Preventing Adhesive Resin Bleed in Microelectronics Assembly through Gas Plasma Technology

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Abstract

Die attach and other bonding operations often use a filled adhesive, typically an epoxy, as a bonding agent. Epoxy resins can separate ("bleed") from the bulk adhesive during bonding and flow outside the bond area, encroaching on surfaces used in later assembly process steps, such as wire bonding. Consequently, assemblies must then be reworked to remove the resin bleed for successful post die attach processing. One method of preventing this unpredictable adhesive flow is through the use of gas plasma technology. By depositing a thin hydrophobic film over the assembly surfaces, the surface energy can be modified to repel the bleed. This method eliminates rework and compensates for the different bonding surfaces and adhesive types and for the relative amounts of resin bleed each combination presents. This article details the plasma deposition methodology, examines its effectiveness at preventing resin bleed and subsequent rework, and verifies the reliability of assemblies treated with the thin hydrophobic films.

Key Words: Resin Bleed, Surface Energy, Plasma Deposition, Thin Films, Adhesive Bonding, Die Attach

1. Introduction

Resin bleed is a phenomena that is commonly encountered when working with filled adhesive systems, such as silver filled epoxies [1] [2]. Adhesive resin components as well as possibly some cross-linking agents are observed to separate from the bulk adhesive when it is applied to substrate surfaces during a bonding operation. The separated resin, as shown in Figure 1, appears as a clear liquid that flows out from the edges of the adhesive fillet and wets adjacent surfaces. If the resin bleed covers wire bond pads or solder pads, it will interfere with or even prevent the formation of wire bonds or solder joints.

Figure 1 . Resin Bleed

The epoxy bleed phenomena is driven by the minimization of the substrates' Gibb's surface free energy (G^S) in the adhesive/substrate system [3]. Uncured filled adhesive systems are typically formulated to have a higher surface free energy than the substrates they bond to, which corresponds to a positive energy differential between adhesive and substrate ($+\Delta G^S_{ls}$) [4]. This fact insures that the adhesive will wet and form strong bonds to these surfaces. However, if the free energy of the bonding surfaces rises above the adhesive free energy ($-\Delta G^S_{sl}$), then the adhesive resin will spontaneously wet out areas adjacent to the die attach fillet. In this case, the adhesive resin has a stronger affinity to the bonding surface than to its own filler.

Resin bleed is especially a problem for high energy surfaces such as those made of metal or ceramic. These surfaces will often have a higher energy than many filled adhesive systems. This problem is compounded by cleaning operations, especially low pressure plasma cleaning, prior to adhesive bonding [1]. The cleaning raises the substrate surface free energy further by eliminating minor organic contaminants that do much to lower surface free energies. Consequently, many microelectronic assemblies such as HTCC hermetic MCMs or COB PWAs with plated gold surfaces can experience severe resin bleed issues.

Past efforts to control resin bleed have been focused on modifying adhesive formulations by adding polar functional groups to the polymer matrix [5] or hydrophilic functional groups to the fillers [4]. While this is ultimately the best solution to this problem, it is not one which is available to an assembler. The manufacturer must work with the adhesives and substrates in their "as-is" state. In this situation, the traditional approach to eliminate bleed has been to vacuum bake the substrates prior to die attach [2] or to "burn off" the bleed after die attach with a low pressure oxygen plasma.

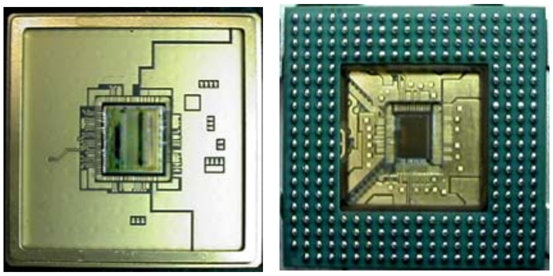

(a) 400Mhz ADC/DMUX CGA (b) 20 GHz DAC BGA

Figure 2 . Assemblies with Resin Bleed Problems

Perpetual problems with resin bleed on numerous assemblies (see Figure 2) and studies of the effectiveness of vacuum baking method led to the development at Stellar Microelectronics of a novel method to suppress resin bleed [1]. This rapid, simple technique requires no modification of the adhesive system. Instead, it seeks to alter the free energy of a bonding surface through the controlled application of a thin film of low surface energy material. A nonpolar, hydrophobic temporary organic or permanent inorganic film is applied to the substrate. The monolayer thick films are most effectively and uniformly applied via a low pressure RF plasma deposition process. Fluorocarbon and SiOx films were initially selected as candidate materials, since these form hydrophobic surfaces [6]. Die attach, die shear and wire bond test results indicated that these materials did indeed prevent resin bleed while preserving adhesive bond strength and wire bondability.

Further work has been performed since these initial results were obtained. The fluorocarbon material was abandoned in favor of the SiOx because of reliability concerns with residual fluorine [7] and the unknown effects of fluorocarbons on adhesive bond strength. This paper evaluates two approaches in the application of SiOx films: complete coating versus selective coating of assembly bonding surfaces. Results of evaluation and reliability tests of the SiOx coatings on HTCC assemblies are reported.

2. Experimental

Two adhesive systems known to exhibit severe resin bleed were used for evaluating the two approaches: a silver filled epoxy and a boron nitride filled epoxy. The silver filled system cures 1 hour at 150°C while the boron-nitride system cures 20 minutes at 60°C followed by 1 hour at 150°C. Nickel-gold plated Kovar lids and nickel-gold plated HTCC packages (NTK, Inc., see Figure 2(a)) were used as substrate vehicles for the tests.

Figure 3 . March AP-1000 Plasma System

A March Plasma Systems batch type plasma system was used for all of the coating work. A typical March system is displayed in Figure 3. The SiOx films were generated by reactive RF plasma deposition using argon with a concentration of 40 to 60 percent by volume of siloxane monomer. The deposition was carried out between 1 to 15 minutes at 28 mTorr and with 800 Watts of forward RF power. The thickness of the coating was a linear function of the length of the deposition.

Rather than monitor the thickness of the SiOx films, the contact angle of DI water on the coated surfaces was measured instead. Contact angle measurements were made using a Rame'-Hart Contact Angle meter. All contact angle measurements were made only on the plated gold surfaces of the Kovar lids and the HTCC packages.

Contact angle measurements give a more direct estimate of surface free energy. The water's contact angle can be directly related to the surface energy by equilibrium expression [6] (Young's equation):

$$\gamma_l \cos\theta = \gamma_s - \gamma_{sl}$$

where γ_s is the surface energy of the solid surface, γ_l is the surface energy (or surface tension) of the liquid and γ_{sl} is the interfacial surface energy.

When a liquid contacts and interacts with a solid surface, it can either reduce or increase the surface energy at the interface. The magnitude of that energy change is equal to $\gamma_l \cos\theta$. For angles between 0° and 90°, $\gamma_{sl} < \gamma_s$ and the liquid reduces the energy at the interface: a necessary condition to achieve good wetting and adhesion. However, for angles between 90° and 180°, $\gamma_{sl} > \gamma_s$ and the liquid increases the energy at the interface, creating a non-wetting condition.

3. SiOx Resin Bleed Control

3.1 Complete Coating of the Substrate

3.1.1 Silver Epoxy Evaluation

The simplest and most cost effective approach is to coat the entire part with the SiOx material, masking off only areas that are to be soldered or welded, such as package leads or seal rings. However, since the SiOx film is not displaced or absorbed by the adhesive resin system it will affect the bond strength of the adhesive. The challenge then is to find the optimal range of coating thickness that will prevent resin bleed while maintaining adhesive bond strength.

Several nickel gold plated kovar lids were coated with varying thicknesses of SiOx. The thickness was initially correlated to the coating time rather than the contact angle. Twenty microcircuit die (1.27 mm x 1.27 mm) were bonded to each of the lids using the silver filled epoxy. All the die were sheared and the results are plotted in Figure 4. The blue line indicates the minimum allowable die shear strength for a die of this size. In general, a die shear strength of at least 2 to 3 times the minimum requirement is preferred.

Between approximately 2 and 2.5 minutes of coating time, there is a clear inflection of the die shear strength curve. To the left of the inflection point, the die shear strength approaches that of the reference specimen and the shear failure mode is largely cohesive with some adhesive failure (i.e., the adhesive shears cleanly from the substrate surface leaving no adhesive residue). This region of the curve corresponds to bonding onto a surface that is partially coated or the coating is thin enough to allow the adhesive to bond partially to the underlying gold. In this region of the curve, significant resin bleed is also observed.

To the right of the inflection point, the die shear strength drops away and the failure mode becomes completely adhesive. This portion of the curve corresponds to bonding to a surface that is completely coated with SiOx. The adhesive is poorly adherent to the SiOx and consequently exhibits poor die shear strength. However, in this region of the curve, the resin bleed is completely suppressed.

The optimal coating thickness should be that which corresponds to the inflection point of the curve, about 2.25 minutes. This coating thickness, the "sweet spot", it was hoped would suppress the resin bleed while still yielding joints with acceptable shear strength.

3.1.2 Boron-Nitride Epoxy Evaluation

In searching for this optimal coating thickness, it soon became apparent that other factors were influencing the results. The Kovar lids were taken from a number of different manufacturing lots. These different lots had variations in platings and surface finishes which gave conflicting results. The various lots of silver adhesive also behaved quite differently from each other.

A different adhesive system, the boron-nitride filled epoxy and a different substrate, the HTCC package, were selected to minimize the aforementioned difficulties. The epoxy was taken from two lots which exhibited similar resin bleed characteristics while all the substrates were taken from a single manufacturing lot.

The same experiments that were performed with the silver epoxy were repeated with the boron-nitride epoxy. Once again, the objective was to search for the optimal coating thickness that would provide resin bleed suppression while maintaining die shear strength. Die (1.27 mm x 1.27 mm) were bonded to the plated gold surface of the package. The die shear results are plotted in Figure 5 versus contact angle.

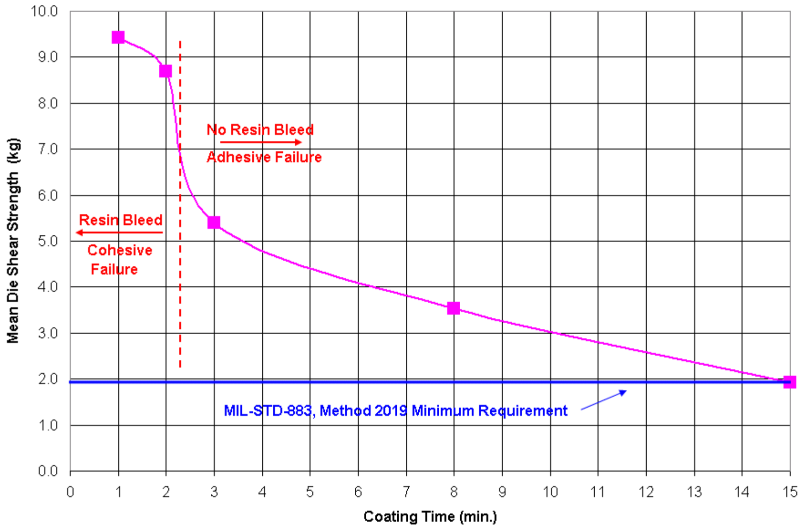


Figure 4 . Die Shear Strength vs. Coating Time

Contact angle was used instead of coating time as there was better correlation with the die shear results. The die shear strengths of the silver epoxy are also plotted in Figure 5 for reference. With an R^2 fit of 88.7%, the silver epoxy data exhibited strong linear correlation with the contact angle. Consequently, similarly strong correlation would be expected for the other adhesive and is indeed the case: the shear strength of the boron nitride epoxy appears to decay almost exponentially with the contact angle.

The point at which resin bleed was suppressed on the HTCC packages was between 44° and 47°. The bleed suppression point on the kovar lids with the silver epoxy was at approximately the same point though it tended to shift depending on the lid and epoxy lots. Unfortunately, the die shear strength of the boron-nitride epoxy at the bleed suppression point is only half that of the epoxy bonded to a pristine surface. Additionally, the shear failure mode is entirely adhesive at this point, indicating poor adhesion. Consequently, for this particular adhesive/ substrate system, there was no optimal coating thickness, no sweet spot.

3.1.3 Conclusion

From the data and discussion above, it is apparent that there are numerous problems with this approach to resin bleed suppression:

- The resin bleed and die shear strength correlate fairly closely with surface contact angle. Other factors, such as adhesive formulation, plating finish and surface roughness also strongly influence bleed. Adhesive formulations and plating finish can vary significantly from lot to lot. Consequently, the bleed suppression point can shift significantly. Each substrate/adhesive type and lot combination then would have to be evaluated to determine the optimal coating thickness.
- The optimal coating thickness range is extremely narrow for some adhesives and can be difficult to pinpoint. If coating thickness lies slightly outside of this range, one will lose significant bond strength or experience substantial resin bleed.
- It is difficult to determine the optimal coating thickness range, since it is very narrow. In many cases (as with the boron-nitride adhesive), it may simply not exist: the point at which bleed is suppressed may yield poorly adherent adhesive bonds.

Given these considerations, this approach was abandoned in favor of an alternate approach where the SiOx film is selectively applied to certain areas of the substrate.

3.2 Selective Coating of the Substrate

In this approach, the SiOx is applied as a “window frame” around the bond areas. The window frame coating then acts as a dam, confining the resin bleed within the area enclosed by it. The SiOx coating thickness may be any thickness which suppresses

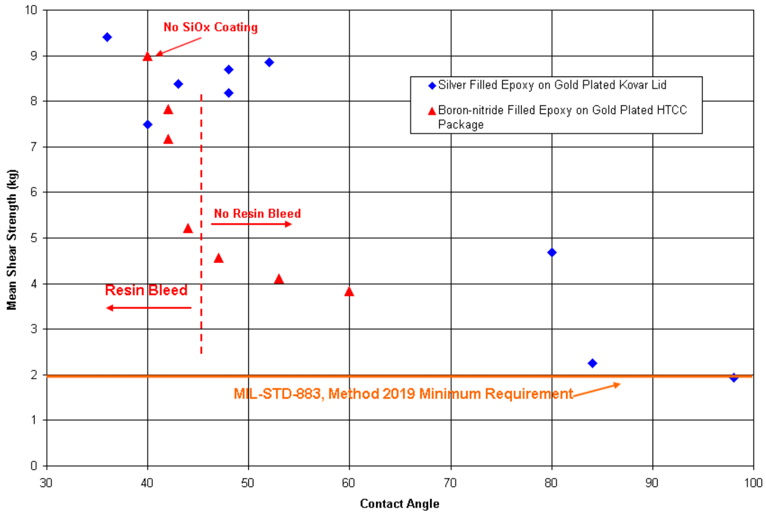


Figure 5 . Die Shear Strength vs. Contact Angle

bleed. For the HTCC package and boron-nitride epoxy system, this will be a film thickness having a contact angle of 47° or greater. This method is then more robust, since there does not need to be tight control on the coating thickness and, with the appropriate thickness, it should be largely insensitive to lot to lot variations of the substrate and adhesive. Additionally, since the SiOx film is stable, an entire inventory of assemblies can all be coated simultaneously, thereby forever eliminating bleed as an issue with the part before assembly has even begun.

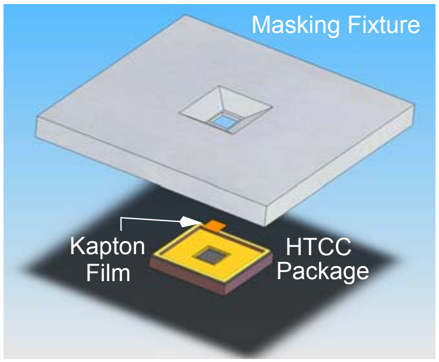
3.2.1 Masking

Since the low pressure plasma uniformly deposits the SiOx coating over all exposed surfaces in the chamber, it is necessary to mask all other surfaces, such as wire bond pads, seal rings, and solder pads, not requiring a coating. There are numerous ways to mask off assembly surfaces, such as with photomask, kapton tape or fixturing. In the interest of simplicity and of minimizing contamination of the assembly substrate, a masking fixture was developed for the following tests. The fixture was designed around the HTCC package and is shown in Figure 6.

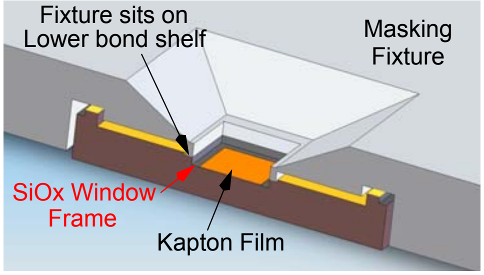
The fixture is designed to rest upon the lower wire bond shelf of the package (Figure 6(b)), masking all surfaces up to the lip of the die attach cavity. In the center of the cavity, a rectangular piece of 50 µm thick kapton film was placed in center of the die attach cavity to mask the actual die attach area. The fixture and kapton masking leave only the edges of the die attach cavity and the cavity walls exposed to the SiOx film, creating the SiOx window frame.

3.2.2 Preliminary Evaluation

An HTCC package was masked and coated with SiOx. The same coating conditions that were used to generate a 60° contact angle film in



(a) Overview of Masking Fixture and Package Mating



(b) Cross-Section View of Fixture sitting on Package

Figure 6 . Masking Fixture for Selective Coating of HTCC Package

Section 3.1.2 were used to coat this sample. The effectiveness of the coating was evaluated with fresh boron-nitride epoxy heated to 90°C. At this temperature, the rate of resin separation substantially accelerates. Figure 7 shows the outline of the SiOx window frame and the resin bleed in the die attach cavity. The resin bleed and wetting of the epoxy clearly outlines the edges of the SiOx window frame. The window frame acts as a dam, preventing spread of the bleed beyond it to the wire bond pads.

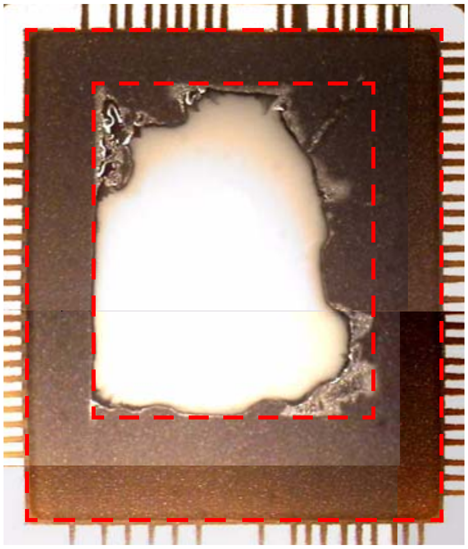


Figure 7 . Resin Bleed Suppression with SiOx Window Frame ***(Note: SiOx deposited only in area between two dashed red rectangles)***

Another package was coated with a narrower SiOx window frame (60° contact angle film) and die attached with an actual ADC die. An uncoated package was similarly die attached and resin bleed was compared between the two. High magnification images of the lower bond pads of each assembly are shown in Figure 8. Examining the assembly coated with the SiOx window frame, there is no visible resin bleed. These results contrast sharply with the assembly that had no SiOx coating where bleed is visible (as a shiny film which also darkens the pads at the edges) on many of the gold wire bond pads and the ceramic.

3.2.3 Reliability Testing

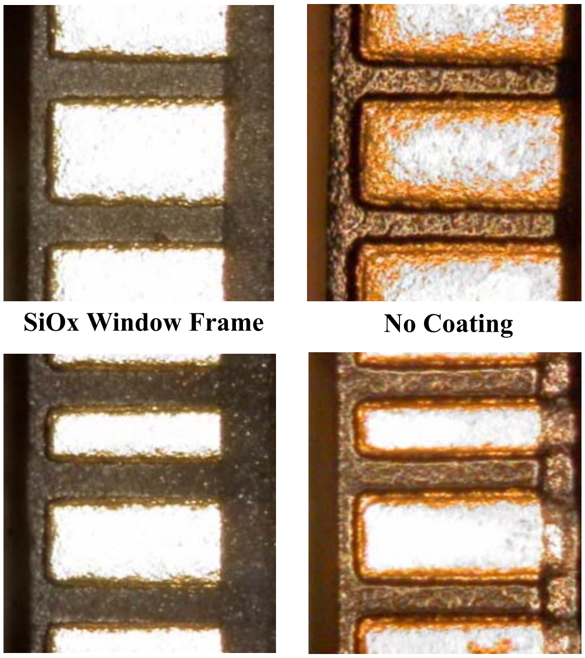
Having established that this approach effectively controls the resin bleed, a series of tests were performed to evaluate:

- Film composition and robustness
- Solderability of coated assemblies
- Reliability of wire bonds on coated assemblies
- Reliability of die attach on coated assemblies

The objective of these tests was to insure that all production or reliability issues with assemblies coated with the SiOx window frame were rooted out.

3.2.3.1 Film Composition & Robustness

The composition of the film was verified to insure that there were no contaminants deposited with the film that could cause reliability issues with wire bonds or die pad metallization [7]. The composition was verified using an XPS/ESCA Kratos Analytical AXIS HSi system. The SiOx film was found to be pure oxygen and silicon with a stoichimetric ratio of approximately 4:1. Consequently, this film is not a source of contamination.



SiOx Window Frame

No Coating

Figure 8 . RF DAC HTCC Assemblies, Lower Wire Bond Shelf: SiOx Dam vs. No SiOx Coating, Mag. 300X ***(Note: Resin bleed appears as shiny coating in right hand pictures above)***

After an assembly has been coated with the SiOx window, it must be cleaned prior to die attach. The film must then be able to survive the cleaning processes. Coated HTCC assemblies were subjected to ultrasonic cleaning (132 kHz, 75 Watts, 5 min.) in Asahiklin AK225-T and vapor degreasing in this same solvent. There was no effect on the bleed suppression. However, cleaning in an argon plasma

(March PX1000 cleaner, 99.9999% argon, 300 mTorr, 400 Watts) for just 5 min. damaged the film: resin bleed was seen to traverse the SiOx barrier. Extended cleaning in argon plasma completely eliminated the film's ability to block the resin flow, as shown in Figure 9. The argon plasma damages the film, breaking Si-O bonds and creating defects in the film. This damage has the effect of raising the free energy of the film and reducing its hydrophobicity. Consequently, it no longer acts as a barrier to resin flow.

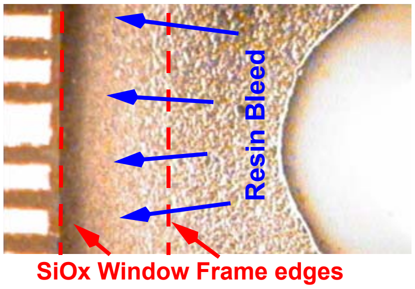


Figure 9 . Damaged SiOx Film No Longer Suppresses Resin Bleed, Mag. 150X

3.2.3.2 Solderability

The solderability of the coated assemblies was verified to ascertain the effectiveness of the masking fixture. If the fixture did not properly mask it would yield areas of the assembly that would no longer be solderable. A lead-tin solder with RMA flux was wetted to several gold plated areas on one of the SiOx coated assemblies. The solder had no difficulty wetting all surfaces.

3.2.3.3 Wire Bond Reliability

The masking fixture may not perfectly mask off the wire bond pads, allowing contamination of the pads with SiOx. Since the film has no contaminants, this should actually not have any effect on wire bond reliability, though it may affect the wire bondability. To verify that this assumption is true and to check the wire bondability, two packages, one with an SiOx dam and one without, were die attached and wire bonded with 50 aluminum (25.4 µm diameter, 99% aluminum/1% silicon, ultrasonic wedge bond) wires. The SiOx coated sample was plasma cleaned in argon prior to wire bond. The uncoated sample, however, had excessive resin bleed and, in order to be bondable, had to cleaned in an argon-oxygen plasma prior to wire bond.

Half the wires were immediately destructively pull tested using a Dage 4000. The remainder were baked at 300°C for 1 hour and then destructively pull tested. The results of the tests are shown in Table I. All wires met the minimum pull strength requirements. There was no statistical difference between the two types of samples.

Table I . Wire Bond Pull Tests

Coating	Temp. Pre-condition	Mean Pull Strength (g)[1]	Spec. Min. (g)[2]
None	None	9.32 ± 1.06	2.5
	1 hr. 300°C in Air	4.61 ± 0.75	1.5
SiOx Dam	None	9.78 ± 1.41	2.5
	1 hr. 300°C in Air	5.07 ± 0.76	1.5

[1] Mean pull strength of 25 wires.

[2] MIL-STD-883, Rev. E, Method 2011.

3.2.3.4 Die Attach Reliability

Given the poor adhesion obtained on SiOx films with 47° or greater contact angles, there was a concern that presence of SiOx could affect die attach reliability. The presence of the hydrophobic film underneath a die attach fillet might reduce the adhesive bond strength in the long term: the adhesive to film interface, where the adhesive bonding is the weakest, could potentially serve as a location where the adhesive might disbond, initiating and propagating a crack, leading to bond failure. A series of die shear tests were performed in an attempt induce this type of failure.

Three sets of test sample HTCC packages were fabricated. Each set consisted of one uncoated package and one package with the SiOx dam (60° contact angle) in the die attach cavity. Nine die (1.27 mm x 1.27 mm) were bonded into the die attach cavity of each package. The die bonded in the SiOx coated packages were placed such that their fillets overlapped the SiOx window frame. The first set of samples were treated as a control and were die sheared without any environmental pre-conditioning. The die shear results are presented in Table II. There was not a statistically significant difference between the results from the coated versus the uncoated assembly.

The other two samples sets were pre-conditioned by one of two methods: (1) extended high temperature bake and (2) high pressure steam conditioning (using a pressure cooker) followed by temperature cycling. The objective of the high temperature bake was to accelerate thermal degradation of the epoxy and thereby weaken the die attach interface. The samples were baked at 150°C for nearly 300 hours and then die sheared. The results are presented in Table II. Although the shear failure mode remained cohesive in nature, there was significant thermal degradation of the epoxy. However, the presence or absence of the SiOx coating had no effect on the results.

The objective of the steam conditioning and thermal cycling was to saturate the adhesive with moisture and then induce adhesive failure and delamination at the SiOx to adhesive interface by extreme temperature cycling [3]. The die shear results are presented in Table II. The die shear failure mode in both samples was largely adhesive but only at the die to adhesive interface rather than the die to substrate interface. Bond strength degradation is clearly evident and may attributed to the extreme moisture and temperature exposure. Yet, again, the presence or absence of the SiOx coating had no effect on the results.

Table II . Die Shear Test Results

Test	Coating	Mean Shear Strength (kg)[1]	Spec. Min. (kg)[2]
Control	None	9.1 ± 1.2	1.9
	SiOx Dam	10.4 ± 2.3	
Extended 150°C Bake[3]	None	6.6 ± 1.4	
	SiOx Dam	6.5 ± 1.4	
Pressure Cooker + Temp. Cycle[4]	None	6.8 ± 1.4	
	SiOx Dam	6.5 ± 1.3	

[1] Mean shear strength of 9 Die (1.27 mm x 1.27 mm).

[2] MIL-STD-883, Rev. E, Method 2019.

[3] Die attached assembly baked for 288 hr. at 150°C

[4] Pressure cook 2 hr., 121°C, 2 atm. followed by 25 cycles, -65°C to 150°C, per MIL-STD-883, Method 1012.

4. Conclusions

Two approaches that use a gas plasma deposited SiOx thin film to control resin bleed were evaluated: complete substrate coating and selective coating deposition. The authors concluded that:

- Coating the entire substrate surface with SiOx film to control resin bleed is not a practical approach.
- Selective deposition of SiOx film to encircle bonding areas and contain the bleed within those areas is a simple and effective approach to resin bleed suppression. It allows one to pretreat an entire inventory of parts prior to assembly, permanently eliminating bleed as a problem.
- The selective deposition approach does not contaminate substrate surfaces and is insensitive to variations in adhesive formulation or substrate fabrication.
- The selective deposition approach does not noticeably affect assembly manufacturability or reliability.

Work is in progress to evaluate the selective deposition method on other substrates, such as PWB laminates and thick film alumina.

5. References

[1] M. Burmeister, “Elimination of Epoxy Resin Bleed Through Thin Film Plasma Deposition”, Proceedings of the 36th International IMAPS Conference, Boston, Massachusetts, pp.780-785, 2003.

[2] J. Ireland, “Epoxy Bleedout in Ceramic Chip Carriers”, International Journal of Hybrid Microelectronics, Vol. 5, No. 1, 1982.

[3] A. Kinloch, “Adhesion and Adhesives: Science and Technology”, Kluwer Academic Publishers, 1987.

[4] N. Iwamoto, J. Pedigo, “Property Trend Analysis and Simulations of Adhesive Formulation Effects in the Microelectronics Packaging Industry Using Molecular Modeling”, Proceedings of 1998 Electronic Components and Technology Conference, Seattle, Washington, May 25 - 28, pp. 1241-1246, 1998.

[5] M. Marks, J. Thompson, R. Gopalakrishnan, “An Experimental Study of Die Attach Polymer Bleedout In Ceramic Packages”, Thin Solid Films, Vol. 252, pp. 54-60, 1994.

[6] J. Israelchavili, “Intermolecular and Surface Forces”, Second Edition, Academic Press, 1992.

[7] George Harman, “Wire Bonding in Microelectronics”, Second Edition, McGraw-Hill Publishers, New York, Chapter 5, 1997.