FAILURE ANALYSIS OF DIE BOND ADHESION FAILURES CAUSED BY SILICONE CONTAMINATION

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Abstract

This paper presents a case history of a failure analysis performed on die bond adhesion failures. Silicone contamination caused intermittent adhesive failures at the die back metallization/conductive epoxy interface. The source of the silicone contamination was identified as the adhesive film used to mount the wafer during the die sawing operation. The analytical equipment and methodology used to determine the failure mechanism are described. Auger Electron Spectroscopy and X-ray Photoelectron spectroscopy are used to identify the elements and their chemical states on the die bonding surfaces. The wafer mounting film is analyzed by Fourier Transform Infrared Spectroscopy. A process related failure in conductive die attach systems is described and corrective actions are presented. This analytical approach can be extended to other epoxy attach materials systems.

Introduction

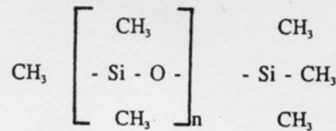
Silicone contamination has been a recurring reliability problem that reduces adhesion strengths of organic adhesives used in the assembly and packaging of microelectronics devices. Since silicones are so versatile in their materials applications, they can be ubiquitous as contaminants when improperly controlled.[1,2] The purpose of this paper is to describe reliability problems associated with silicone contamination, and to provide a better understanding of the analytical techniques used to determine its presence. The capability of detecting silicone contamination is a prerequisite for preventing future occurrences of such failures. Some examples of failures resulting from silicone contamination are described below. Because silicone oils can bleed or migrate, they can result in high contact resistance in electrical contacts in relays, connectors, and other devices.[3,4,5] Bleed-out of silicone particle getters can cause lid seal failures. Peel and stick labels with a silicone adhesive were used on plastic carriers and were found to contaminate the enclosed hybrid devices. The contamination was introduced by removing the labels, cleaning the carriers, and reusing them. The contaminated substrates exhibited reduced adhesion strengths in the conductive epoxy component attaches. In another case, titanium alloys that were machined with silicone bearing cutting fluids did not bond to organic adhesives. Silicones are also known to cause delaminations in printed circuit boards.[1]

Adhesion failures typically result from inadequate control of surface preparation or the cleaning processes of adherends. Adhesive bonding of organic adhesives is a surface phenomenon in which the cleanliness of the adherend surfaces is critical. If unwanted silicone forms a weak attachment to the substrate, the result is the formation of a "weak-boundary layer". The silicone prevents the direct contact between the adhesive and the adherend. When the adhesion failure is inspected, it visually appears to have occurred as an adhesive failure at the adhesive-adherend interface.[2] However, a closer examination by surface analysis usually shows that the failure actually occurs as a cohesive break within the silicone contaminant layer.

Silicones have the unusual properties of either preventing adhesion when used as release agents, oils, and lubricants or promoting adhesion as adhesives, sealants, and protective encapsulants. Silicones have excellent chemical resistance and thermal stability which often results in inadequate removal by common cleaning procedures.

Silicones are polymers, or more specifically, polyorganosiloxanes. Their physical and chemical properties are determined by their molecular weight distribution, the types of organic functional groups bonded to the silicon atoms, and by the degree of cross-linking between the polymer chains.[2]

Polydimethyl siloxane in a common silicone whose structure is shown below:



The backbone of the polymer consists of silicon to oxygen bonds similar to those in silica glasses. These bonds provide for the silicone's high degree of thermal stability. The silicon atoms are also bonded to organic radicals such as methyl, ethyl, and phenyl groups. The chemistry of the radicals determine the extent of cross-linking and provide for water resistance.[2,6] Polyorganosiloxanes are surface active polymers which can bond to surfaces via the formation of Si-O-substrate bonds following a reaction of the methoxy polymer end-groups with hydroxy groups on the substrate. The presence of moisture is required for proper curing, cross-linking, and bonding of silicones to surfaces, for silicones do not bond well to dry surfaces.[7]

Case History

A case history of an analysis of epoxy die attach failures is presented below. Intermittent die shear test failures were observed with a failure rate of approximately 1 to 3 percent. The failures occurred at the adhesive-die back metallization interface, and were caused by silicone contamination on the die back metallization. The silicone was introduced during the die separation and attachment processes. The source of the silicone was identified as the wafer backing sheet on which the wafer was mounted during the die separation and die attachment processes. The silicone is suspected to be an additive in the adhesive on the wafer backing sheet. The silicone additive moderates the wafer backing sheet tack in order to facilitate die pick and place.

Multiple analytical techniques were used to analyze for silicone in samples from the fabrication line and the die shear test failures. A wafer backing sheet and the attached wafer were analyzed following die separation. Failed die shear test samples included the dice and their mating residual epoxy fillets on PCB coupons. We intend to demonstrate the application of Fourier Transform Infrared Spectroscopy (FTIR), Auger Electron Spectroscopy (AES), and X-ray Photoelectron Spectroscopy (XPS) in determining die bonding materials and materials-process related failures. The corrective actions entailed removal of the silicone contamination by plasma cleaning the die back metallization. Surface analysis of a test matrix of plasma cleaned samples was performed to optimize the plasma cleaning conditions.

Failure Analysis

A. Sample Background

By properly selecting samples for analysis, the failure analyst can identify the source of contamination and recommend corrective actions. The following samples were analyzed:

1. Wafer Sample: A four inch wafer mounted to an adhesive backing sheet with separated dice, Figures 1.a, 2.a, and 2.b. The wafer backing sheet is a flexible polyvinyl chloride with a proprietary synthetic acrylic adhesive applied to one side. The wafer backing sheet is available in various adhesion strengths.

2. Die shear failures including dice and their corresponding printed circuit board coupons, Figure 1.b.

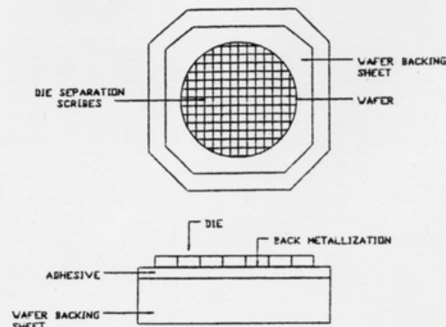


Figure 1.a: The wafer was mounted on the wafer backing sheet for die separation and pick and place

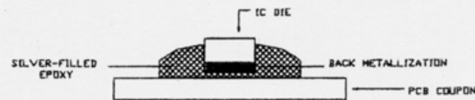


Figure 1.b: Die shear testing was performed on conductive epoxy die attaches to PCB coupons

B. Inspection of the adhesion failures by Light Microscopy, Fluorescence Light Microscopy, and Scanning Electron Microscopy

The analysis of adhesion failures begins with the visual inspection of both sides of the failed interface. A thorough examination of the appearance, color, texture, and the apparent

location of the failure interface provides important clues in establishing the failure mechanism.[8] A "look-a-metric" analysis enables the design of an efficient, cost-effective, and successful analytical test plan. The die shear failure initially appeared to be an adhesive failure at the die back metallization-epoxy interface rather than a cohesive failure within the gold-filled conductive epoxy. The die back metallization exhibited plating nodules and voids, Figures 2.a and 2.b. However, neither of these were related to the failure mechanism. Voids were observed in residual epoxy on the PCB coupons where the epoxy adhered to the back of the die, Figures 3.a and 3.b.

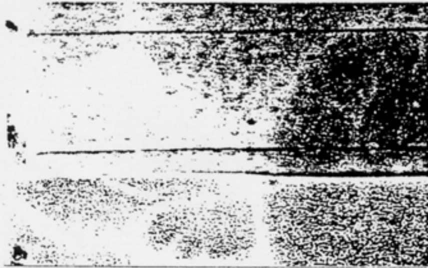


Figure 2.a: Light micrograph of wafer backing sheet and die back metallization

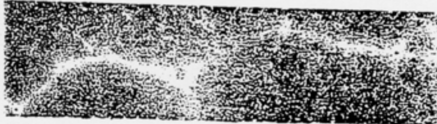


Figure 2.b: FLM of back metallization on die shear failure

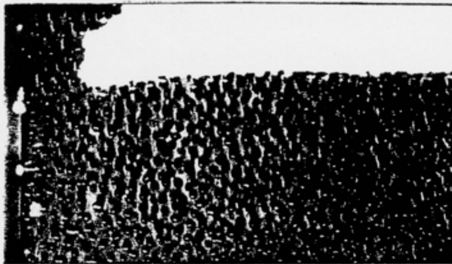


Figure 3.a: FLM of wafer backing sheet and die back metallization

Figure 3.b: FLM of residual epoxy on PCB coupon

Fluorescence Light Microscopy (FLM), was also used to inspect the samples. Microscopes with FLM accessories use color filters to monochromate a high power broadband light source. Excitation of fluorescence by monochromatic UV or visible light allows one to observe the fluorescence of certain materials, particularly organics, in a light microscope. FLM is quite useful in identifying the presence of organic contaminants on metals and semiconductor devices. Increased exposure of samples to moisture can reduce the intensity of fluorescence in some materials.

The residual epoxy fillet on the PCB coupon contained a thin film of material which was different from the bulk epoxy, Figure 3.b. The exact nature of this film is not completely understood. One explanation is that the film was created by the segregation of the resin component from the conductive epoxy matrix. This type of segregation has been observed to cause high contact resistances in conductive epoxy die attaches.[9] On the other hand, the film may have been a product of a reaction between the residual adhesive on the die back metallization and the die attach epoxy.

Absorbed current images corroborate the presence of the film observed by FLM. Images were observed using the Physical Electronics Model 590 Scanning Auger Microprobe. In this technique, the incident electron beam is rastered over the sample which is biased with a positive voltage. An image of the current absorbed by the sample is displayed as a gray scale on an oscilloscope. Areas which appear bright in an absorbed current image are indicative of conducting materials.[9] Voids in the film where both the bulk gold-filled epoxy and PCB metallization were exposed conducted better than the film itself.

C. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is a valuable technique in the analysis of organic materials and contamination. Proper sample preparation and

a sufficient quantity of sample are required for a successful analysis. Organic contaminants as small as 20 microns in diameter can be analyzed by an FTIR instrument with a microscope attachment. When a sample is analyzed by IR spectroscopy, it absorbs energies of IR radiation that are characteristic of vibrational energies of organic functional groups within the sample and transmits the rest. IR data is interpreted by assigning organic functional groups such as alcohols, ethers, esters, carboxylic acids, amines, etc. to the observed spectral features.

FTIR spectroscopy can be used to study reactions of silicones with process related materials such as cleaning solvents or outgassing products from packaging materials. The effect of exposure to non-process related materials can also be determined. The effect of outdoor exposure on the insulating performance of RTV silicones has been studied by Vlastos.[11] Here, FTIR was used to characterize differences in chemical structure between the surfaces of aged silicone and material from the bulk. In another application, FTIR was used to determine the extent of polymerization of silicone gels used as a moisture corrosion resistant coating in non-hermetic packaging technology.[6] The dependance of the silicone's moisture resistance on process parameters such as gel-cure temperature was evaluated. A third example entailed the use of FTIR and other techniques in identifying the cause of incomplete cure of fluorogel encapsulants used in automotive applications. This failure analysis showed that evaporation of the cross-linking agent during polymerization resulted in an insufficient amount of cross-linker for proper curing.[12]

In the analysis of the die shear failures, the thickness of the residual material on die back metallization was insufficient for analysis in the reflectance mode. The film observed on the residual epoxy fillet was better analyzed by Auger, XPS, or static SIMS. However, the wafer backing sheet was ideally suited for analysis in the Attenuated Total Reflection (ATR) mode, Figure 4.a. The depth of analysis in an ATR experiment depends on the refractive index of the sample and is typically 10-20 microns (80 micron wafer backing sheet thickness). Spectra were collected on the adhesive side and the PVC side of the sheet, Figure 4.b. The spectrum of the PVC side is indicative of a mixture of plasticizers and PVC. The spectrum of the adhesive side (plotted on top), exhibited peaks at 2150cm^{-1} and 1740cm^{1} which were assigned as a nitrile and an ester, respectively. Esters are commonly used in acrylic adhesives. Silicone peaks area not readily apparent in the spectrum of the adhesive side. This is not surprising given the small amount of adhesive on the sheet and spectral overlaps with other materials in the adhesive.[10] The presence of silicone in the wafer backing sheet adhesive was verified in the XPS analysis.

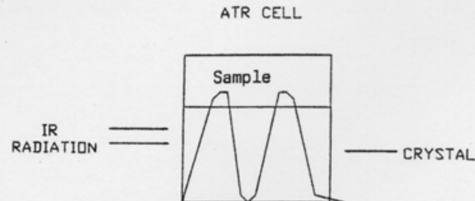


Figure 4.a: FTIR experimental configurations

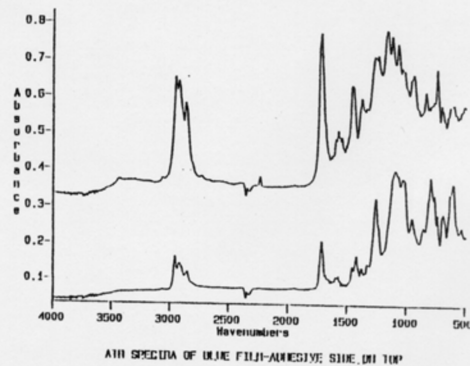


Figure 4.b: FTIR spectra of wafer backing sheet adhesive (top) and PVC sheet material without adhesive (bottom)

D. Auger Electron Spectroscopy (AES)

AES uses a finely focused electron beam (0.01 - 3 micron spot size) to stimulate the ejection of Auger electrons from the top 10-50 angstroms of the surface. AES provides an elemental analysis of the surface with chemical state information available from Auger peak shapes and peak energy shifts. Advantages of AES include excellent spatial resolution; rapid elemental survey and depth profile data acquisition; relative ease of data interpretation; and elemental mapping capabilities.

Auger elemental surveys were collected on the die back metallization and the residual epoxy to provide a more exact location of the failure interface than that provided by visual inspection.

1. Back Metallization on Freshly Peeled Die

Surveys of the die back metallization display high levels of silicon contamination, Figure 5.a. XPS analysis showed that the silicon was present in the form of a silicone.

2. Back Metallization on Die Shear Failure

Surveys of voids in the die back metallization exhibit silicon in an oxide form. The silicon in the voids is associated with the exposed die material. Surveys of representative areas of the die back metallization which had continuous plating coverage displayed low levels of silicon near or below the detection limit, Figure 5.b.

3. Residual Epoxy Fillet on the PCB Coupon

Surveys collected on the residual epoxy displayed high levels of carbon, oxygen, and silicon, Figure 5.c. The residual epoxy contained much higher levels of silicon than the die back metallization, Figure 5.b. This indicated that the silicon had preferentially adhered to the epoxy. The silicon may have been chemically bonded to the epoxy.

AES can be used to distinguish silicones and elemental silicon or silica by measuring shifts in auger peak positions as listed below:[3,13,14,15]

	Si LMM (eV)	Si KLL (ev)
Elemental Silicon	92	1619
Silicate	76	1606
Silicone Oil	84	1626
Silicone Resin	80	1619

We chose to verify the presence of silicone by XPS to reduce the risk of Auger peak shifts resulting from specimen charging and electron beam related artifacts.

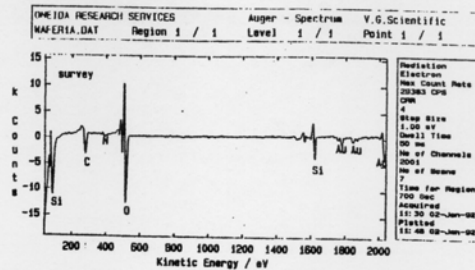


Figure 5.a: Auger elemental survey of back metallization on die freshly peeled from wafer backing sheet

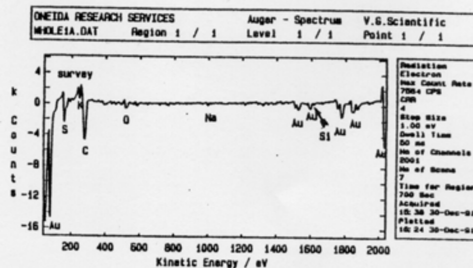


Figure 5.b: Auger elemental survey of back metallization on die shear failure

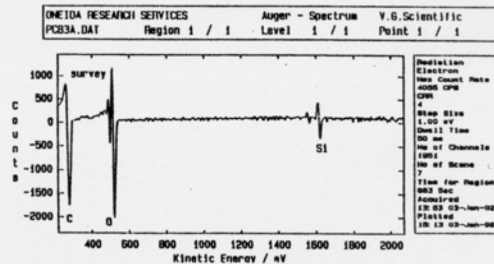


Figure 5.c: Auger elemental survey of residual epoxy on PCB coupon

E. X-ray Photoelectron Spectroscopy (XPS)

In XPS, and x-ray beam ejects electrons from the top 10-50 angstroms of the surface by the photoelectron effect. Auger electrons and photoelectronics are emitted in the same energy range so they can be analyzed simultaneously in an XPS experiment. XPS photoelectrons have kinetic energies equal to the incident x-ray minus its binding energy. XPS spectral features have narrower line widths than Auger peaks. Consequently, XPS can resolve subtle binding energy shifts that provide chemical

state information, even though in many cases the magnitude of the Auger peak shifts are greater than XPS peak shifts.[16] An advantage of XPS is that the x-ray beam is less destructive to the sample than the electron beam used in AES so analysis by XPS is less likely to induce chemical changes in the sample. A major disadvantage in XPS analysis is the lower spatial resolution (30-200 micron diameter spot size).

XPS can distinguish silicones from elemental silicon and silicates. The primary objective of the XPS analysis was to verify that the film on the residual epoxy-PCB coupon contained silicone, and that the source of the silicone was from the wafer backing sheet. Analysis of the adhesive on the wafer backing sheet was readily performed by XPS. Lower resolution scans provided an elemental analysis. Higher resolution multiplex data were collected to determine the chemical state of silicon and semiquantitative atomic concentrations, Table I.

An XPS multiplex of the silicon 2p peak collected on wafer backing sheet adhesive is shown in Figure 6.a. The energies of the silicon 2p photoelectron and Auger transitions were found to be at 102.5 eV and -355.2 eV, respectively, following applications of the appropriate charge corrections. This indicated that silicon was present in the form of a silicone. Silicon was also present as silicone on the other samples listed in Table I. Silicates and elemental silicon exhibit peaks at 103.4 eV and 99.5 eV, respectively.

The highest levels of silicone were detected on the back metallization of a die freshly peeled from the wafer backing sheet. Therefore, silicone was transferred from the wafer backing sheet to the die back metallization during removal of the die. Both sides of the die shear failure interface contained significant levels of silicon in the form of silicone. This confirmed that the failure was a cohesive failure within a silicone bearing layer at the adhesive-die back metallization interface.

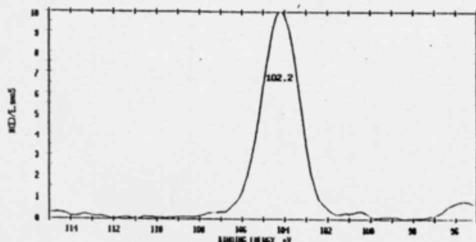


Figure 6.a: XPS multiplex of wafer backing sheet adhesive, silicon 2p peak

X-ray Photoelectron Spectroscopy

Atomic Concentration Table

	O	N	C	Si	Au
Back Metallization - Shear Failure	16.91	2.17	59.00	5.74	16.17
Residual Epoxy - PCB Coupon	37.32	1.44	50.66	10.07	0.51
Backing Sheet Adhesive	23.18	1.45	68.06	7.31	
Back Metallization - Freshly Peeled Die	34.70	3.44	41.61	16.62	3.63

Table I

The curve fitting of the carbon multiplexes provided additional information on the chemistry of the die shear failure interface and the adhesive from the wafer backing film. Carbon was primarily present as hydrocarbons in all of the samples. Esters were observed such that equal areas of *O=C O (~288.5 eV) and O=C O* (~286 eV) are required. Any excess area at 286 eV is due to ethers and/or alcohols which are indistinguishable by XPS. The presence of esters can be indicative of hydrocarbon degradation. The acrylic adhesive is another source of ester(s). The curve fits of the wafer backing sheet and the freshly peeled die exhibit a significant amount of esters, Figures 7.a and 7.b. The presence of esters was confirmed by the FTIR spectrum of the wafer backing sheet.

The XPS analysis of the die back metallization on the die shear failure showed the presence of a carbonyl, C=O (~287.7 eV), Figure 7.c. The relative amounts of ketone versus ester indicated by the peak fits should be viewed with caution due to the poor spectral resolution. However, the amount of ketone plus the amount of ester relative to other forms of carbon is more certain. The absence of a ketone in the wafer adhesive indicates that the source of the carbonyl is probably from the conductive epoxy. It is likely that some epoxy did adhere to the die back metallization and that the weak-boundary layer contained silicone contamination and die attach epoxy. Therefore, the silicone contamination and the conductive epoxy may have reacted to form the weak boundary layer.

The curve fit for the residual epoxy on the PCB exhibited six bands, Figure 7.d. A logical explanation is that these are actually two sets

of three bands. The three bands in each set are due to typical carbon species. One set arises from photoelectron emission of carbon atoms on an insulator, and the other is from carbon atoms on the gold flakes in the conductive epoxy matrix. This interpretation assumes that the same type of material is present on both areas. The material on the gold experiences less sample charging than the material on the insulator so the XPS peaks of material on the gold are observed at lower binding energies.

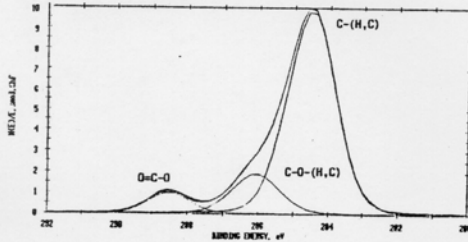


Figure 7.a: XPS multiplex of adhesive on wafer backing sheet, carbon 1s peak

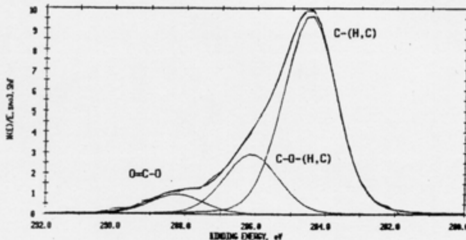


Figure 7.b: XPS multiplex of die back metallization, freshly peeled die, carbon 1s peak

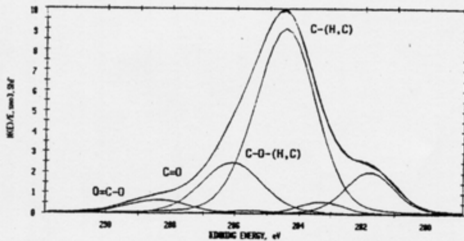


Figure 7.c: XPS multiplex of residual epoxy on PCB coupon, carbon 1s peak

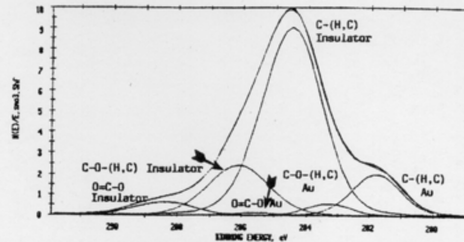


Figure 7.d: XPS multiplex of residual epoxy on PCB coupon, carbon 1s peak

XPS identified silicone as the class of material that caused the failure and the wafer backing film as the source of the silicone. Mass spectroscopy techniques such as static SIMS or Laser Ionization Mass Spectroscopy may have provided additional information. Silicones have a very characteristic positive static SIMS fragmentation pattern with prominent features at m/z 73, 147, 207, 221, 265, and 281.[17] The use of static SIMS and other mass spectroscopy based surface analysis techniques is improving the success rate of solving problems caused by process and non-process related organics.

Corrective Actions

Silicone contamination from the wafer backing sheet was determined to be the cause of the die attach failures. The problem of how to salvage the existing product was then addressed. Silicone contamination is often described as tenacious, yet there are several ways to remove silicones. Gentle abrasion by swabbing with a mixture of alumina powder in methanol has been successfully used for removing silicone contamination from metallization of flexible organic substrates. Mechanical abrasion was preferred over plasma cleaning in this case. Solubility data lists polydimethylsiloxane and Alkyl-Aryl siloxane copolymers as being soluble in chloroform, DMSO, MEK, acetone, and P-Dioxane.[10] Ireland's chemical method for removal of RTV conformal coatings, glob-tops, and other silicone based encapsulants yields excellent results for removing large amounts of silicone.[18] The Tetramethyl Ammonium Hydroxide (TMAH), methanol isopropyl alcohol solution is very selective and is relatively inert to most materials of construction. Open wire bonded hybrid devices where shown to function normally following rework using this procedure.

Plasma cleaning of the dice was performed by non-reactive sputtering with argon using a barrel reactor at 300 watts for 5, 10, 15, and 30 minutes cleaning times. Auger elemental surveys were collected to characterize the relationship of cleaning time and the levels of silicon. Ratios of the silicon

to gold auger peak heights ongoing from 0 to 5, 10, 15, and 30 minute cleaning times were 1.8, 0.9, 1.2, 0.52, and 0.28, respectively. The decrease in the amount of silicon in the auger spectra indicated that silicone was being removed by plasma cleaning. There was some evidence of cross-contamination of potassium and sodium from the barrel reactor. The problem with the intermittent die shear failures was solved following the incorporation of the plasma cleaning step in the assembly process.

Summary and Conclusions

The significant results of this failure analysis are summarized as follows:

1. Improper cleaning of dice exposed to wafer backing sheets with silicone bearing adhesives results in intermittent die shear failures. The presence of silicone contamination can cause adhesion failures in other applications of organics adhesives.

2. The failures were cohesive and occurred within a weak boundary layer which contained silicone and constituents of the conductive epoxy.

3. A film of material was observed on the residual epoxy on the PCB coupon. The film may have been produced by either a segregation of the epoxy resin from the conductive epoxy matrix or a reaction of the silicone contamination with the epoxy.

4. A successful methodology for the detection and removal of silicone contamination has been described to prevent future occurrences of similar adhesion problems.

5. An increased awareness of the potential reliability problems associated with the contamination will improve the quality of the devices produced by the microelectronics industry.

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