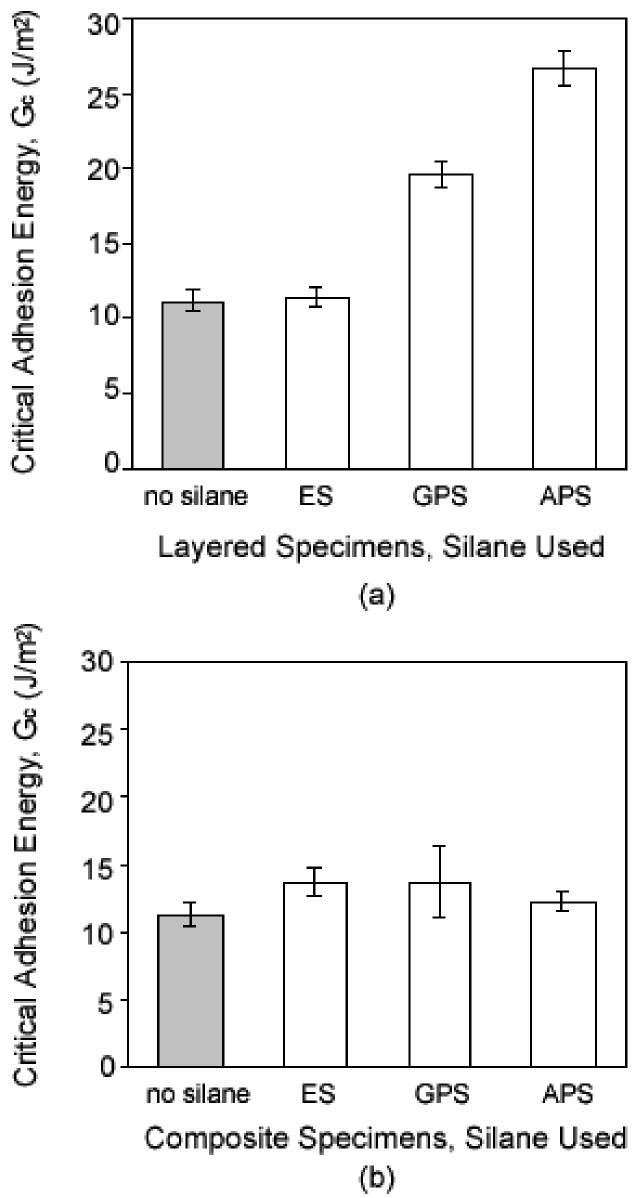

Figure 5. Adhesion energies in bisphenol-f epoxy system. (a) Simple layered structures in which wafer oxide models filler. (b) Composite structures with 40wt% silane-treated filler.

Results from an earlier, preliminary study verify this prediction. In this earlier study, a GPS solution was prepared without an amine catalyst. It is well documented that diminished adhesion energy is observed when no catalyst is included in silane solutions prepared following the most commonly used recipes [25], [26]. The omission of catalyst most likely results in a residue of unreacted silane on the wafer surface. The adhesion energies of the layered test structures prepared with this catalyst-free GPS solution were 10% below that measured when no silane treatment was used (16.9 J/m^2 vs. 15.2 J/m^2). However, the catalyst-free GPS composite specimens were observed to fracture through the composite layer. Adhesion energies of these specimens averaged 60.2 ± 7.0 J/m^2, a full tripling of the adhesion energies presented for specimens prepared with a catalyst (presented in Figure 5b).

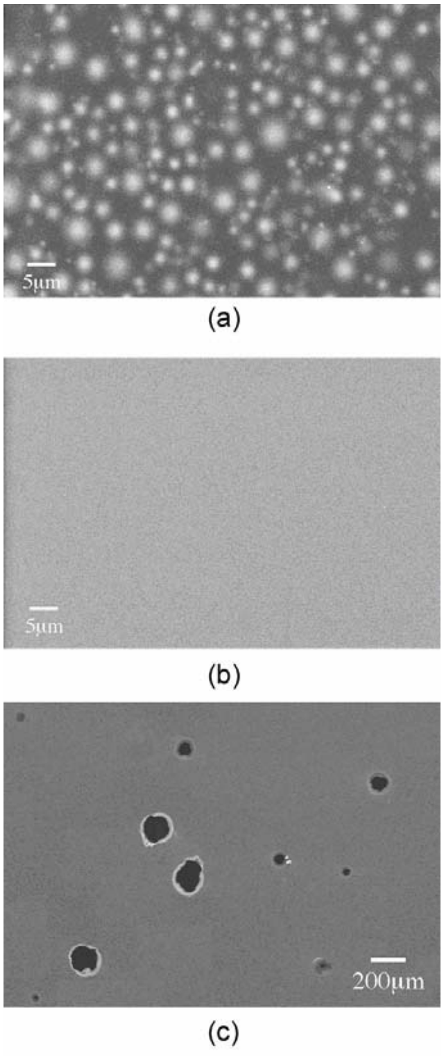

Figure 6. SEM fractography of bisphenol-f composites. (a) Polymer side of typical fracture surface, indicating adhesive failure between epoxy and wafer. (b) Wafer side of same specimen. (c) Lower magnification micrograph of a specimen showing some deformation through epoxy composite layer (wafer side). The direction of crack propagation is from the top of this page to the bottom.

SEM micrographs of mating fracture surfaces of one of these specimens prepared without the catalyst are presented in Figure 7. It is immediately apparent that in these specimens, the crack propagated through the composite layer, rather than at the composite-wafer interface as in other specimens (Figure 6). The smooth, clean filler surfaces evident in Figure 7 are indicative of crack blunting, previously observed in specimens prepared with a release agent [8], [9], [13]. Delamination of the epoxy-filler interface accounts for the dramatic increase in composite adhesion energy. Unlike any of the other specimens in this study, this specimen absorbed energy as it debonded at numerous filler-epoxy interfaces above and below the fracture plane.

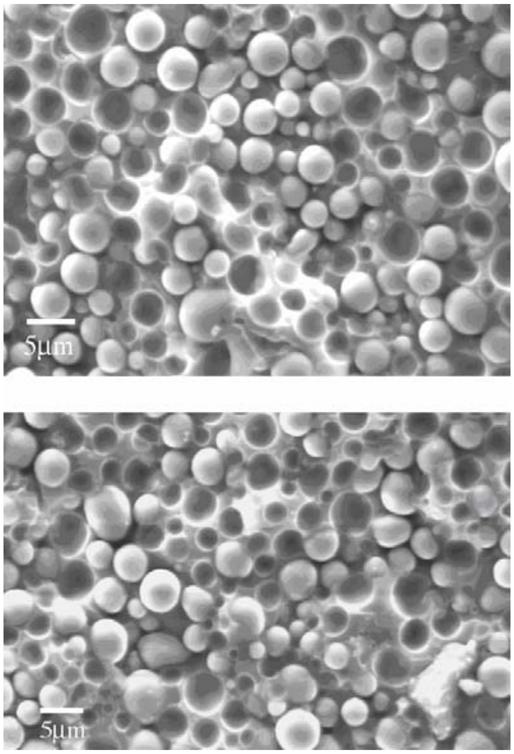

Figure 7. SEM micrographs of mating fracture surfaces of a "mistake" specimen in which silane solution was prepared without a catalyst and acted as a release agent. The direction of crack propagation is from the top of this page to the bottom.

Conclusion

The importance of matching silane reactive functional group to epoxy cure chemistry was verified using two epoxies. Only those functional groups that mimic the epoxies were found to act as effective adhesion promoters between silicon oxide and epoxy. The main focus of the present study, however, was to determine the effect of coating silicon oxide filler with these silanes on adhesion of a thin composite film to a silicon wafer. It was found that silanes which augment epoxy-filler adhesion adversely affect macroscopic adhesion of epoxy composites to adjacent silicon oxide layers.

In most cases, fracture was adhesive, at or near the interface between the epoxy composite and silicon wafers, so deformation similar to that observed in bulk epoxy composites was not observed. In one unique case, the highest adhesion energies were measured for specimens prepared by inadvertent omission of a key silane solution ingredient during an early preparation step. In these specimens, the silane treatment acted as a release agent rather than an adhesion promoter, allowing delamination at filler-epoxy interfaces above and below the fracture plane to dissipate the highest amount of energy.

Ultimately, this study indicates that the highest composite-wafer adhesion energies could be achieved by (1) coating the wafers with a silane which mimics epoxy functional groups involved in the final curing step and (2) coating filler particles with a release agent, such as a silane mixed without a catalyst.

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