

Adhesion and Toughening Mechanisms at Underfill Interfaces for Flip-Chip-on-Organic-Substrate Packaging

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Abstract—The flip-chip-on-organic-substrate packaging technology utilizes a particulate reinforced epoxy as the underfill (UF) to adhere the chip to the package or board. Although the use of underfill encapsulation leads to improved reliability of flip-chip solder interconnections, delamination at various interfaces becomes a major concern for assembly yield loss and package reliability. In spite of their importance, the adhesion and fracture behaviors of the underfill interfaces have not been investigated until recently. Considerable controversy exists over the effects of underfill formulation and the adhesion and toughening mechanisms of the interfaces. The present work focuses on investigating the effects of several key variables on the interface adhesion strengths for UF/chip and UF/organic substrate systems. These variables are underfill organosilane content, filler particle content, rubber particle content, surface morphology and chemistry of the chip and organic substrates. The approach of this study is to measure the effect of these variables on the interfacial fracture energy using the double-cantilever-beam (DCB) techniques. The results demonstrate that the underfill interfacial adhesion and fracture characteristics are controlled by several distinct but competing mechanisms, such as formation of primary bonds, crack-pinning by glass fillers, debonding of glass filler from epoxy matrix (defect formation), and cavitation and shearing induced by rubber particles. Fundamental understanding of the interfacial adhesion and toughening mechanisms can provide guidance for developing new processes and materials to enhance interfacial adhesion and reliability.

Index Terms—Adhesion mechanisms, electronic packaging, flip-chip-on-organic-substrate, glass filler particles, interfacial fracture toughness, organosilane, rubber particles, surface morphology and chemistry, underfill formulations.

I. INTRODUCTION

AS THE performance and functionality of integrated circuits at the chip level continue to improve with increasing device density and reducing device dimensions, the input/output terminal requirements grow accordingly [1]. To utilize the density and performance of the chip technology,

assembly and packaging technology with high performance and I/O counts will have to be developed [2]. The area array flip-chip solder interconnection on organic laminate substrate has the potential to meet these requirements [3]. It has been identified as an enabling technology in the 1997 National Technology Roadmap for Semiconductors [4].

The flip-chip-on-organic-substrate packaging technology utilizes a particulate reinforced epoxy as the underfill to adhere the chip to the package or board. Although the use of underfill encapsulation led to improved reliability of flip-chip solder interconnections, delamination at underfill to chip or/and organic substrate interfaces becomes a major concern for assembly yield loss and package reliability [3], [5]. In spite of their importance, the adhesion and fracture behaviors of the underfill interfaces have not been investigated until recently [3], [6]–[11]. Underfill encapsulant is a filled epoxy system with rather complex chemistry and morphology. A great deal of confusion and controversy exists over the effects of underfill formulation and the adhesion and toughening mechanism of the interfaces. Presumably, once the formulations and mechanisms responsible for good adhesion and increased interface toughness are clearly identified, then the material parameters can be modified to produce an optimal combination of interfacial properties.

The interface fracture energy (or practical adhesion energy) consists of contributions from several distinct mechanisms, such as intrinsic adhesion, plasticity, and roughness (asperity). The interface fracture experiments measure the total energy contributed from all mechanisms, making the interface fracture energy a useful quantity to characterize the materials resistance to interfacial fracture. But it is not a trivial task to separate the intrinsic adhesion energy from energy dissipated in the near-tip crack process zone through other mechanisms, such as plasticity and roughness effects. Much research has been conducted in searching for the correlation between the measured strength of adhesive joints and the thermodynamic work of adhesion (W_A) [12]–[15]. However, some researchers have confirmed such a correlation, while others have found none. The main causes for the discrepancies are: first, the commonly adopted test methods are not suitable for such kind of analysis; secondly, the locus of failure is not truly interfacial; thirdly, when there are primary bonds involved the intrinsic adhesive fracture energy (G_0) is far higher than the thermodynamic work of adhesion (W_A) since the values of W_A assume that only secondary bonds act at the interface. In an effort to correlate the intrinsic adhesion energy

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(G_0) to the measured interface fracture energy G_c , a simple relationship was proposed [16]–[19]:

$$G_c = G_0 \Phi_v(\dot{a}, T, \varepsilon) \quad (1)$$

where $\Phi_v(\dot{a}, T, \varepsilon)$ = mechanical loss function depending on the crack growth rate $\dot{a}$, the test temperature T , and the strain level ε . The validity of this formalism has been demonstrated for a number of systems, such as a cross-linked rubbery adhesive/rigid plastic interface. But it is not clear whether the simple relationship outlined is appropriate for studying epoxy adhesive/substrate interface fracture. Nonetheless, the idea is intriguing and the general dependency of the interface fracture energy on the intrinsic adhesion energy should still hold. The material around the crack tip can be subjected to stress and energy losses only when the chemical and physical bonds acting ahead of the crack tip remain unbroken.

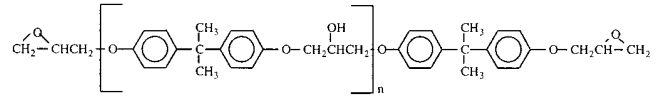
The intrinsic adhesion forces across the interface, especially the nature and the magnitude of such forces, are extremely important to the establishment of good adhesion [20]. The mechanisms of adhesion consider various types of intrinsic forces that may operate at the adhesive/substrate interface. Four major mechanisms have been proposed so far, namely, mechanical interlocking, diffusion theory, electronic theory, and adsorption theory [21]. The adsorption theory is the most widely applicable theory [22] among the four. It proposes that materials adhere because of the interatomic and intermolecular forces established between the atoms and molecules in the surfaces of the adhesive and substrate, provided that there is sufficiently intimate molecular contact at the interface. Depending on the combination of the materials forming the interface, the nature of the bonding can be quite different. Chemisorption involves bonds established across the interface, such as ionic, covalent, and metallic interfacial bonds. Physisorption includes secondary bonds, such as van der Waals forces and hydrogen bonds. While physisorption is most common, chemisorption sometimes may occur.

The objective of this work is to investigate the effects of underfill formulations and the adhesion and toughening mechanism of the interface. The approach is to quantify interfacial fracture energy using the experimental and analytical techniques for the double cantilever beam method developed previously [23] and study the effect of individual variables on interfacial adhesion in UF/chip and UF/organic substrate systems. Discussions will be focused on the effect of underfill filler content, organosilane content, rubber particles, and surface morphology and chemistry of the chip and organic substrates.

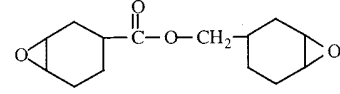
II. MATERIALS

A. Underfill

Underfill encapsulant is normally a filled epoxy-based composite material. Among a variety of polymers considered as potential underfill encapsulants, cycloaliphatic and bisphenol A epoxy resins with anhydride curing agents have been most commonly used as the matrix [24]. In order to reduce the stresses induced by the CTE mismatch between the encapsulant and the substrates, fused silica (SiO_2) filler particles are commonly used to tailor and reduce the coefficient of thermal expansion (CTE) of the encapsulant [25]. In some cases, rubber particles

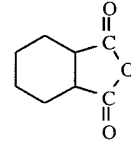


(a) Bisphenol A Epoxy Resin (Diglycidyl Ether of Bisphenol A)

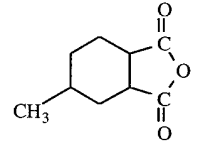


(b) Cycloaliphatic Epoxy Resin

Fig. 1. Structures of the two most commonly used epoxy resins in underfill materials.



(a) Hexahydrophthalic anhydride



(b) Methylhexahydrophthalic anhydride

Fig. 2. Structures of typical acid anhydrides used in underfill.

TABLE I
FORMULATION OF UF-3

Cycloaliphatic / Bisphenol A Epoxy	2:1 ratio
Epoxy Silane	0.40%
Anhydride (stoichiometric)	100%
Elastomer Additive	0.80%
Filler, SiO_2	70%

are added to enhance the bulk fracture toughness of the encapsulant. Organosilanes are frequently used to improve adhesion of the resin matrix to the silica filler particles as well as to the inorganic substrates.

Epoxy resins form hard, tough, cross-linked, three-dimensional polymer networks through reaction with a curing agent (hardener) [26]. Fig. 1 shows the structures of cycloaliphatic and bisphenol A epoxy resins. The basic element of these epoxy resins is the epoxy or oxirane group which is a three-membered ring consisting of one oxygen and two carbon atoms. The strained nature of this three-membered ring makes it highly reactive.

The cross-linking or curing is accomplished through specific chemical reactions with various curing agents and catalysts. Acid anhydrides are widely used as curing agents in underfill encapsulants because of the attractive features of anhydride-cured epoxy resin systems, such as relatively low-viscosity, comparatively long pot lives and low exotherms when cured [24]. Typical curing agents are hexahydrophthalic anhydride and methylhexahydrophthalic anhydride with the structures shown in Fig. 2.

To study the effects of varying the type and amount of each component, a number of underfill materials were formulated and interfacial fracture energy values were measured. Table I lists the formulation of UF-3, which is typical for an anhydride-cured underfill material. All values are in weight percentage unless otherwise specified. Other formulations with

TABLE II
VARIABLES AND VARIATIONS RELATIVE TO UF-3 FOR
CUSTOMER-FORMULATED UNDERFILLS

	UF-3	UF-4	UF-7	UF-8	UF-9
Cycloaliphatic	x	x	x	x	x
Bis phenol A	x	x	x	2X	x
Silane	x	2X	x	x	x
Anhydride	x	x	x	x	0.85X
Elastomer	x	x	0	x	x

(Note: UF-3 is the base-line formulation)

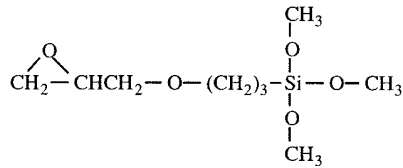


Fig. 3. Structure of gamma-glycidoxypyrtrimethoxysilane.

changes relative to UF-3 (base-line material) are tabulated in Table II. For each custom formulation, there was only one component changed.

An organofunctional silane, glycidoxypyrtrimethoxysilane, was used as an adhesion promoting additive (Fig. 3) in these epoxy resins.

B. SiliconChip and Organic Substrate

Passivated (100) silicon (Si) wafers were used to simulate the surface conditions of silicon chips. Two types of passivation layer were studied. One was silicon nitride (Si_3N_4). The other was the organic coating material, bisbenzocyclobutene (BCB). The organic substrates were epoxy-coated FR4 board (EP-PCB) and polyimide coated FR4 board (PI-PCB).

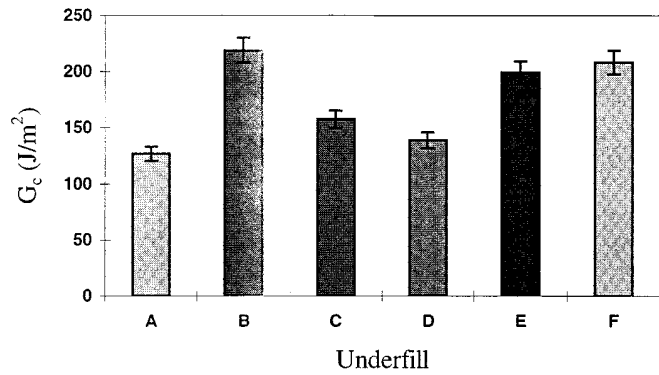
III. RESULTS AND DISCUSSIONS

A. Commercial Underfill Materials

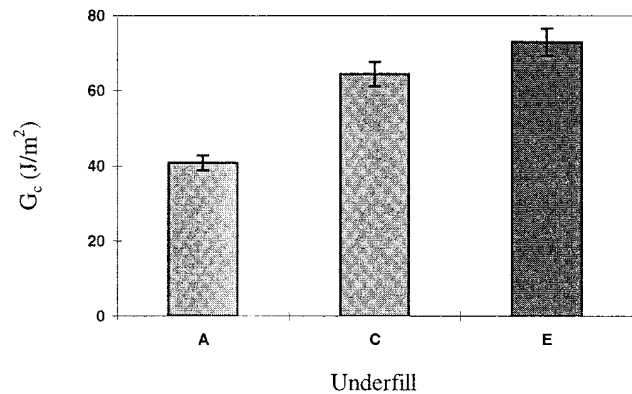
1) *Interfacial Fracture Energy Results:* Fig. 4 shows the interfacial fracture energies measured for different commercial underfill formulations on PCB with epoxy top-layer (EP-PCB), PCB with polyimide top-layer (PI-PCB), and silicon-nitride-passivated-silicon (Si_3N_4 -Si) substrates. From the variation in the values of interfacial fracture energy for different underfill and substrate combinations, it can be seen that adhesion strength is strongly influenced by underfill formulation and substrate type.

From the results presented above, it is evident that the developed techniques for DCB experiments allow reproducible measurements of PCB/underfill and chip/underfill interfacial fracture resistance. It has been shown that the differences between structures of the same underfill with different substrates and different underfills with the same substrate can be distinguished.

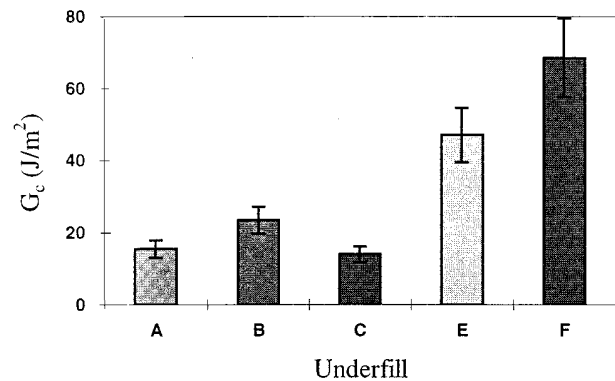
2) *Fracture Characteristics:* Fig. 5 shows the characteristics of unstable brittle crack propagation for UF/PCB interfaces. The load-displacement plot has linear loading lines and saw-tooth shapes. The crack propagates intermittently in a stick-slip manner. An optical micrograph of the fracture surface for a



(a) UF/EP-PCB Interfaces



(b) UF/PI-PCB Interfaces



(c) UF/Si₃N₄-Si Interfaces

Fig. 4. Effects of different underfill formulations on adhesion strength for: (a) UF/EP-PCB interfaces, (b) UF/PI-PCB interfaces, and (c) UF/Si₃N₄-Si interfaces.

PCB/UF/PCB specimen is shown in Fig. 6. On the fracture surface, lines corresponding to jump/arrest event are clearly visible with “stress whitening” zones in between relatively darker regions. The occurrence of a single striation associated with each crack jump/arrest event was confirmed during the test via optical video microscopy.

Crack tip blunting is believed to be responsible for the stick-slip characteristic. In the arrest stage, the crack tip was

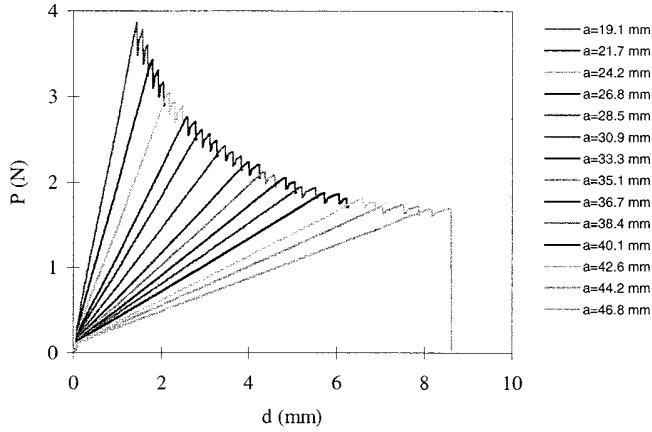


Fig. 5. Typical load-displacement plot for a DCB PCB/UF/PCB specimen.

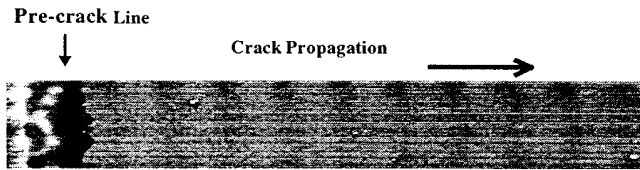


Fig. 6. Fractured surface of the PCB/UF interface with striations marked by crack jump/arrest.

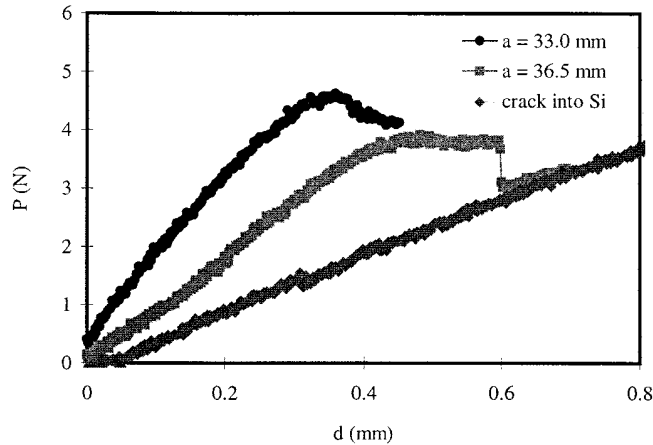


Fig. 7. Typical load-displacement plot for a DCB Si/UF/Si specimen.

blunt resulting from build-up of the near-tip plastic zone and so the crack overloaded until the stress was high enough to resume propagation. Once this occurred the crack tip became sharp and a rapid release in strain energy occurred as the crack propagates rapidly. Consequently, the saw-tooth curve of load against displacement was observed.

By contrast, interfacial fracture at UF/Si₃N₄-Si interface has the characteristics of stable brittle crack propagation as shown in Fig. 7. The load-displacement plot has the non-linear loading portions corresponding to some degree of subcritical crack growth before the peak load is reached. The fracture surface is relatively featureless under the optical microscope. A relatively sharp crack shows a minimum amount of crack-tip plasticity, thus, a lower value of G_c is expected. Similar characteristics were also observed for UF/BCB-Si interfaces.

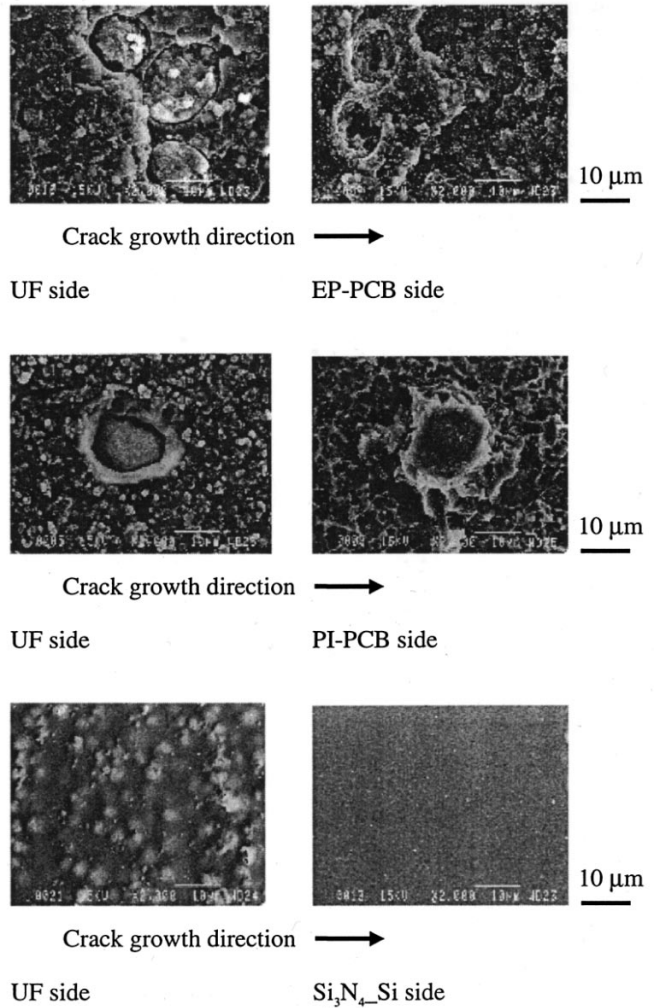
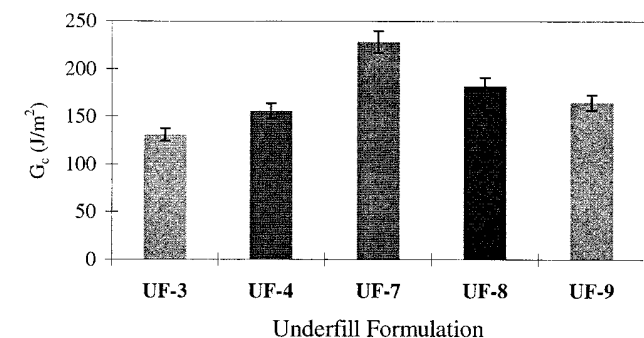


Fig. 8. SEM micrographs of the fractured surfaces for UF/EP-PCB, UF/PI-PCB, and Si₃N₄-Si/UF interfaces.

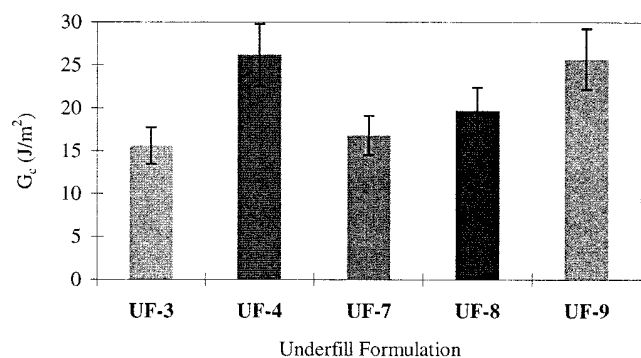
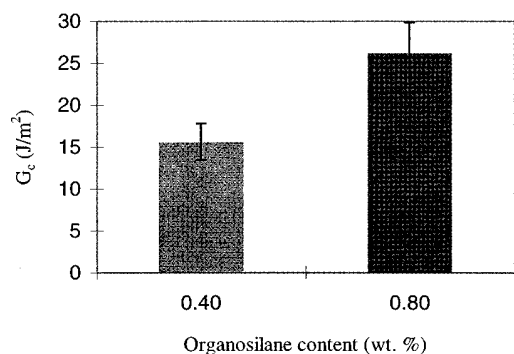
SEM micrographs of the fractured surfaces for UF/EP-PCB, UF/PI-PCB, and Si₃N₄-Si/UF interfaces are shown in Fig. 8. For UF/passivated silicon specimens, the fracture occurred right at the interface. SEM analysis did not show any UF residual left on the passivated silicon. For UF/EP-PCB and UF/PI-PCB specimens, the fracture occurred very close to the interface, but clearly within the underfill since there is underfill left on both sides of the fractured specimens. Fig. 8(a) and (b) also shows that there are epoxy resin/filler particle interfacial failures within the underfill. While most of the filler particles were retained in the underfill epoxy resin, some of them were pulled out and left on the PCB substrate side, and a few were even shattered during the experiment.

B. Results on Custom-Formulated Underfill Materials

1) *Effects of Chemical Formulations:* Fig. 9 highlights the results for UF/EP-PCB and UF/Si₃N₄-Si interfaces for custom-formulated underfill materials. It is quite clear that adhesion strength is strongly influenced by underfill formulation. The mechanisms behind the observed differences in interface fracture energies are believed to be the changes in the nature and



(a) UF/EP-PCB interfaces

Fig. 9. Adhesion energies of custom-formulated underfills for (a) UF/EP-PCB interfaces; (b) UF/Si₃N₄-Si interfaces.Fig. 10. Effect of organosilane content on adhesion energies for UF/Si₃N₄-Si interfaces.

extent of the interfacial bonding and the variations in underfill plasticity. Some of these effects are discussed in the following subsections.

2) *Effect of Organosilane*: The results in Fig. 10 show that by doubling the organosilane content the underfill/Si₃N₄-Si interfacial fracture energy increased by 68% from 15.6 J/m² to 26.2 J/m². A finite element analysis [23] showed that plastic dissipation contributes only about 10% to the total adhesion energy within this fracture energy range for UF/Si interfaces. The crack separation energies can be estimated to be 14.2 and 23.3 J/m² respectively—still a 64% increase. The crack separation energy is believed to be directly proportional to (if not equal to) the intrinsic adhesion energy, which relates to the bonding forces acting across the interface. Therefore, the enhancement

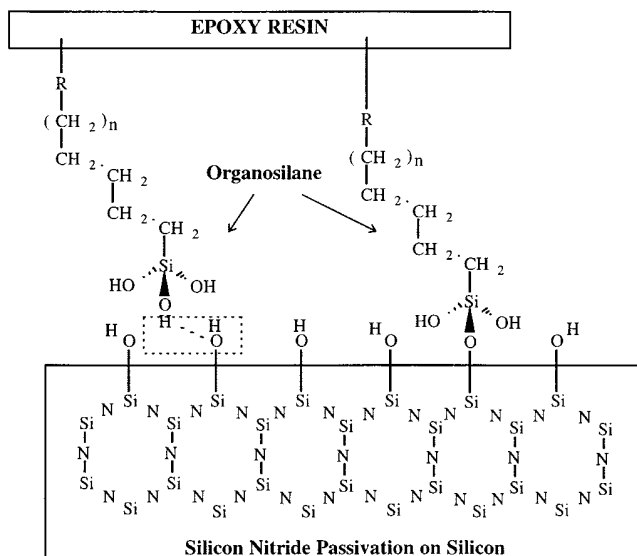


Fig. 11. Schematic of coupling mechanisms through organosilane.

of intrinsic adhesion between underfill and silicon nitride surfaces due to organosilane addition is evident.

A recent study by Vincent *et al.* [27] reported similar effects of organosilane additives to improve underfill adhesion to passivated silicon although the results suffered from large scattering due to the shear test method chosen for their adhesion measurement.

One possible mechanism is illustrated schematically in Fig. 11. The adhesion enhancement can arise from the formation of hydrogen bonds with hydroxyl groups on the substrate surface and Si-O-substrate bonds via condensation reactions between -SiOH group (or Si-OCH₃ group if organosilane is not hydrolyzed) in organosilane and hydroxyl group on the substrate surface. In addition, the epoxy functional group in the organosilane could react with reactive groups in the underfill epoxy resin to form strong covalent bonds. Although the formation of covalent bonds alone may not fully account for the observed difference in the adhesion energy, additional mechanisms, such as localized plastic dissipation, roughness effects, and cohesive failure of the polymer, may also be induced during fracture and contribute to the total energy dissipated. Recent investigations by Swadener *et al.* [28] on the fracture of a glass-epoxy interface have shown some evidence for breakage of covalent bonds in the epoxy molecule and for localized inelastic deformation in epoxy on the nanoscale.

Organosilane coupling agents for structural adhesives and composites have been studied previously [29]–[32]. They have been used to enhance adhesion between organic matrices and inorganic reinforcements (fillers) or between adhesives and inorganic substrates. A number of previous studies also reported adhesion enhancements through silane coupling agents in similar systems of polymer on either glass substrate or glass filler [33]–[35]. The generally, but not universally, accepted mechanism of adhesion is the formation of strong primary interfacial bonds. Similar to the one shown in Fig. 11, it arises from the formation of Si-O-substrate (or Si-O-filler surface) bonds and from the reaction of the organo-functional group of

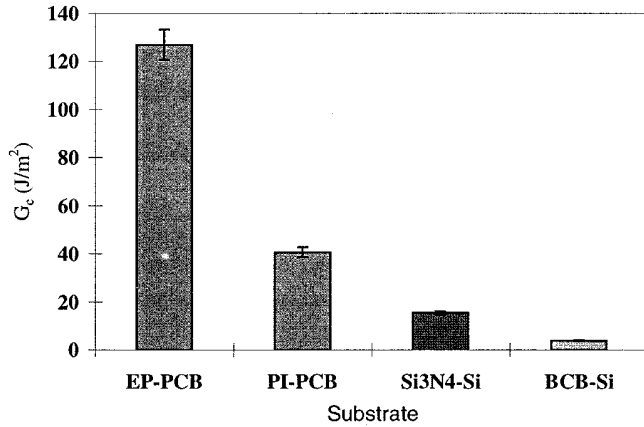


Fig. 12. Adhesion energies of the UF-A/EP-PCB, UF-A/PI-PCB, UF-A/Si₃N₄-Si, and UF-A/BCB-Si interfaces.

the silane with reactive groups in the adhesive (or the organic matrix). The structure shown in Fig. 11 is a simplified one because some form of interpenetrating network structure, which is not shown, may be formed on both ends of the organosilane molecule. It was found that an increased silane content may not always be beneficial and optimum adhesion can be reached at certain intermediate levels corresponding to one or two mono-layers of silane on the inorganic substrate or filler surface. This is because higher content can result in the formation of brittle polysiloxane and lower content does not provide enough coverage for coupling. Neither case is desirable for optimum adhesion strength.

Elucidating the exact mechanism and establishing the presence of Si-O-Si bonding across the organosilane/SiN interface would require experimental investigation of the interfacial structure using modern surface analysis techniques. Such an experiment using Internal Reflection Spectroscopy (IRS) to analyze the interface region directly could be proposed for future work based on the approach demonstrated by Garton [36].

Several investigations like this have been carried out on similar systems, largely for silane coatings on glass surfaces from aqueous solution. Most noticeable are the studies by Chiang *et al.* [37] employing Fourier transform infrared spectroscopy and by Koenig and Shih [38] using laser Raman spectroscopy. They have clearly shown the presence of Si-O-Si bonding across silane/glass interfaces.

3) *Effect of Substrate*: Fig. 12 highlights the interfacial fracture energies of the UF-A/EP-PCB, UF-A/PI-PCB, UF-A/Si₃N₄-Si, and UF-A/BCB-on-Si interfaces. The results indicate that the underfill adhesion strength in this case is strongly dependent on the type of top-layer on the PCB substrate and the passivation layer on the silicon. Also, the PCB interfaces are significantly more robust than the passivated silicon interfaces. This is in agreement with failure analysis results for plastic flip-chip packages, which indicate that delamination almost always occurs at the underfill/die (passivated silicon chip) interface. Similar trends in the relative strength of underfill adhesion to these substrates have also been observed for other underfill materials. The difference can be attributed to difference in the type and extent of bonds that are formed

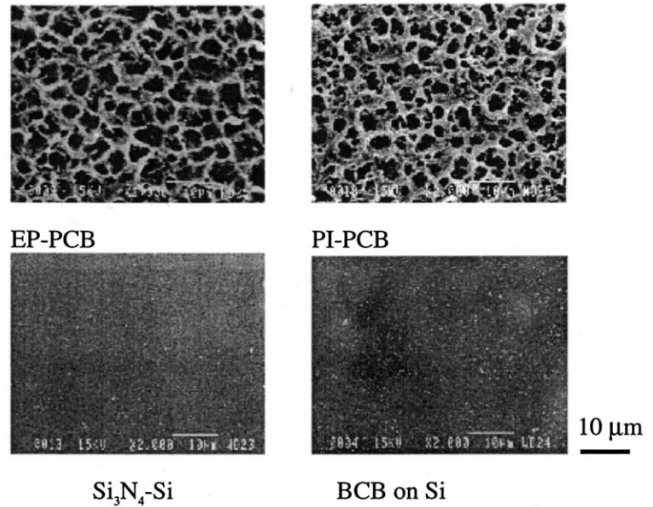


Fig. 13. SEM micrographs of the substrate surfaces before testing.

across the interfaces as well as to substrate surface roughness and polymer plasticity.

Fig. 13 shows SEM micrographs of the substrate surfaces before test. It is evident that the surfaces of EP-PCB and PI-PCB substrates are significantly rougher than silicon nitride passivated silicon and BCB on silicon.

For both EP-PCB and PI-PCB, the surface has porous micro-fibrous features that represent the negative imprint of the copper foil treatment after the copper has been etched away. As noted by Evans and Packham [39] in the study of polyethylene/fibrous oxide interface, this kind of surface topography can lead to a greater area for interfacial contact and enhancement of localized energy dissipation if the adhesive can wet the porous surface. The topography of the PCB substrate causes high shear stresses around the tips of the porous fibrous texture. Hence, failure at the interface region would occur by plastic deformation of the underfill resin initially around the fibrous tips, going further into the bulk of the underfill as the stress concentration is relieved. A much greater volume of the underfill resin will be plastically deformed during fracture, compared to the volume that is deformed when bonding to a chemically similar but smooth surface. It is evident that there is a significantly larger degree of plastic deformation in the UF/PCB interface region than in the UF/passivated silicon interface region as we compare the appearances of the fractography (Fig. 8). This large amount of localized plastic deformation accounts for the high fracture energy measured for UF/PCB interfaces. This localized plastic deformation was not modeled by the finite element model which was based on continuum fracture mechanics and treated the underfill as a homogeneous material without separating epoxy resin and filler particles.

As we compare the UF/EP-PCB and UF/PI-PCB interfaces, the difference in the fracture energy is believed to originate from the difference in the intrinsic adhesion between the underfill epoxy resin to the epoxy top-layer and to the polyimide top-layer since the two interfaces have very similar (physical) morphology. Although the degree of plastic dissipation at the crack tip could also differ, they could well be caused by the

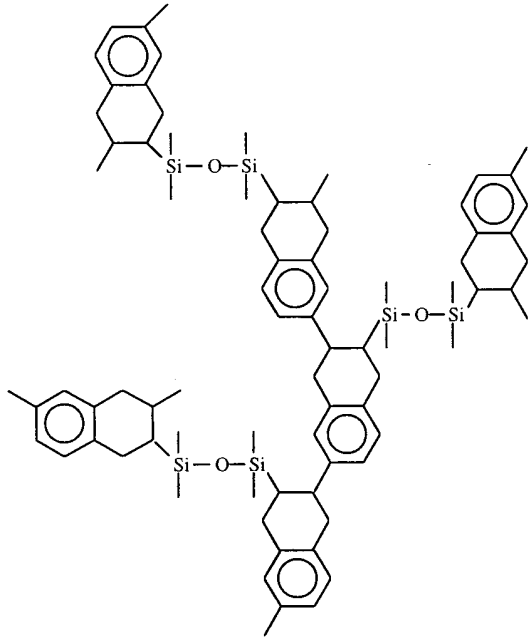


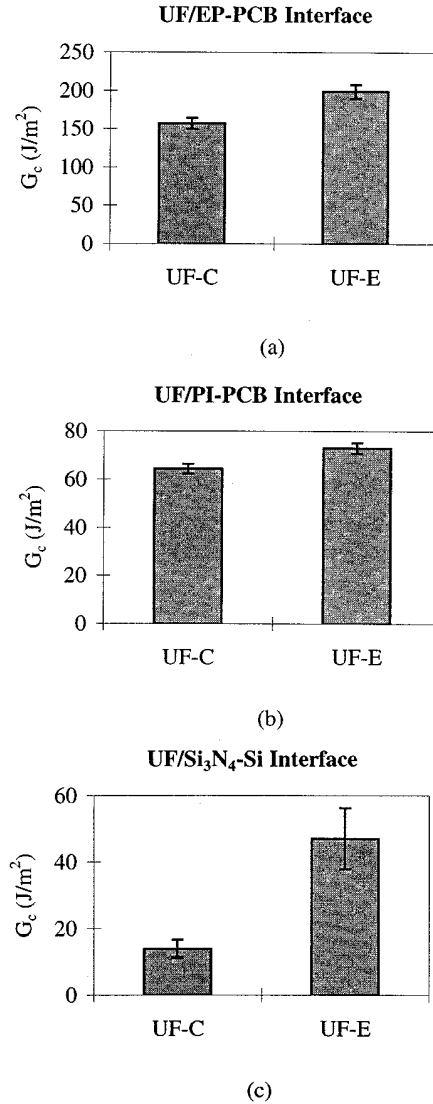
Fig. 14. Chemical structure of BCB.

difference in the intrinsic adhesion. At this time the nature of the bonding is not clear. But it is quite certain that there are stronger intermolecular interactions (secondary or primary) for epoxy to epoxy as opposed to epoxy to polyimide.

In comparing Si_3N_4 passivation and BCB coating on Si, the observed difference in underfill adhesion may be accounted for by different surface chemistry. BCB (as shown in Fig. 14) has a very stable and “inert” chemical structure once it is cured. The mechanism of adhesion through organosilane proposed for silicon nitride (Fig. 11) is very unlikely to take place for UF/BCB adhesion because of the following two reasons. First, it is difficult to introduce the hydroxyl group into such a non-polar structure. Secondly, the density of silicon atoms is quite low on the BCB surface.

4) *Effect of Filler Content:* Among the underfills studied, UF-C and UF-E are known to have the same resin chemistry but different filler (silica particle) contents. The filler content is about 70% for UF-C and about 55% for UF-E. The results in Fig. 15 show that the underfill with lower filler content has better adhesion than the underfill with higher filler content to all the three substrates. These effects of filler content are rather complicated. There are a number of mechanisms that could be postulated. The effect could be a result of some or all of these mechanisms.

One mechanism can be explained using the data shown in Table III, which takes into consideration the change in underfill plasticity caused by differences in filler content. The underlying assumption is that the plasticity of underfill is due to yielding of epoxy resin matrix rather than the filler particles. The ratio of available epoxy resin per unit volume for UF-E vs. UF-C is estimated to be 1.5. The plastic dissipation component of the total energy can be scaled by this ratio. As a result, the separation energies are estimated to be the same for UF/EP-PCB and UF/PI-PCB, regardless of the difference in filler contents

Fig. 15. Adhesion energies of (a) UF/EP-PCB and (b) UF/PI-PCB interfaces for UF-C and UF-E. (c) UF/ Si_3N_4 -Si interfaces for UF-C and UF-E.TABLE III
ESTIMATION OF THE ENERGY DISSIPATION COMPONENTS (UNIT: J/m^2)

Substrate	G_c UF-C	G_c UF-E	G_p UF-C	G_p UF-E	G_s UF-C	G_s UF-E
EP-PCB	157.5	199.3	50.4	95.7	107.1	103.6
PI-PCB	64.4	73	12.9	21.9	51.5	51.1
Si_3N_4 -Si	14	47.1	1.3	6.6	12.7	40.5

of these two underfills. The localized plastic deformation due to the micro-fibrous topography of the PCB substrates was not modeled by the finite element model, which was based on the continuum fracture mechanics [23]. The actual values for the plastic dissipation G_p should be larger and the values for the separation energy, G_s , should be smaller. This simplified model seems to offer one explanation for the effect of filler content on UF/PCB adhesion.

However, the difference in the plastic dissipation can not explain the difference in the intrinsic adhesion energy of the

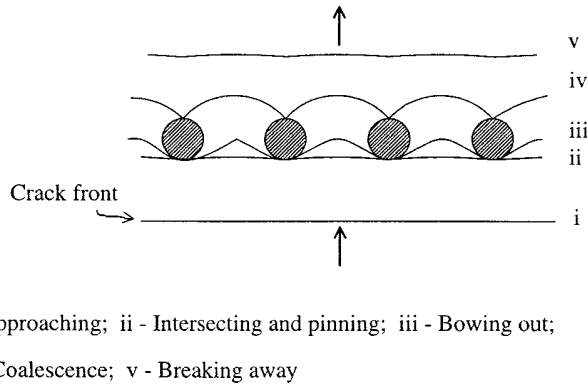


Fig. 16. Schematic of crack-pinning mechanism in a rigid particle-filled epoxy.

UF/Si₃N₄ Specimens. The mechanism of adhesion through silane coupling could be invoked to explain this discrepancy. The organosilane molecules first have to diffuse to the interface before they can react and couple the underfill resin to the substrate. More organosilane molecules might have reacted but been consumed at the silica filler particle/epoxy resin interfaces if there are more filler particles in the underfill. In this case, there will be less organosilane molecules that can reach the UF/passivated silicon interface to promote adhesion. Therefore, the adhesion strength of UF/passivated silicon is expected to be weaker for the underfill with higher filler content.

The effect of filler on the fracture toughness of particulate-filled polymer composites has been studied previously [40], [41]. Many studies observed that the fracture toughness increases with filler content. Crack pinning is the most commonly accepted mechanism. The mechanism is illustrated in Fig. 16. It [42]–[44] has been demonstrated that with rigid particulate, the dominant mechanism of energy absorption is the interaction of the crack front and the dispersed phase. The increase in fracture energy is due to the energy required to move the crack between particles.

In the regime where the filler content was higher than that required to reach the maxima in fracture energy, it was shown that defects within the composites, like voids or poor particle-matrix bonding could have a significant impact on the overall fracture energies [45]. Composites with the volume fraction of particulate beyond a certain maximum level usually have lower fracture energy, and crack pinning steps are not evident. This is because defect population increases with increasing particulate volume fraction. Thus, the spectrum of fracture energy versus volume fraction can be divided into two regions (Fig. 17). The pinning mechanism controls the fracture energy up to the maxima, and beyond the maxima it is controlled to a large extent by defects in the composites. This could explain our case since the filler contents for UF-C and UF-E are quite high and fall within the defect controlled region.

5) *Effect of Rubber Particles:* Fig. 18 shows that the addition of rubber particles resulted in a significant decrease in fracture energy of UF/PCB interfaces, which seems to be contradictory to previous findings for bulk fracture of rubber-modified epoxy systems [46]–[50].

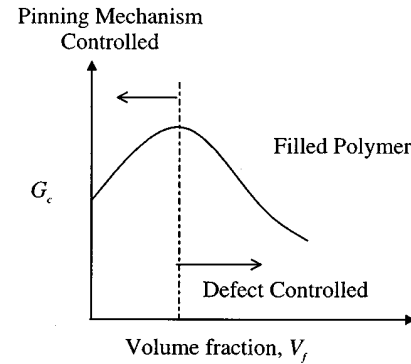


Fig. 17. Two competing mechanisms influencing fracture in rigid particulate-filled polymers. There is a maximum in the fracture energy versus filler content curve.

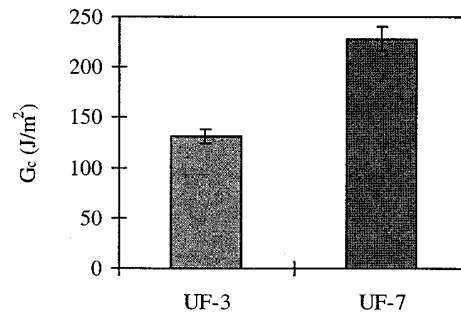


Fig. 18. Effect of rubber particles on the fracture energy of UF/PCB interfaces. UF-3 has 0.8 wt.% rubber particles whereas UF-7 has none.

Rubber-toughening of epoxy systems has been clearly demonstrated and its mechanism has been studied extensively. The toughening was typically achieved by introducing 10 wt.% of small dispersed rubber particles into the epoxy matrix. The generally accepted toughening mechanism is the cavitation of the rubber particles followed by large scale shear yielding of the epoxy matrix [14], [47]–[50]. More recently, it has also been reported that the synergistic toughening could also be promoted in hybrid epoxy composites. Hybrid epoxy composites are epoxy materials modified with both rubbery particles and rigid fillers. Some established evidence showed that the simultaneous occurrence of cavitation/shear banding induced by rubber particles and crack tip pinning mechanisms [49]. Underfill materials certainly belong into the hybrid epoxy composite category. However, there are at least two major complications in the underfill/substrate system. First, the total volume or weight fractions of the rubber and glass fillers in previous work are usually about 10% to 30%. In our case it is much higher, about 70% by weight. Secondly, the previous work described only bulk fracture of the epoxy composites under study whereas in our case the main focus is the fracture of UF/PCB interfaces.

Fig. 19 shows the scanning electron micrographs of fracture surfaces of the UF-3 and PCB sides, where the apparent “holes” in the micrograph are believed to be associated with cavitated rubber particles. In Fig. 20, there is no sign of any cavitation on the fracture surface of UF-7 (the underfill with no rubber

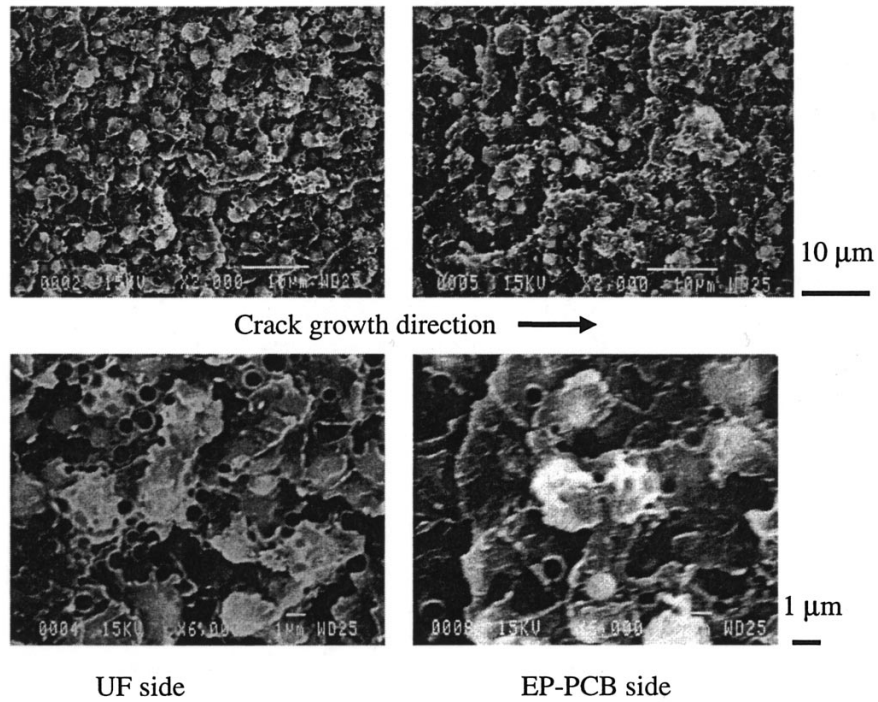


Fig. 19. Scanning electron micrographs of the UF-3/PCB fracture surfaces.

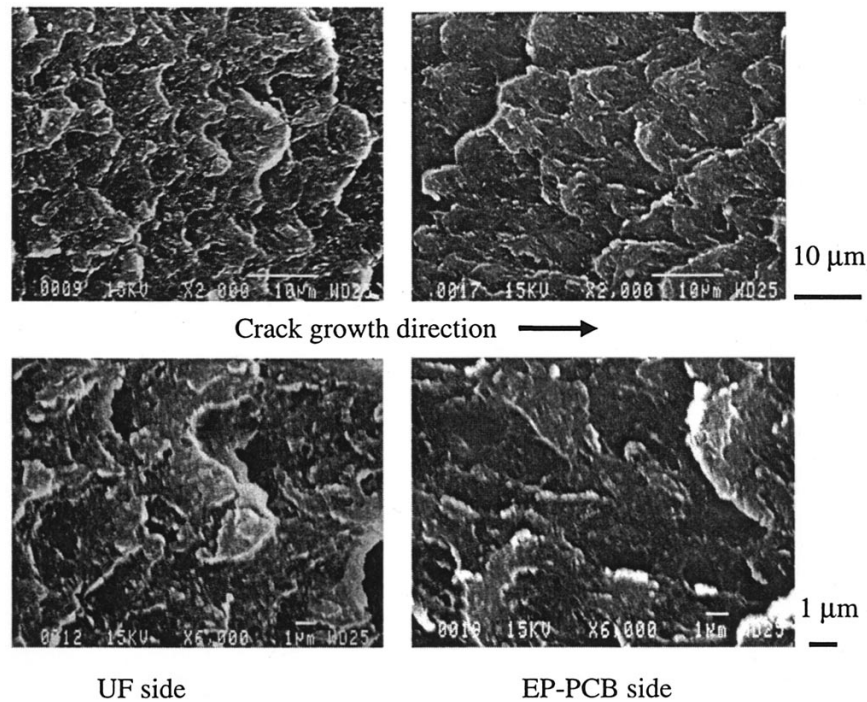


Fig. 20. Scanning electron micrographs of the UF-7/PCB fracture surfaces.

particles). But pronounced fish-scale-like features exist in both cases. These features might be evidence for the operation of crack-pinning mechanism caused by the silica filler particles. A closer look at the vicinity of the filler particles leads to an interesting observation: many filler particles were pulled out and visible on both fractured surfaces of UF-3/PCB system whereas very few filler particles are visible in the case of UF-7/PCB

system. This might be an indication that cavitation of rubber particles near filler particles promoted failure near the filler/resin matrix interface and reduced the effectiveness of the crack pinning by filler particles. At this time it is not clear whether this is the root mechanism for the observed reduction in fracture energy due to the addition of rubber particles. More work is needed to shed light on this matter.

IV. CONCLUSION

The fracture energies of UF/silicon chip and UF/organic substrate interfaces were determined through DCB interfacial fracture experiments and analyses. As demonstrated, the developed techniques allow reproducible measurements of the interfacial fracture resistance. Practical adhesion of the same underfill with different substrates and different underfills with the same substrate can be distinguished.

In order to identify the adhesion and toughening mechanisms, the study focused on the effects of several key variables of UF/chip and UF/organic substrate systems on the interface fracture resistance. These variables were underfill organosilane content, filler particle content, rubber particle content, and substrate surface morphology and chemistry.

Based on the results obtained from this study, the following observations and conclusions can be made.

- 1) Organosilane additive into underfill can enhance the practical adhesion between the underfill and passivated silicon. The adhesion mechanism is through formation of primary bonds between organosilane and passivation and between organosilane and epoxy resin. The availability of the organosilane molecule and the surface chemistry of the silicon passivation layer control the effectiveness of the coupling.
- 2) The fracture energies of the UF/organic substrate and UF/silicon chip interfaces decrease with increasing silica filler content. Crack pinning is not a dominating mechanism for filler content levels greater than 50-wt.%, which is typical for underfill materials. The causes for the lowered interfacial fracture toughness might be associated with higher filler content, which leads to higher defect density, smaller plastic deformation, and possibly a lower silane concentration at the epoxy resin/silicon interface.
- 3) Surface morphology and chemistry are crucial to achieving good practical adhesion of UF/chip and organic substrate interfaces. The toughening of the UF/organic substrate interfaces can be the result of an increased area of interfacial contact and localized plastic deformation promoted by the morphology of the organic substrate if the wetting of underfill is good. The UF/silicon chip adhesion can be enhanced by the use of a desirable surface chemistry for the silicon passivation.
- 4) The UF/organic substrate interface was not toughened by the addition of rubber particles to the underfill. Silica particle debonding from the epoxy matrix is promoted when rubber particles cavitate in the vicinity of the silica particles.
- 5) The adhesion and fracture behaviors at underfill interfaces are complicated because of the nature of underfill as a hybrid composite material. They are controlled by many distinct mechanisms, such as, formation of primary bonds, crack pinning by silica fillers, debonding of silica filler particles from the epoxy matrix (defect formation), and cavitation and shearing induced by rubber particles. All these mechanisms are operating and competing with each other. Further work is needed to shed more light on the correlation between the interfacial adhesion/fracture behavior and the chemistry, morphology, and properties of the materials.

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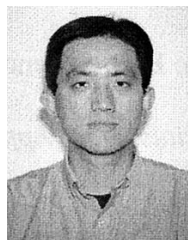
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REFERENCES

- [1] R. R. Tummala, E. J. Rymaszewski, and A. Klopfenstein, *Microelectronics Packaging Handbook*, 1997.
- [2] P. A. Totta, "Roadmap of packaging interconnect technology," *Adv. Electron. Packag.*, vol. 19, pp. 323–327, 1997.
- [3] T. Y. Wu, Y. Tsukada, and W. T. Chen, "Materials and mechanics issues in flip-chip organic packaging," in *Proc. 46th Electron. Comp. Technol. Conf.*, 1996.
- [4] The National Technology Roadmap for Semiconductors. San Jose, CA: Semiconductor Industry Association, 1997.
- [5] W. T. Chen, D. Questad, D. Read, and S. Bahgat, "Opportunities and needs for interfacial fracture mechanics in microelectronic packaging industry," presented at the International Mechanical Engineering Congress and Exposition, Application of Fracture Mechanics in Microelectronic Packaging, Dallas, TX, 1997.
- [6] R. A. Pearson, R. M. Hydro, T. B. Lloyd, and H. F. Nied, "The effect of temperature and humidity exposure on adhesion," in *Proc. ASME Int. Mech. Eng. Congr. Expo., Applicat. Fracture Mech. Electron. Packag.*, Dallas, TX, 1997.
- [7] J. M. Snodgrass, S.-Y. Kook, A. Kirtikar, and R. H. Dauskardt, "Adhesion and reliability of polymer/inorganic interfaces in microelectronic applications," in *Proc. ASME Int. Mech. Eng. Congr. Expo., Applicat. Fracture Mech. Electron. Packag.*, Dallas, TX, 1997.
- [8] C. K. Gurumurthy, J. Jiao, L. G. Norris, C.-Y. Hui, and E. J. Kramer, "A new approach for thermal fatigue testing of the underfill/passivation interface," in *Proc. ASME Int. Mech. Eng. Congr. Expo., Applicat. Fracture Mech. Electron. Packag.*, Dallas, TX, 1997.
- [9] J. Jiao, C. K. Burumurthy, E. J. Kramer, Y. Sha, C.-Y. Hui, and P. Borgesen, "Effect of thermal residual stress on the measurement of the adhesion between polyimide and underfill using an asymmetric double cantilever beam specimen," in *Proc. ASME Int. Mech. Eng. Congr. Expo., Applicat. Fracture Mech. Electron. Packag.*, Dallas, TX, 1997, presented at.
- [10] X. Dai, M. V. Brillhart, and P. S. Ho, "Investigation of underfill adhesion in plastic flip-chip packages," in *Proc. ASME Symp. Proc. Applicat. Fracture Mech. Microelectron. Packag.*, 1997, pp. 115–124.
- [11] X. Dai, M. V. Brillhart, and P. S. Ho, "Polymer interfacial adhesion in microelectronic assemblies," in *Proc. IEEE/CPMT 48th Electron. Comp. Technol. Conf. Proc.*, 1998, pp. 132–137.
- [12] C. A. Dahlquist, *Aspects of Adhesion*, D. J. Alner, Ed. London, U.K.: Univ. of London Press, 1969, p. 193.
- [13] B. W. Cherry and S. L. Muddarris, "Wetting kinetics and the strength of adhesive joints," *J. Adhesion*, vol. 2, pp. 42–48, 1970.
- [14] D. Maugis, *J. Mater. Sci.*, vol. 20, pp. 3041–3073, 1985.
- [15] R. A. Pearson and T. B. Lloyd, "On relating thermodynamic work of adhesion to interfacial fracture toughness," presented at the Electronic Packaging Materials Science IX, Boston, MA, 1996.
- [16] A. N. Gent and A. J. Kinloch, "Adhesion of viscoelastic materials to rigid substrates. III energy criterion for failure," *J. Polym. Sci.*, vol. 9, pp. 659–668, 1971.
- [17] A. N. Gent and J. Schultz, "Effect of wetting liquids on the strength of adhesion of viscoelastic materials," *J. Adhesion*, vol. 3, pp. 281–294, 1972.
- [18] E. H. Andrews and A. J. Kinloch, "Mechanism of adhesive failure. I," *Proc. R. Soc. Lond. A*, vol. A. 332, pp. 385–399, 1973.
- [19] E. H. Andrews and A. J. Kinloch, "Mechanism of adhesive failure. II," *Proc. R. Soc. Lond. A*, vol. A. 332, pp. 401–414, 1973.
- [20] L.-H. Lee, *Fundamentals of Adhesion*. New York: Plenum, 1991.
- [21] L.-H. Lee, *Adhesive Bonding*. New York: Plenum, 1991.
- [22] A. J. Kinloch, *Adhesion and Adhesives: Science and Technology*. London, U.K.: Chapman & Hall, 1990.

- [23] X. Dai, M. V. Brillhart, and P. S. Ho, "Adhesion Measurement for Electronic Packaging Applications using Double Cantilever Beam Specimens," *IEEE Trans. Comp. Packag. Technol.*, vol. 23, pp. 717–732, Mar. 1999.
- [24] R. S. Bauer, "Application of epoxy resins in electronics," in *Polymers for Electronic and Photonic Applications*, C. P. Wang, Ed. San Diego, CA: Academic, 1993, pp. 287–331.
- [25] D. Suryanarayana, T. W. Wu, and J. A. Varcoe, "Encapsulants used in flip-chip packages," *IEEE Trans. Comp., Hybrids, Manufact. Technol.*, vol. 16, pp. 858–962, Dec. 1993.
- [26] L. S. Penn and T. T. Chiao, "Epoxy Resins," in *Handbook of Composites*, G. Lubin, Ed. New York: Van Nostrand Reinhold, 1982, pp. 57–88.
- [27] M. B. Vincent, L. Meyers, and C. P. Wong, "Enhancement of underfill performance for flip-chip applications by use of silane additives," presented at the IEEE/CPMT 48th Electronic Components and Technology Conference, Seattle, WA, 1998.
- [28] J. G. Swadener, K. M. Liechti, and A. L. deLozanne, "The intrinsic toughness and adhesion mechanisms of a glass/epoxy interface," *J. Mech. Phys. Solids*, 1998.
- [29] E. P. Plueddemann, *Mechanism of Adhesion through Silane Coupling Agents*, E. P. Plueddemann, Ed. New York: Academic, 1974, vol. 6.
- [30] Y. Eckstein and E. J. Berger, "Effect of silane on glass/resin adhesion strength," in *Adhesive Chemistry, Developments and Trends*, L.-H. Lee, Ed. New York: Plenum, 1983, pp. 139–168.
- [31] J. Comyn, "Silane coupling agents," in *Structural Adhesives*, A. J. Kinloch, Ed. London, U.K.: Elsevier, 1986, pp. 269–312.
- [32] E. P. Plueddemann, "Adhesion through silane coupling agents," in *Fundamentals of Adhesion*, L. H. Lee, Ed. New York: Plenum, 1991, pp. 279–290.
- [33] E. H. Andrews, P. He, and C. Vlachos, "Adhesion of epoxy resin to glass," *Proc. R. Soc. Lond. A*, vol. 381, pp. 345–360, 1982.
- [34] A. J. Kinloch, W. A. Dukes, and R. A. Gledhill, "Durability of adhesive joints," in *Adhesion Science and Technology*, L. H. Lee, Ed. New York: Plenum, 1975, pp. 597–618.
- [35] D. Suryanarayana and K. L. Mittal, "Effect of pH of silane solution on the adhesion of polyimide to silica substrate," *J. Appl. Polym. Sci.*, vol. 29, pp. 2039–2043, 1984.
- [36] A. Garton, "The crosslinking of epoxy resins at interfaces. I. Germanium, germanium dioxide, and silane-treated germanium," *J. Polym. Sci.*, vol. 22, pp. 1495–1506, 1984.
- [37] C. H. Chiang, H. Ishida, and J. L. Koenig, "The structure of γ -aminopropyltriethoxysilane on glass surface," *J. Colloid Interface Sci.*, vol. 74, pp. 397–404, 1980.
- [38] J. L. Koenig and P. T. K. Shih, "Raman studies of the glass fiber-silane-resin interface," *J. Colloid Interface Sci.*, vol. 36, p. 1971, 1971.
- [39] J. R. G. Evans and D. E. Packham, "Adhesion of polyethylene to metals: The role of surface topography," *J. Adhesion*, vol. 10, pp. 177–191, 1979.
- [40] D. Maxwell, R. J. Young, and A. J. Kinloch, "Hybrid particulate-filled epoxy-polymers," *J. Mater. Sci. Lett.*, vol. 3, pp. 9–12, 1984.
- [41] R. J. Young, "Rigid-particulate reinforced thermosetting polymers," in *Structural Adhesives: Developments in Resins and Primers*, A. J. Kinloch, Ed. New York: Elsevier, 1986, pp. 163–200.
- [42] F. F. Lange, "The interaction of a crack front with a second-phase dispersion," *Philos. Mag.*, vol. 22, pp. 983–992, 1970.
- [43] F. F. Lange and K. C. Radford, "Fracture energy of an epoxy composite system," *J. Mater. Sci.*, vol. 6, pp. 1197–1203, 1971.
- [44] A. G. Evans, "The strength of brittle materials containing second phase dispersions," *Philos. Mag.*, vol. 26, pp. 1327–1344, 1972.
- [45] S. K. Joneja and G. M. Newaz, "Fracture toughness and impact characteristics of a hybrid system: Glass-fiber/sand/polyester," in *Effects of Defects in Composite Materials*, D. J. Wilkins, Ed. Philadelphia, PA: American Society for Testing and Materials, 1984, vol. ASTM STP 836, pp. 3–20.
- [46] A. J. Kinloch, "Rubber-toughened thermosetting polymers," in *Structural Adhesives: Developments in Resins and Primers*, A. J. Kinloch, Ed. New York: Elsevier, 1986, p. 127.
- [47] A. F. Yee and R. A. Pearson, "Toughening mechanisms in elastomer-modified epoxies part 1 mechanical studies," *J. Mater. Sci.*, vol. 21, pp. 2462–2474, 1986.
- [48] R. A. Pearson and A. F. Yee, "Toughening mechanisms in elastomer-modified epoxies part 2 microscopy studies," *J. Mater. Sci.*, vol. 21, pp. 2475–2488, 1986.
- [49] H. R. Azimi, R. A. Pearson, and R. W. Hertzberg, "Role of crack tip shielding mechanisms in fatigue of hybrid epoxy composites containing rubber and solid glass spheres," *J. Appl. Polym. Sci.*, vol. 58, pp. 449–463, 1995.

- [50] H.-J. Sue, F. I. Garcia-Meitin, and D. M. Pickelman, "Fracture behavior of rubber-modified high-performance epoxies," in *Polymer Toughening*, C. B. Arends, Ed. New York: Marcel Dekker, 1996, p. 131.



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