

Effect of Silicone Contamination on Assembly Processes

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Abstract

Silicone contamination is known to have a negative impact on assembly processes such as soldering, adhesive bonding, coating, and wire bonding. In particular, silicone is known to cause de-wetting of materials from surfaces and can result in adhesive failures. There are many sources for silicone contamination with common sources being mold releases or lubricants on manufacturing tools, offgassing during cure of silicone paste adhesives, and residue from pressure sensitive tape. This effort addresses silicone contamination by quantifying adhesive effects under known silicone contaminations. The first step in this effort identified an FT-IR spectroscopic detection limit for surface silicone utilizing the area under the 1263 cm^{-1} (Si-CH_3) absorbance peak as a function of concentration ($\mu\text{g}/\text{cm}^2$). The next step was to pre-contaminate surfaces with known concentrations of silicone oil and assess the effects on surface wetting and adhesion. This information will be used to establish guidelines for silicone contamination in different manufacturing areas within Harris Corporation.

Introduction

In an effort to increase productivity, a manufacturing process may consist of numerous operations undertaken simultaneously which can complicate process control and cause unexpected failures due to contamination. One particular type of contamination that is of great concern to the microelectronics industry is silicone. Common sources of silicone contamination are cosmetics such as hand lotion and mold releases or lubricants on manufacturing equipment. Silicone based adhesives, sealants, or films may be used in the manufactured product so that these uncured silicone materials also will be present in the manufacturing facility. In addition to these uncured silicone materials which can be transferred between manufacturing operations by poor housekeeping, the silicone curing process itself can fail if silicones which cure with the aid of a platinum catalyst are "poisoned" by contaminants such as sulfur or nitrogen containing compounds. Silicone oils also may be added to silicone materials to act as a plasticizing or softening agent, and this silicone oil later can escape the cured polymer matrix. The end result is a potential for non-curable silicone (such as oil) to contaminate hardware during the manufacturing process. The ability of silicone oil to migrate across a surface and spread into a thin, transparent and often invisible film can cause considerable consternation to manufacturing personnel who are working to control sensitive processes.

While it is generally documented that silicone contamination can lead to bonding failures,^[1,2] there is limited guidance available as to the concentration of silicone that will lead to failure. Space hardware manufacturing activities rank among the most sensitive to silicone oil contamination, due mainly to the necessity of extremely high hardware reliability requirements because of the impossibility of servicing deployed hardware. NASA advisory NA-MSFC-01^[3] cautions against wearing silicone wristbands in manufacturing areas because "silicone is easily transferred (cross contamination) and inhibits bonding. Less than $0.250\text{ mg}/\text{ft}^2$ causes a shift in failure modes." On the other hand, other reports by companies which manufacture assemblies for space applications indicate that silicone concentrations as low as $0.1\text{ mg}/\text{ft}^2$ ^[4] can cause failure while in other cases, silicone concentration as high as $50\text{ mg}/\text{ft}^2$ ^[5] had no impact. While these studies establish that adhesive failures can be affected by silicone contamination, there is a lack of significant information regarding single-lap shear, which is an industry standard test for evaluating adhesive bonding.

Hardware cleaning efforts involving silicone detection and silicone removal are a costly activity and can typically slow or even stop manufacturing activities, thus pushing these valuable activities behind schedule or over budget. Increasingly, manufacturing activities are on lean time and budget restraints and must remain vigilant by eliminating unnecessary activities. In the spirit of minimizing costly activities, this effort will be the first of several that when combined will address two important questions: (1) What level of silicone is actually present? and (2) What level and type of threat to assembly bonding processes do these levels of silicone pose?

This paper represents the initial undertaking to answer the aforementioned questions by (1) quantifying non-curable silicone contamination levels on aluminum and gold surfaces using Fourier Transform Infrared spectroscopy (FT-IR) and (2) analyzing the effect of known non-curable silicone contamination levels on unfilled epoxy adhesive bonded single-lap specimens.

Epoxies are routinely utilized in hybrid microelectronic manufacturing. The adhesives used may be highly filled epoxies to conduct heat or electricity, thixotropic epoxies to prevent sag on surfaces, or unfilled low viscosity epoxies for potting or gap

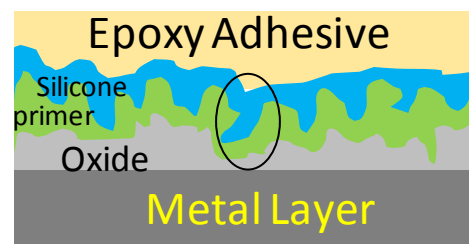
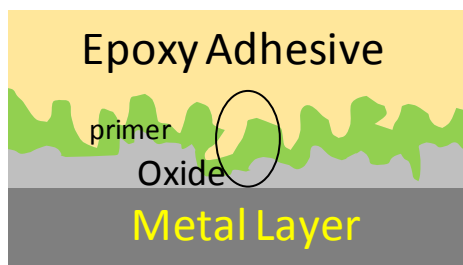
filling. The adhesion mechanisms for any of these types of epoxies are similar, but the behavior of these epoxy adhesive variants in response to silicone oil contamination may differ. At this point in the investigation, the focus is on the behavior of non-filled epoxies applied to rough adherend surfaces.

Introduction to Adhesive Bonding

The advantages of adhesives instead of mechanical fasteners in joining operations include (1) absorb stress, (2) absorb vibration, (3) act as an electrical insulator and allow dissimilar materials to be joined, (4) join complex geometries, (5) seal against environmental conditions, and (6) are lightweight.

With these advantages over fasteners, adhesives are widely used in nearly all industries including microelectronics and space. One challenge to using adhesives is the sensitivity of the bond integrity to the cleaning and surface preparation processes for the adherends. A proper bonding surface must be free of contaminants that can potentially interfere with bonding.

For good adhesion between an adhesive and an adherend, it is necessary for the adherend surface to be “rough” and clean in order for all of the possible adhesive mechanisms to be active. Adhesion is a combination of (1) mechanical interlocking; (2) weak intermolecular attractive forces (e.g. Van der Waals bond); and depending upon the substrate, (3) covalent bonds between the adherend surface and adhesive (as depicted in Figure 1). Silicone oil contamination has the potential to strongly interfere with all three of these mechanisms by acting as an interstitial and blocking contact locations for physical dovetailing or chemical bonding.



Mechanisms of bonding:

1. Physical dovetailing into adherend (strong bond)
2. Attractive forces – e.g. Van der Waals (weak bond)
3. Possible chemical reactions between any uncured epoxide terminations in primer, if used (strong bond)

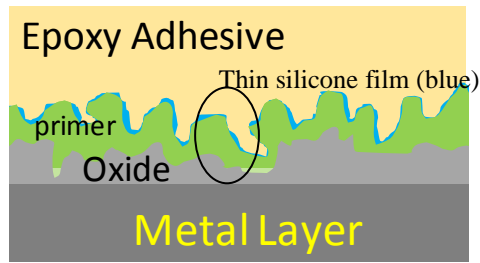
A contaminant has the potential to affect bonding mechanisms by:

1. limiting physical dovetailing into adherend by blocking pores,
2. cancelling weak bonding forces, and
3. preventing contact between the adhesive and adherend surface and blocking favorable chemical reactions.

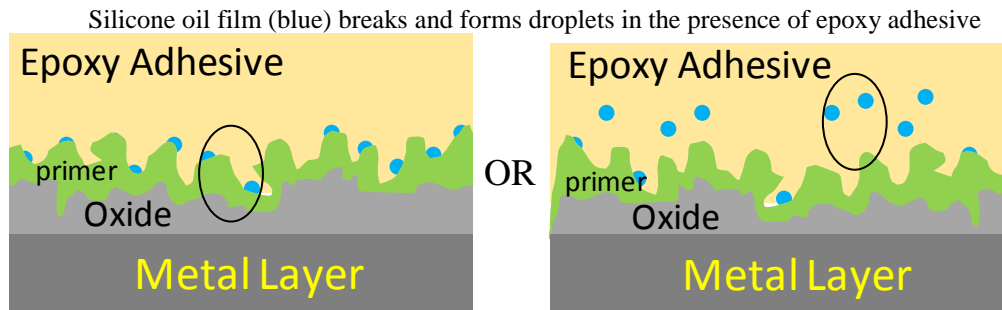
The result is a potential bond failure.

Figure 1. Diagram of adhesive bonding mechanisms and the threat posed by contaminants (silicone)

Since silicone oil is a readily flowing liquid, there are other effects that could potentially reduce the impact of silicone oil on adhesive bonding. These factors are depicted in Figure 2. The film of silicone oil may spread so thin that the contamination coating would not prevent mechanical interlocking of the adhesive with the adherend surface. Another possibility is that the thin film of silicone oil could break and bead in the presence of an epoxy adhesive thereby minimizing its contact area on the surface or emulsifying in the adhesive itself. Any of these events or a combination of these events acting in concert would counter the negative effects of silicone oil contamination.



Silicone oil will spread, and the thin coating would not fully inhibit dovetailing. The remaining sites for mechanical interlocking would allow for a strong bond in the presence of silicone oil.



Silicone oil and epoxy adhesive are two immiscible fluids, and they will separate to minimize contact. Silicone may disperse into the adhesive away from the adhesion interface.

Figure 2. Diagram of the properties of silicone oil which could counteract the impact of contamination on adhesive bonding

Quantifying Silicone Contamination on a Metal Surface

One method to detect silicone is FT-IR spectroscopy as silicone is particularly visible with infrared (IR) radiation. The siloxane (Si-O-Si) asymmetric stretch (1068 and 1100 cm^{-1}) along with the silicon-methyl (Si-CH₃) umbrella (1263 cm^{-1}) give a clear and readily identifiable IR signature confirming the presence of silicone. The FT-IR spectrum of a typical silicone oil (polydimethylsiloxane) is shown in Figure 3. The silicon-methyl peak has been used to quantify silicone concentration levels.

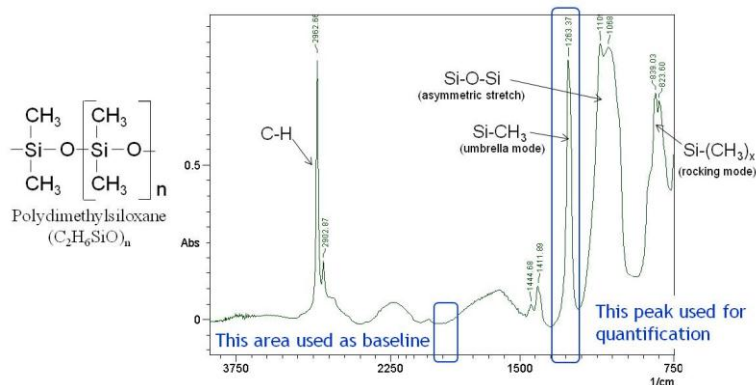


Figure 3. FT-IR spectrum of silicone oil and identification of the silicon-methyl peak that is used for quantification

There are differing means to apply the IR energy to a sample, each with advantages and disadvantages. The three most common FT-IR methods are reflectance, transmittance, and attenuated total reflectance (ATR). Of these three methods, ATR has been found to be the most sensitive measurement mode. In fact, by using the FT-IR/ATR method, the sensitivity is

sufficient to detect silicone well below the threshold of human visibility. Without quantification and corresponding information on the impact of silicone at varying concentration levels, this high degree of measurement sensitivity introduces a dilemma as to whether or not to clean hardware if the presence of silicone is detected.

ATR is so effective at detecting silicone because the sample comes into intimate contact with an evanescent IR wave, thus allowing a stronger IR response for the same volume of analyte (Figure 4). In order to quantify the silicone IR response on a surface using the ATR sampling accessory, several conditions must be satisfied: (1) The layers of silicone stack together to form a film that does not exceed the penetration depth of the ATR crystal, (2) The measuring surface permits IR reflectance back to the ATR crystal, (3) The silicone does not migrate sufficiently to spread the layer, (4) The pressure on the sample is sufficient to make good contact with the ATR crystal, and (5) Silicone is not pushed away by the force necessary to keep good contact with the ATR crystal.

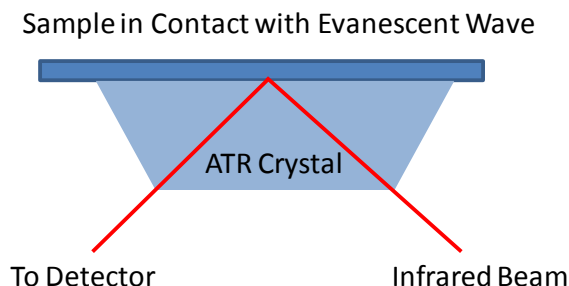


Figure 4. Diagram showing the sample interface of the ATR sampling accessory

As previously mentioned, the IR wave penetrates into the supporting substrate so that other factors affecting ATR analysis are refractive index and reflectivity of the measured surface. Aluminum and gold were chosen to represent typical metal surfaces used in microelectronic manufacturing. Aluminum is widely used in structural applications because of its light weight with respect to strength. Gold is widely employed as a plating to protect metallic surfaces from corrosion. Gold and aluminum oxide (native oxide coating exists on all aluminum surfaces) have differing refractive and reflective properties as shown in Figure 5^[6] so that the FT-IR response to silicone concentration is expected to differ for each material.

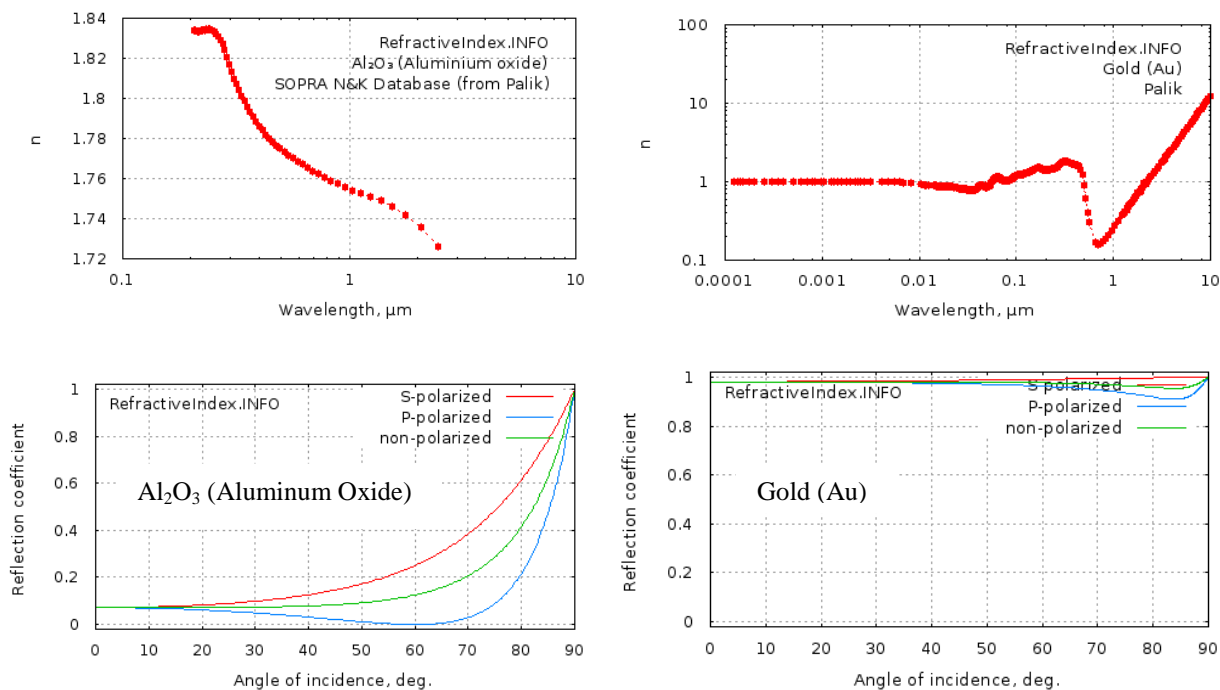


Figure 5. Refractive index and reflection coefficients of aluminum oxide and gold^[6]

For these experiments, DC-200 (polydimethylsiloxane oil) was selected as the source of non-curable silicone contamination. This oil has a somewhat low viscosity of approximately 20 Centistokes, can be used as a silicone rubber thinning agent, and

is fully terminated (non-polymerizing); thus it is a suitable representative of uncured or non-curable silicone. A series of contamination standards were prepared by first dissolving 1 gram of DC-200 into 100 mL of heptane and serially diluting this standard by 10 each time.

For quantification of silicone on the aluminum surface, a non-corrugated aluminum weighing pan was filled with at least enough silicone standard solution to completely cover the bottom of the pan, and the heptane was allowed to evaporate (Figure 6). The amount of standard to be added to the pan was calculated from the surface area of the bottom of the pan and was weighed using an analytical balance.

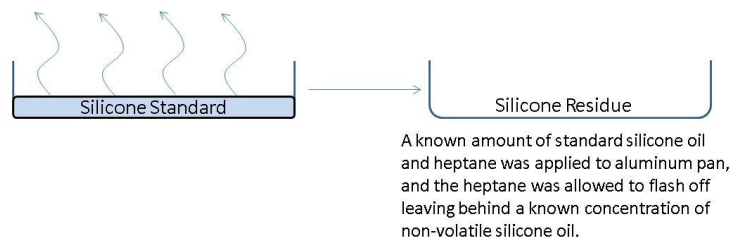


Figure 6. Diagram of method used to contaminate aluminum surface for silicone quantification by FT-IR/ATR analysis

The quantification measurements on a gold surface were performed on microscope slides that were sputter deposited with 1000 Å gold over a 50 Å sputter deposited chromium adhesion layer. Since these slides are without edges to contain the standard silicone solution, a micropipette was used to administer the standard silicone infused heptane onto the surface, allowing the heptane to evaporate (Figure 7). The volume of standard to be administered was calculated for a 0.5" x 1" surface area scribed into the gold surface. For aluminum, the measured silicone concentration levels were 0.5, 1, 2, 4, 8, 16, 32 and 64 $\mu\text{g}/\text{cm}^2$ and for the gold sputtered microscope slide, 0.25 $\mu\text{g}/\text{cm}^2$ was measured in addition to the aforementioned concentrations.

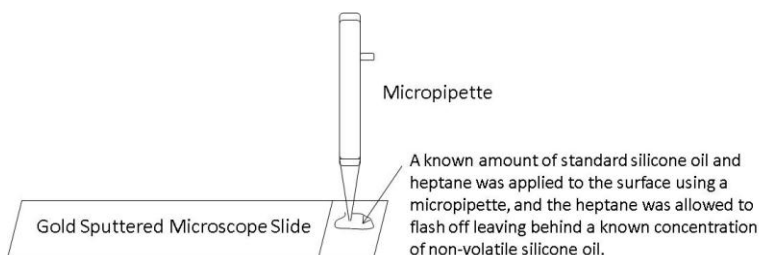


Figure 7. Diagram of method used to contaminate gold surface for silicone quantification by FT-IR/ATR analysis

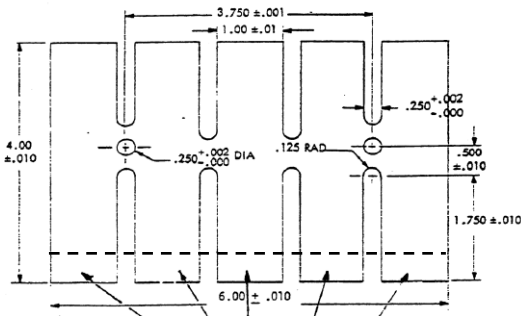
Once prepared, samples were pressed onto a single reflectance diamond ATR crystal attached to a FT-IR spectrometer. The FT-IR spectrometer uses mid-IR radiation with a range of 4000 cm^{-1} ($2.5\ \mu\text{m}$) to 550 cm^{-1} ($18\ \mu\text{m}$), and the single reflection diamond crystal plate ATR sampling accessory (45 degree nominal angle of incidence) has approximately a $2\ \mu\text{m}$ penetration depth. A torque limited press attached to the ATR accessory applied a consistent pressure to the selected test point. Spectra were collected for 60 seconds using a resolution of 4 cm^{-1} . A transect of points (minimum of three) was measured across both the aluminum pan and the gold sputtered microscope slide, and the average FT-IR/ATR absorbance response area (corrected) at $1259\text{-}1263\text{ cm}^{-1}$ (silicon-methyl vibration) was calculated. The average FT-IR/ATR response area was then plotted as a function of silicone concentration to construct a calibration curve in accordance with the Beer-Lambert Law. The Beer-Lambert Law, $A = \lambda bc$, where A is absorbance, λ is the wavelength dependent absorptivity coefficient, b is concentration, and c is the path length states that IR absorbance is directly proportional to concentration.

Determining Impact of Silicone Contamination on Adhesive Bonding

A widely used adhesive bonding performance test is ASTM D1002 "Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (metal-to-metal)". The single-lap specimen test is practical for evaluating manufacturing control of bonded products, including adherend surface preparation. For this study, two types of single-lap specimens were tested: (1) 2024-T3 aluminum treated with FPL etch (chromic/sulfuric acid solution) and then spray coated with Cytac BR-127 corrosion inhibiting epoxy primer to a nominal 0.0002" thickness and (2) 2024-T3 aluminum electroplated with gold over electroplated nickel. The primed aluminum surface was chosen because most

aluminum structures at Harris utilize this primer to improve adhesive bond strength and bonding directly to untreated aluminum is atypical.

Silicone contamination of the single-lap specimen surface was performed using a micropipette to apply a precise volume of silicone/heptane standard solution to the critical 0.5" x 1" (0.5 in²) overlap region on each single-lap specimen test panel. Figure 8 indicates the overlap region on each test panel that was contaminated and subsequently bonded. This contamination method was very similar to the method described earlier (depicted in Figure 7) which was used to apply silicone to the gold sputtered microscope slides.



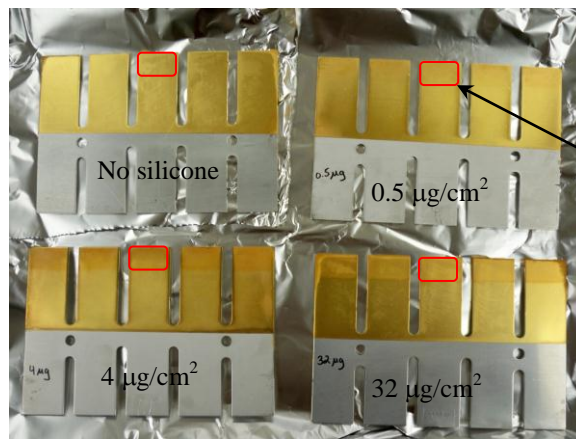
Apply silicone and adhesive to this 0.5" x 1" overlap region

Figure 8. Single-lap specimen test panel

The opposing single-lap specimen panel was left uncontaminated to serve as a comparison for the silicone contaminated panel. In addition, the silicone contaminated electroplated gold panel was bonded to an uncontaminated BR-127 primed panel to induce failure at the gold interface. Single-lap specimen test panels were bonded immediately with Epon 828 resin mixed 1:1 by weight with Versamid 140 hardener, and cured for 1 hour at 93°C. After cure, the single-lap specimen panel was cut into five individual single-lap coupons for mechanical testing. Five test coupons were tested for each silicone contamination level. The contamination levels on each single-lap specimen type are shown in Table 1. Note that prior to bonding, it was noted on the gold plated single-lap specimen panel that the silicone contamination is visible to the naked eye even at the lowest concentration of 0.5 µg/cm² (Figure 9).

Table 1. Silicone Contamination Levels for Single-Lap Specimens

Sample	Silicone Contamination (µg/cm ²)	
	BR-127 Primed	Gold Plated
1	0	0
2	0.5	0.5
3	4	4
4	16	32
5	32	-----
6	64	-----



Silicone oil somewhat visible at $0.5 \mu\text{g}/\text{cm}^2$ and becomes more pronounced as concentration is increased to $32 \mu\text{g}/\text{cm}^2$.

Figure 9: Silicone contaminated gold plated single-lap specimen panels

FT-IR/ATR Results

The FT-IR/ATR responses for silicone contamination on an aluminum surface are shown in Figure 10. The response is linear up to at least $64 \mu\text{g}/\text{cm}^2$ with absorbance increasing approximately 0.03 peak area units under the 1263 cm^{-1} peak for every one $\mu\text{g}/\text{cm}^2$ of silicone. Each calibration point represents an average value of at least three points along the pan diameter, with the coefficients of variation ranging from 9% to as high as 71%. The resulting calibration curve of the averages is well correlated with silicone concentration ($R^2 = 0.997$) so that on this surface, the FT-IR/ATR technique satisfies the necessary conditions for the Beer-Lambert Law. The variation in absorbance response along the transect was elevated which suggests that the evaporation method tended to concentrate the silicone more on one side of the pan over the other and that an improvement in the sample preparation method is desirable.

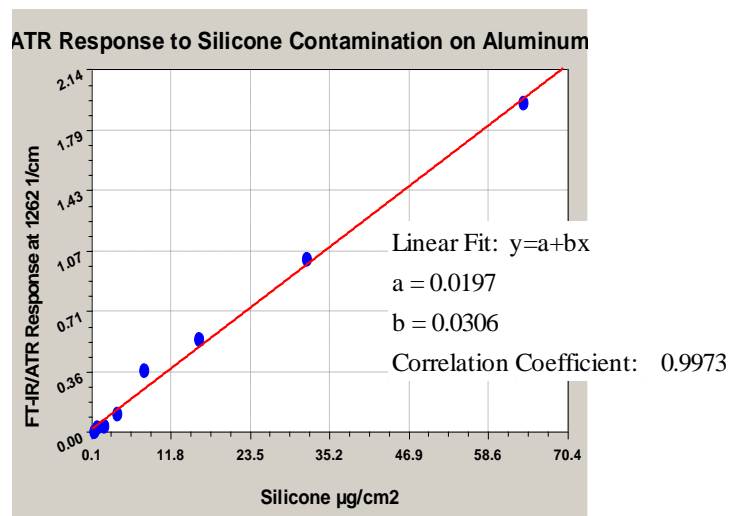


Figure 10. FT-IR/ATR response to silicone contamination on aluminum

The gold sputtered microscope slide samples exhibited a stronger FT-IR/ATR response than aluminum for the same silicone contamination. The absorbance increased approximately 0.1 peak area units under the 1263 cm^{-1} peak per one $\mu\text{g}/\text{cm}^2$ of silicone, which is nearly 350% higher than for an aluminum surface. Unlike the aluminum surface, the linear response of absorbance area as a function of silicone concentration begins to falter after $32 \mu\text{g}/\text{cm}^2$ (Figure 11a). With the highest concentration level included ($64 \mu\text{g}/\text{cm}^2$), an exponential relationship of absorbance to silicone concentration was a much better fit for the calibration (Figure 11b).

The method detection limit for silicone on an aluminum surface is estimated to be $0.036 \mu\text{g}/\text{cm}^2$ or $0.006 \mu\text{g}/\text{cm}^2$ on a gold sputtered microscope slide surface. This limit was calculated by measuring the area of the baseline at $1780\text{-}1810 \text{ cm}^{-1}$, multiplying the area by three^[7] (signal to noise ratio of 3), and determining the corresponding concentration value from the best linear fit on aluminum (forcing the intercept to zero) or exponential fit on gold.

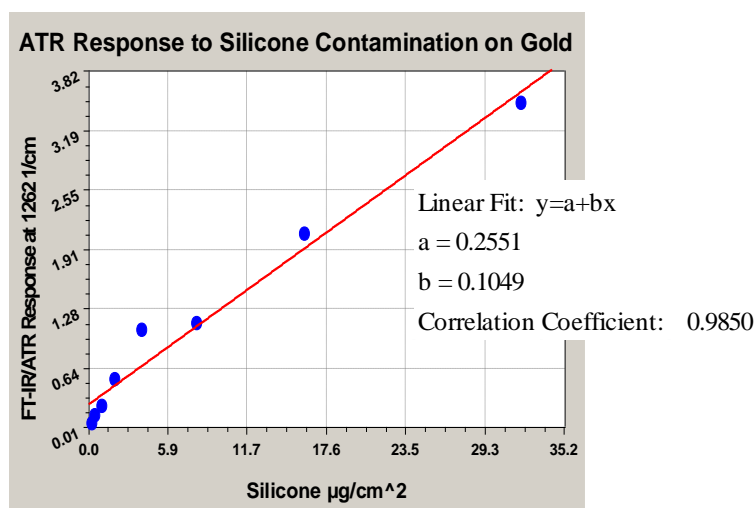


Figure 11a. FT-IR/ATR response to silicone contamination on gold is linear up to $32 \mu\text{g}/\text{cm}^2$ silicone

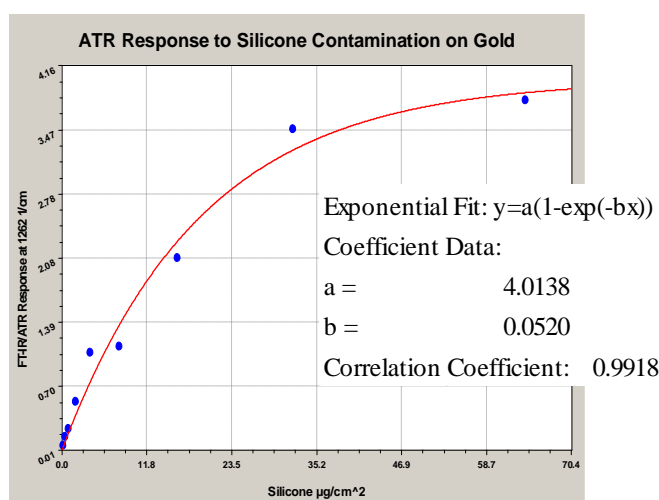


Figure 11b. FT-IR/ATR response to silicone contamination on gold is non-linear for concentrations $> 32 \mu\text{g}/\text{cm}^2$. An exponential relationship of FT-IR/ATR response with concentration exists for all concentrations up to $64 \mu\text{g}/\text{cm}^2$ silicone.

Evidence of the ability of silicone oil to migrate across a surface is apparent when silicone is spread onto the gold sputtered microscope slides used to create the FT-IR/ATR calibration curve. As shown in Figure 12, at a silicone concentration of $32 \mu\text{g}/\text{cm}^2$, in a span of less than an hour, the silicone had visibly spread an additional 25% beyond the original defined contamination border. In the same time frame, silicone at a concentration of $16 \mu\text{g}/\text{cm}^2$ does not migrate. The notorious silicone oil migration property is a result of a very low surface energy liquid in contact with a higher energy surface. At a value of $24 \text{ dyne}/\text{cm}^{[8]}$, silicone has one of the lowest surface energies found among the polymers, with the fluoro-polymers being the exception (PTFE is $18 \text{ dyne}/\text{cm}$).

The reason that this spreading effect was not readily observed on the aluminum may be due to surface roughness. Scanning electron microscope (SEM) micrographs as shown in Figure 13 reveal a significant difference in surface roughness between the aluminum and gold sputtered microscope slide surfaces. The aluminum pan has visible marks from the forming operation on the surface whereas the gold was so smooth that focusing was difficult due to a lack of topography. In addition to differences in reflectivity between aluminum (oxide) and gold, these surface topography features (or lack thereof) may help to explain the difference in slope of the best fit trendline for the two calibration curves as well as the more rapid migration of silicone across the smooth gold surface. As silicone begins to build layers upon itself, it is more inclined to spread across the surface, effectively thinning the silicone layer over time. Aluminum, in contrast, with its relatively rough surface, provides more surface area to prevent silicone from building as thick a uniform film layer. This behavior results in a lower calibration curve slope for aluminum, but a curve that remains linear to higher concentrations. The resulting thicker silicone film on gold at higher concentrations of silicone may approach the penetration depth of the evanescent wave from the ATR crystal so that the IR response will approach a maximum absorbance for silicone measured directly on the ATR crystal (no substrate).

This data clearly indicates that an FT-IR/ATR calibration has limitations both in the concentration of silicone and type of surface that can be measured, and one calibration curve cannot be substituted for another surface type.

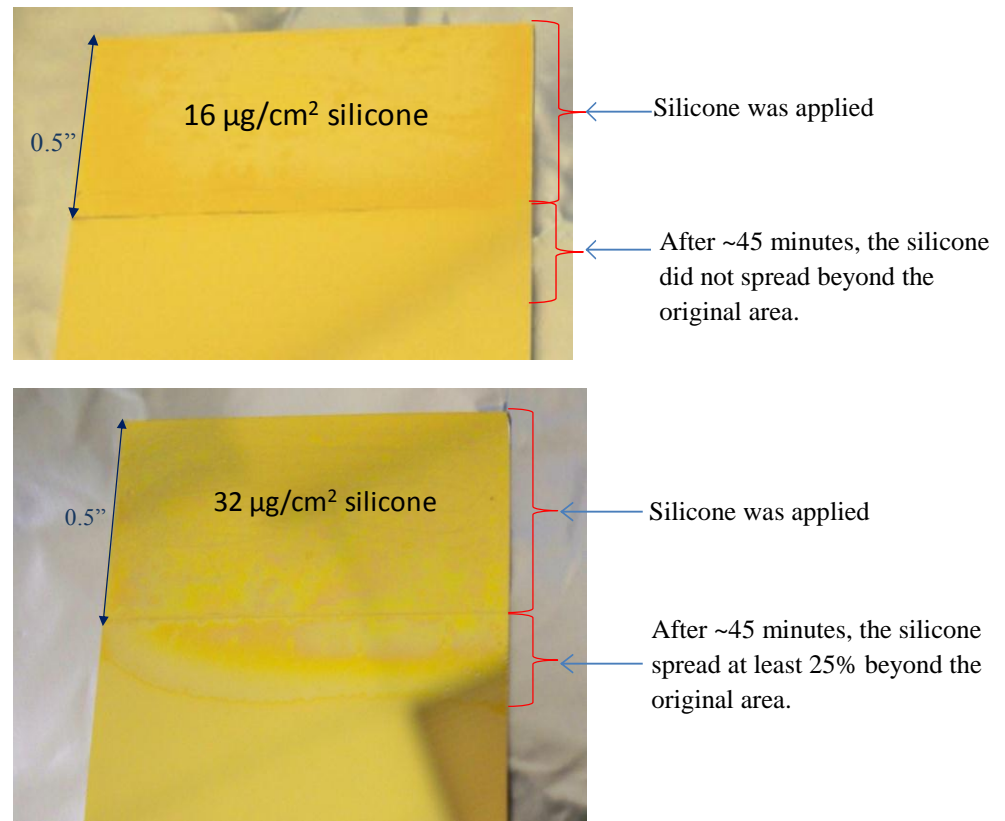


Figure 12. Silicone oil contamination on a gold sputtered microscope slide spreads beyond the originally contaminated area at a concentration of 32 $\mu\text{g}/\text{cm}^2$.

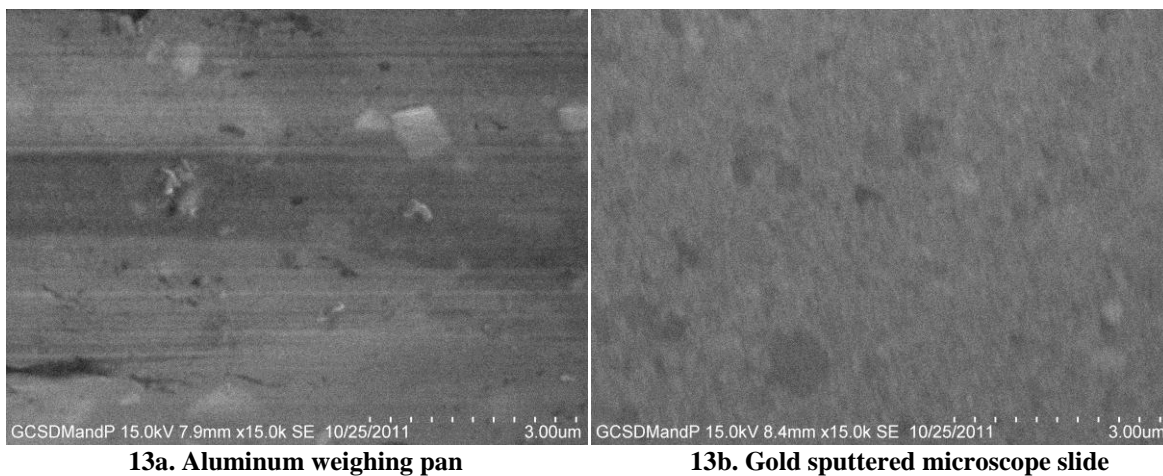
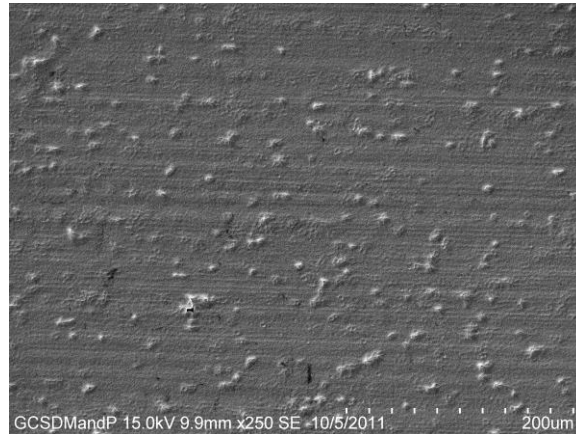


Figure 13. Representative SEM images (15,000x) of (a) the aluminum weighing pan and (b) the gold sputtered microscope slide

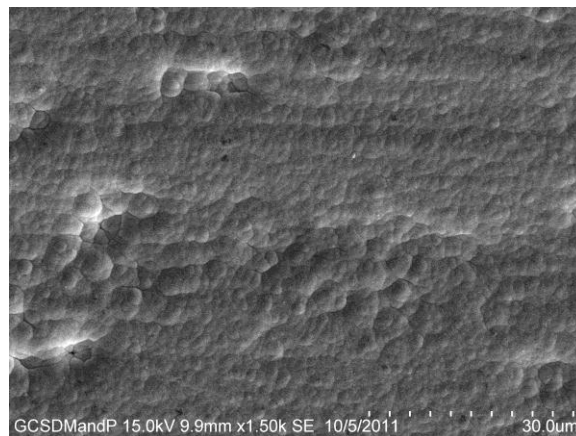
Single-lap Specimen Results

Unlike the gold sputtered microscope slides, the gold plated aluminum panels had a more complex surface. The surface roughness was readily apparent in the SEM images shown in Figure 14. The gold deposit exhibits a nodular appearance at low magnification with evidence of irregular discontinuities on some coupons. BR-127 also had a complex surface, which is expected for a film that is spray deposited and cured (Figure 15). The primer contains filler particles of strontium and

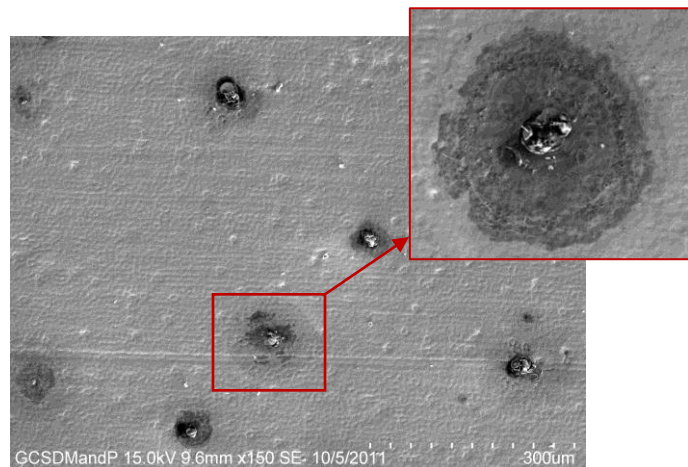
chromium in an epoxy matrix. Because of this surface complexity, the epoxy adhesion to both adherend types is expected to be fairly strong since mechanical interlocking components will be abundant. In addition, Epon 828/V140 is a low viscosity epoxy that would easily flow into the available surface features.



14a. Low magnification (250x) SEM image showing nodules in gold plating deposit



14b. Higher magnification (1500x) SEM image showing deposit roughness



14c. Gold plating irregularity

Figure 14. Representative surface SEM images of the gold plated single-lap specimens. Both nodules (a) and plating imperfections (c) are apparent on some coupons.

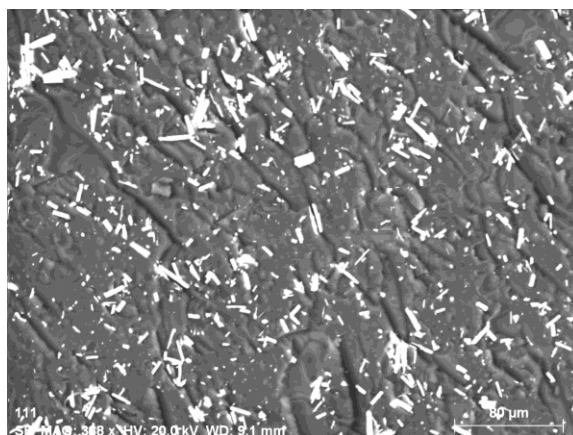
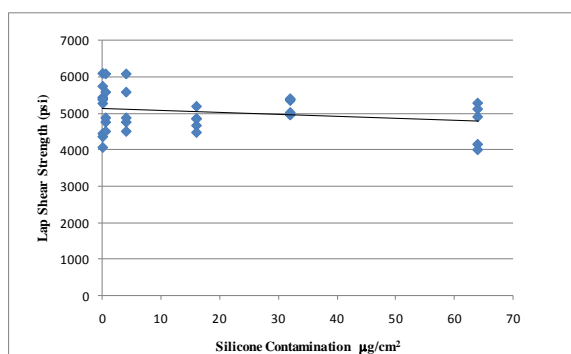


Figure 15. Representative surface SEM Image of the BR-127 primed single-lap specimens. The particles are comprised of strontium and chromium.

The single-lap specimen results for BR-127 primed aluminum are shown in Figure 16. The single-lap shear strength appeared to decrease slightly from an average of 5100 psi to 4700 psi; however, the level of process variance exceeds this trend, and the correlation is a low 83% confidence. In this adhesion mode, both BR-127 and Epon 828/V140 appear to be insensitive to silicone contamination. More data is required to determine if any trend does indeed exist.

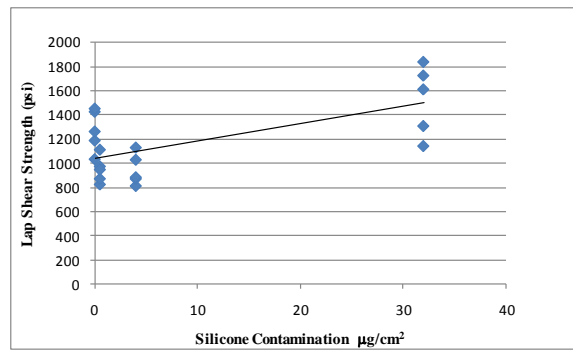


Regression Statistics	
Multiple R	0.2383
R Square	0.0568
Adjusted R Square	0.0273
Standard Error	546.2701
Observations	34

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	574865.225	574865.23	1.9264	0.1747
Residual	32	9549154.38	298411.07		
Total	33	10124019.6			

Figure 16. Single-lap specimen results for BR-127 primed aluminum

The single-lap specimen results for gold plated aluminum are shown in Figure 17 and actually appeared to increase from a low of approximately 1100 psi with no silicone contamination to 1500 psi at a silicone contamination of 32 μg/cm². The higher single-lap shear values observed at a silicone contamination of 32 μg/cm² are statistically different; however, there appears to be a significant plating issue with the gold plated single-lap specimen panels which may explain the difference in adhesion behavior. The gold plated single-lap specimens were found to have considerable variation from coupon to coupon. As noted in Figure 14, the gold plated single-lap specimen panels would occasionally display plating defects. These discontinuities in the plated surface would negatively impact adhesive bonding and decrease the single-lap shear values of those coupons. A coupon without a significant number of defects would obtain higher single-lap shear values.



Regression Statistics	
Multiple R	0.6506
R Square	0.4233
Adjusted R Square	0.3913
Standard Error	236.8662
Observations	20

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	741381.43	741381.43	13.2140	0.0019
Residual	18	1009900.5	56105.585		
Total	19	1751282			

Figure 17. Single-lap specimen results for gold plated aluminum

In general, the single-lap specimen results for both the BR-127 primed and gold plated single-lap panels reveal that Epon 828/V140 bonding is insensitive to silicone contamination when tested in an overlap shear mode. These results are in contrast to those findings by Caldwell, et al^[4] whereby testing in tensile mode revealed sensitivity to silicone contamination at 0.11 µg/cm². The reason for this difference in silicone sensitivity is postulated to be due to the rough, complex surfaces for both BR-127 primed and gold plated samples. The surface features allow significant mechanical interlocking of the adhesive into the adherend. In a single-lap shear test mode, the mechanical interlocking is particularly effective since the adhesive must move against/slide past the adherend surface, preventing premature failure. In addition, the silicone contamination layer may break and form beads which pull away from the adherend/adhesive interface or emulsify into the epoxy adhesive.

Summary and Conclusions

This effort found that FT-IR/ATR can be used as a quantitative tool to determine non-curable silicone contamination. A calibration for each surface type of interest must be completed because the ATR response is unique for each surface. As a result, each surface has a unique slope to the calibration curve. Smooth gold surfaces appear to be limited to quantify silicone from approximately 0.006 µg/cm² up to 32 µg/cm² whereas a rougher aluminum surface only can detect silicone concentrations as low as 0.035 µg/cm² but can quantify silicone up to 64 µg/cm².

As for silicone contamination and its effects on adhesion, bonding Epon 828/V140 to BR-127 primed aluminum and gold plated aluminum surfaces appears to be insensitive to silicone contamination concentrations of up to 64 and 32 µg/cm², respectively. The reason for this insensitivity appears to be a result of the good mechanical interlocking between the relatively rough surfaces and the low viscosity epoxy adhesive. Such interlocking would interfere with premature failure since the interlocking regions must break in order for the adhesive to fail. Additionally, the silicone layer may bead and disperse into the adhesive. Future work will examine silicone contamination on a smooth adherend surface in an attempt to separate out these different effects since a smooth surface will minimize interlocking, and the other, weaker forces will become the primary adhesion mechanism.

Acknowledgments

The authors wish to thank Bob Stoddart for preparing the primed single-lap specimen panels, Louie Smith for testing all bonded single-lap coupons, and Deborah Taylor and Jeff Jennings for meaningful discussions of the results.

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Effect of Silicone Contamination on Assembly Processes

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Introduction

- Silicone materials have many desirable qualities such as flexibility, constant physical properties over a wide temperature range, and good chemical resistance which are useful in various applications
- One drawback to using silicones in manufacturing areas is the potential for non-curable silicone (e.g. oil) to contaminate surfaces and cause unexpected process failures
- Industry guidance is limited with sometimes contradictory information on the concentration of silicone that will lead to failure
- As a result, the risk of costly and potentially unnecessary contamination remediation efforts is increased
- This study is the first of several in an attempt to establish guidelines for allowable non-curable silicone contamination
- This initial undertaking will establish a calibration curve and detection limit for silicone on metal surfaces as well as investigate the impact of silicone on adhesive bonding (unfilled epoxy)

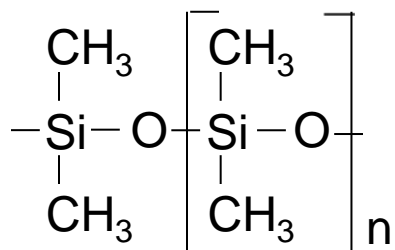


Quantify Silicone on Metal Surface

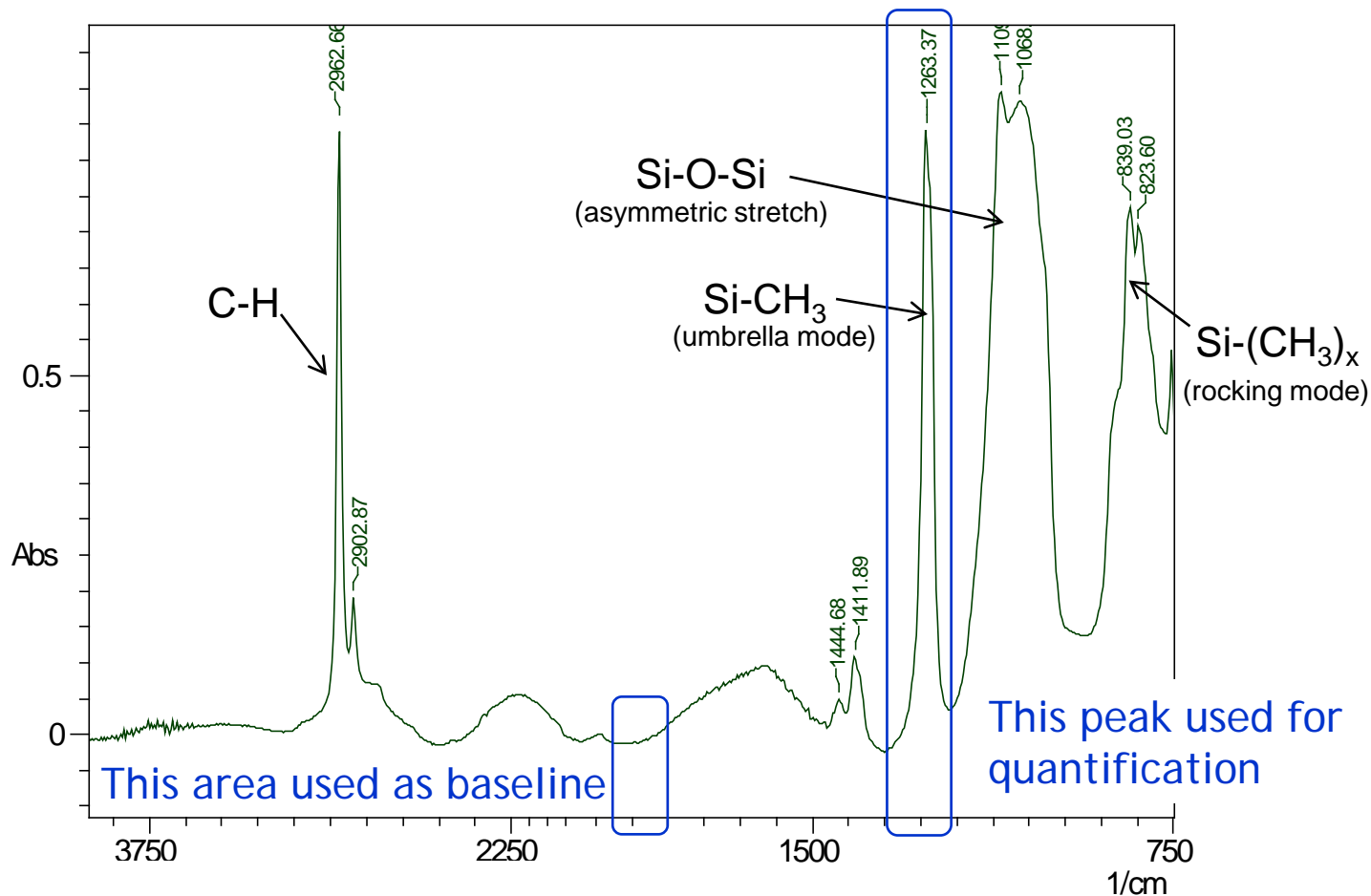
- Prepare standard solutions (mg silicone/ml heptane) by diluting a known weight of silicone oil (DC-200) into known volume of heptane
 - Heptane readily dissolves silicone oil and evaporates quickly from surfaces
- Contaminate aluminum and gold surfaces with silicone standards
 - Pour silicone solution into aluminum weighing pan and allow heptane to evaporate leaving behind non-volatile silicone
 - Micropipette solution onto marked area of gold/chromium sputter deposited microscope slide and allow heptane to evaporate
- Measure contamination level on surface ($0.5 - 64 \mu\text{g}/\text{cm}^2$) using FT-IR spectroscopy in attenuated total reflection (ATR) mode
- Construct calibration curve for area of FT-IR/ATR response under 1263 cm^{-1} peak as a function of silicone concentration
- Estimate detection limit from 3x baseline area at $\sim 1800 \text{ cm}^{-1}$



FT-IR Spectrum of Silicone Oil

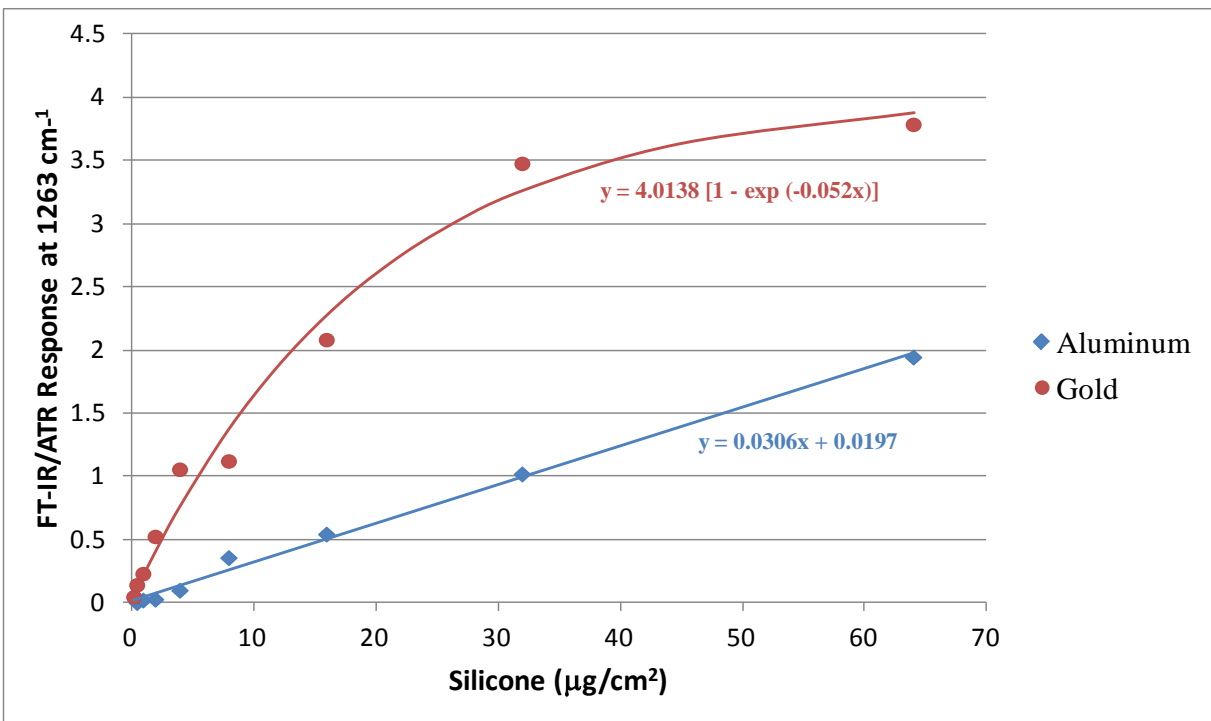


Polydimethylsiloxane
(C₂H₆SiO)_n





FT-IR/ATR Response to Silicone Contamination

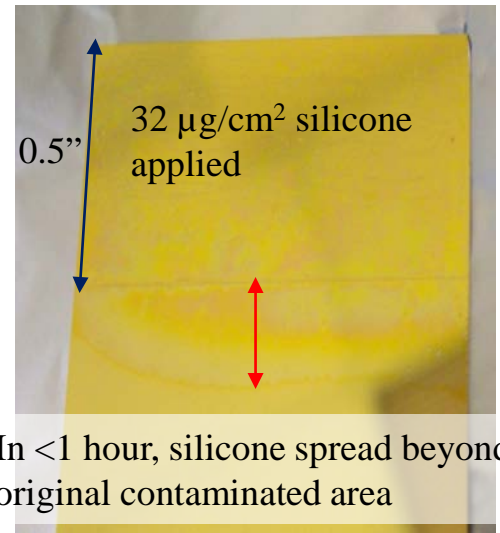
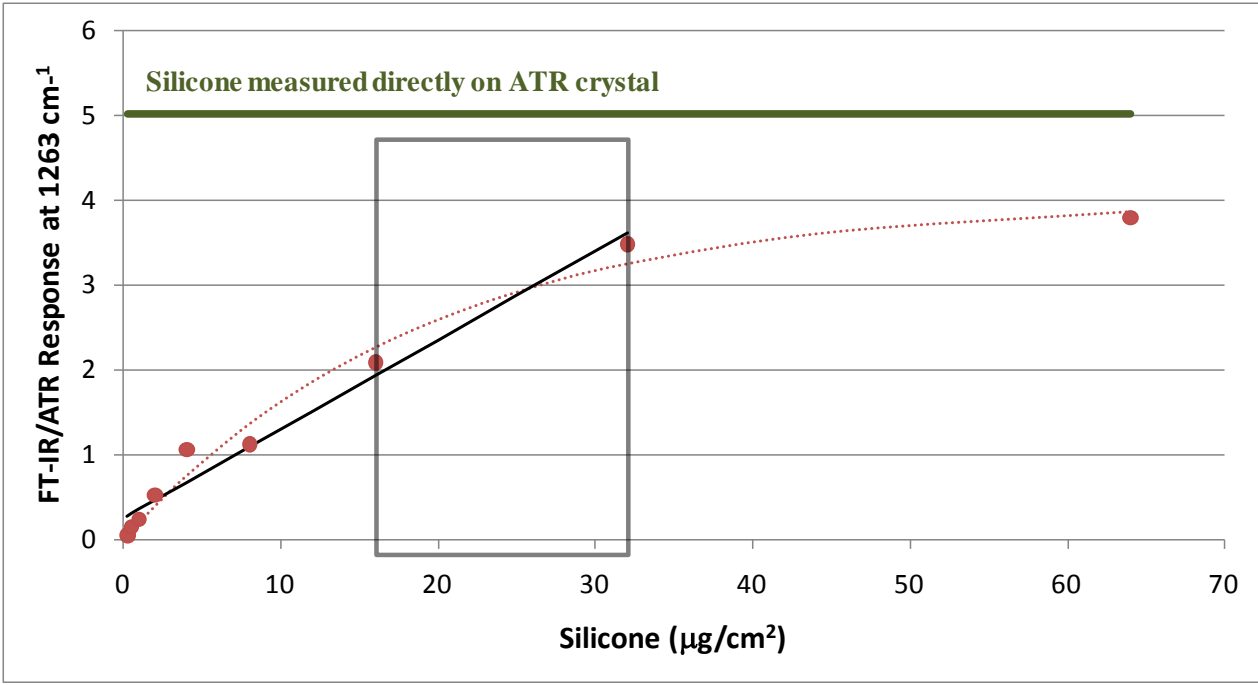


Substrate	Method Detection Limit (µg/cm²)
Aluminum	0.036
Gold	0.006

- Gold response ~350% greater than that of aluminum
 - Need calibration curve for each surface type



Behavior at Higher Silicone Concentrations



- At silicone concentrations above 32 $\mu\text{g}/\text{cm}^2$, FT-IR/ATR response on gold no longer follows linear relationship with concentration and silicone begins to spread in reasonable timeframe (30-60 minutes)



Adhesion

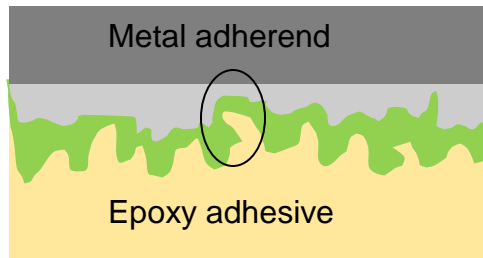
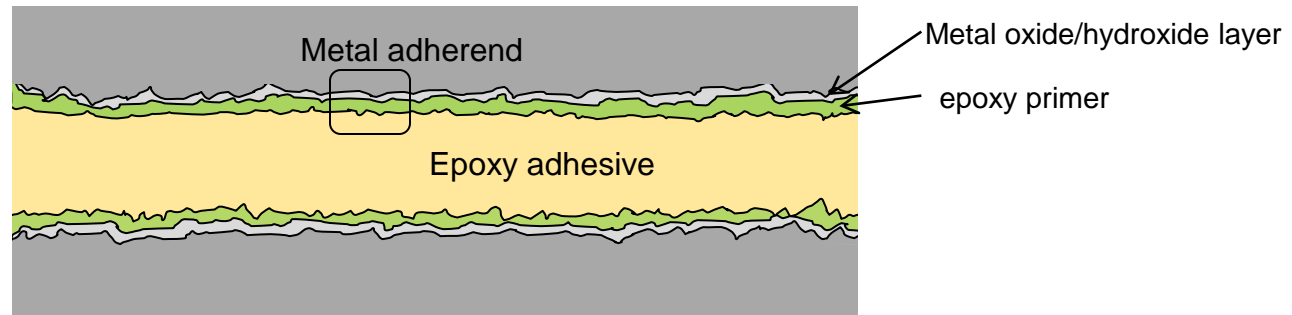
- Major requirements for good adhesion are
 - Adherends with sufficiently rough surfaces to allow for physical “dove-tailing” of the adhesive into the substrate
 - Adhesive with a lower surface tension than the surface energy of the adherend to allow the adhesive to effectively wet the surface

Material	Surface Energy (dyne/cm)
Aluminum	>500
Epoxy	39-52
Silicone	24
PTFE	18

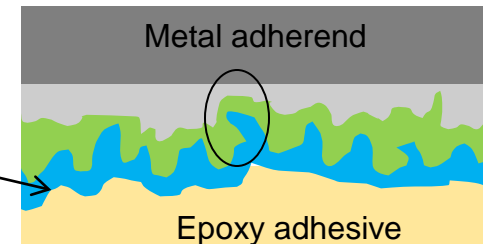
- Adherend surface and adhesive free from contamination
- Silicone oil has the potential to impact adhesion because it has lower surface energy than most adhesives and is a structurally weak boundary layer between the adhesive and the adherend surface



Adhesion and Contamination



Contaminant
(e.g. silicone oil)



Mechanisms of bonding

1. Physical dovetailing into adherend (strong)
2. Attractive forces – e.g. Van der Waals (weak)
3. Possible chemical reactions between uncured epoxide terminations in a primer, if used (strong)

A contaminant has the potential to affect bonding mechanisms by:

1. Limiting physical dovetailing into adherend
2. Cancelling weak bonding forces
3. Preventing contact between adhesive and adherend surface and blocking favorable chemical reactions.

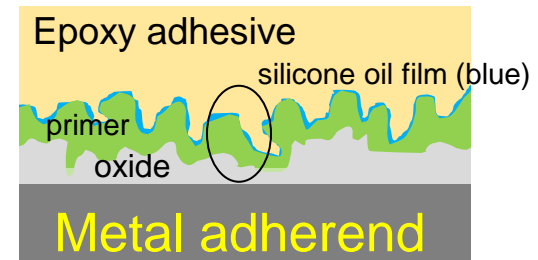
- Higher surface energy of metal allows adhesive to wet surface
- Low surface energy of silicone can cause it to coat adherend surface and lead to bond failure



Silicone Contamination in Adhesive Bond

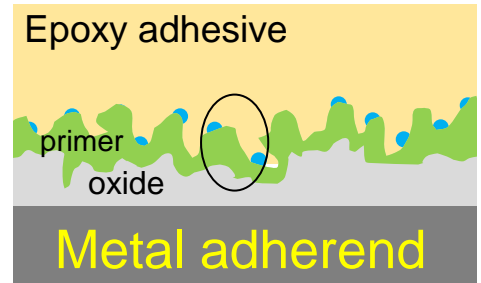
Option 1:

Silicone oil will spread, and the thin coating may not fully inhibit dovetailing. The remaining sites for mechanical interlocking would allow for a strong bond in the presence of silicone oil.

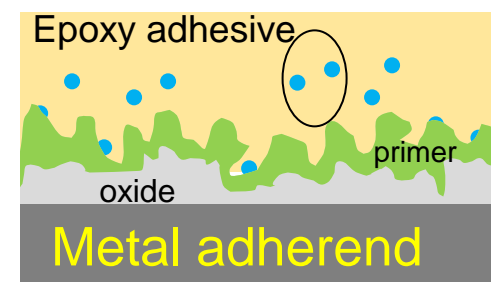


Option 2:

Silicone oil film (blue) breaks and forms droplets in the presence of an epoxy adhesive. Silicone oil and epoxy adhesive are two immiscible fluids. They will separate to minimize contact. Silicone may disperse into the adhesive away from the adhesion interface.



OR



- Significant dovetailing or beading could minimize presence of silicone oil contamination on bonding

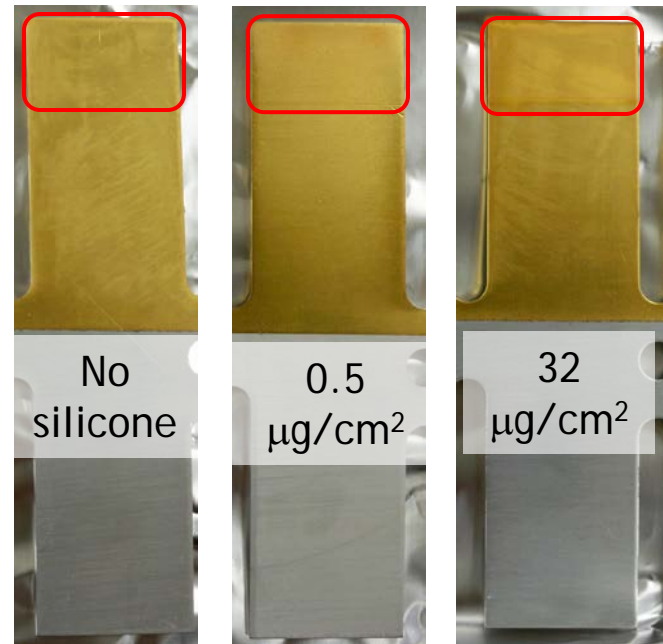
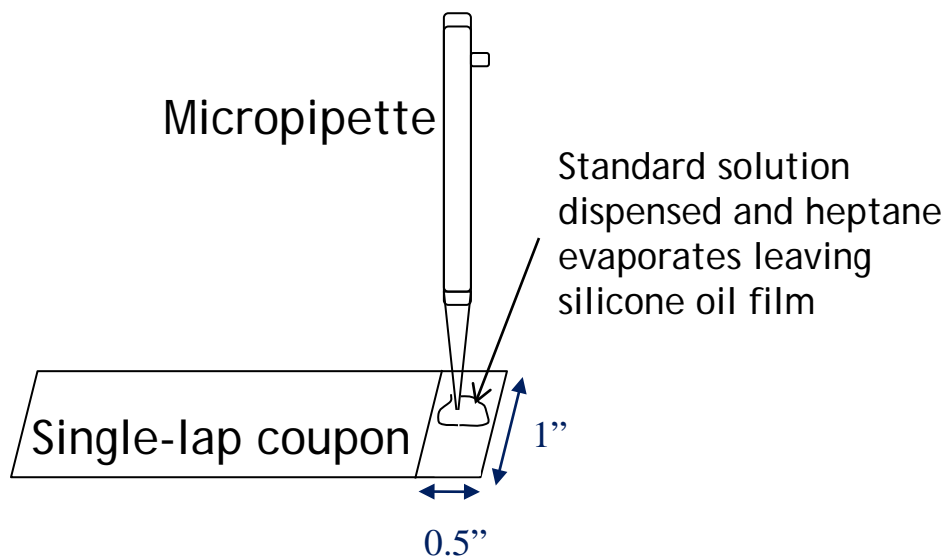


Determine Impact of Silicone on Adhesive Bond (unfilled epoxy)

- Single-lap joint specimens are commonly used to measure adhesion strength of bonded metals (test method ASTM D1002)
- Two types of bond surfaces were tested
 - BR-127 primer/FPL etch/Aluminum
 - Electroplated gold/Electroplated nickel/Aluminum
- Contaminate 0.5" x 1" overlap area of test panel with previously prepared silicone standard solutions
 - Micropipette solution onto marked area of primed or gold plated panel and allow heptane to evaporate
 - Only one panel of each bonded set contaminated to induce failure at contaminated interface
- Bond panels immediately with unfilled epoxy (Epon 828 with Versamid 140 mixed 1:1 by weight) and cure at 93° C for 1 hour
- Cut panels into 5 individual coupons for mechanical test



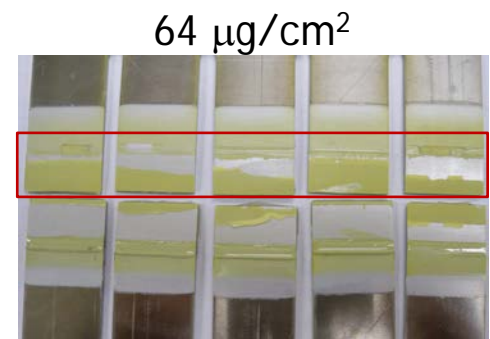
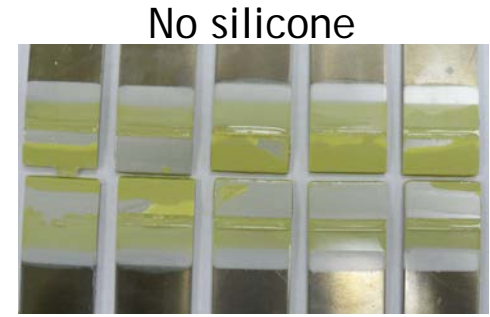
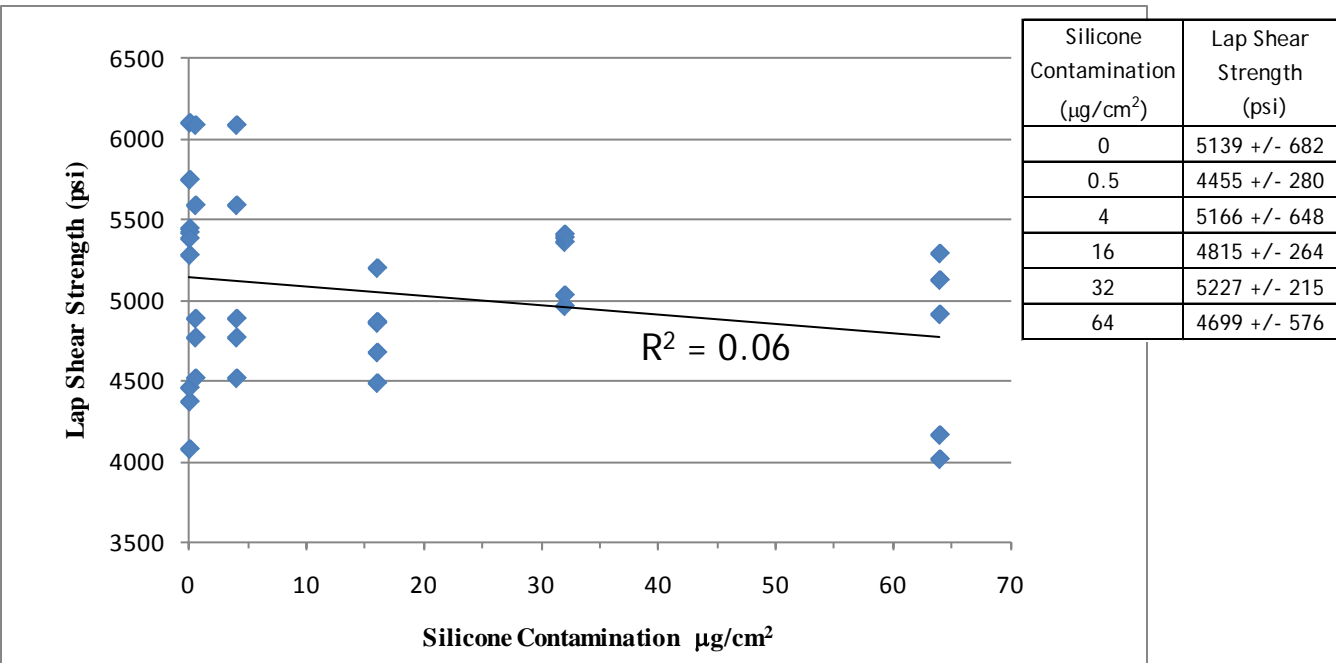
Single-lap Specimen Contamination



- Known weight of silicone oil diluted in known volume of heptane is dispensed onto the overlap region and the heptane evaporates leaving behind the non-volatile silicone oil
- Silicone oil contamination visible on primed panels at 16 $\mu\text{g}/\text{cm}^2$ but visible on gold plated panels at concentration as low as 0.5 $\mu\text{g}/\text{cm}^2$



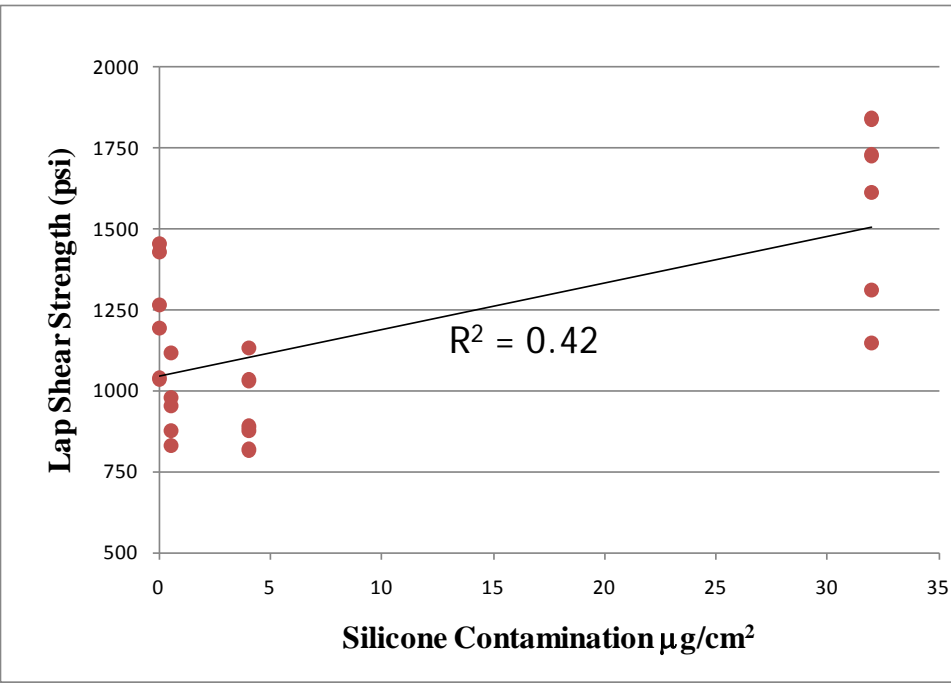
Primed Single-lap Specimen Results



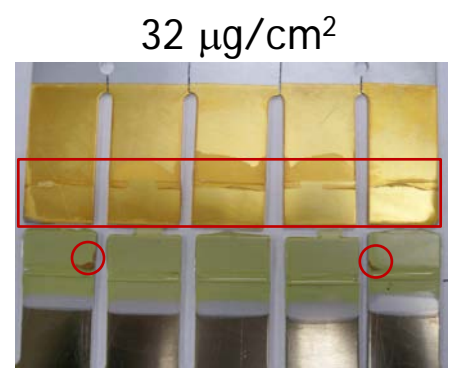
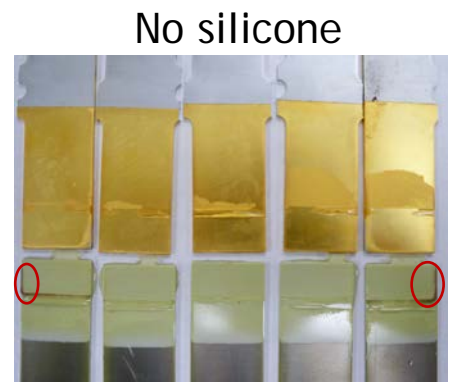
- No statistically significant difference in adhesive bond strength with silicone contamination up to 64 µg/cm²
- No significant difference in failure mode with contamination



Gold Plated Single-lap Specimen Results



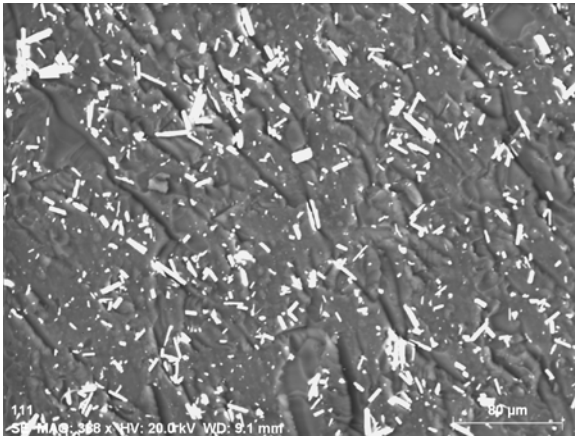
Silicone Contamination (µg/cm ²)	Lap Shear Strength (psi)
0	1276 +/- 173
0.5	950 +/- 110
4	949 +/- 130
32	1527 +/- 290



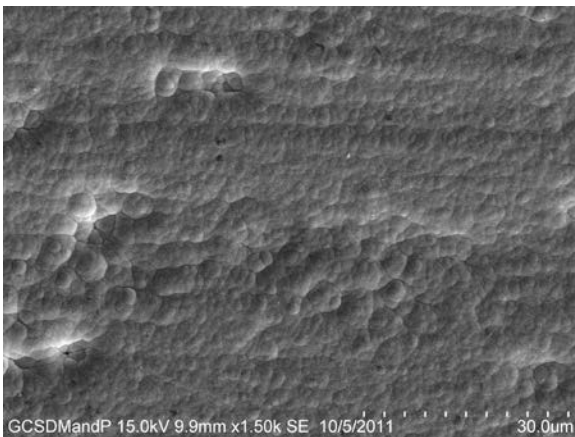
- Positive trend in adhesive bond strength with silicone contamination up to 32 µg/cm²
 - Plating imperfections most likely cause of significant variation in coupon results and lower bond strength values on some test specimens



Primed and Gold Plated Adherend Surfaces

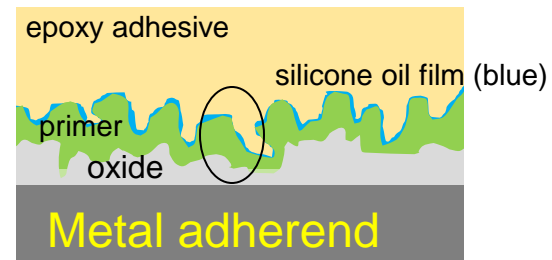


Primer consists of filler in epoxy matrix

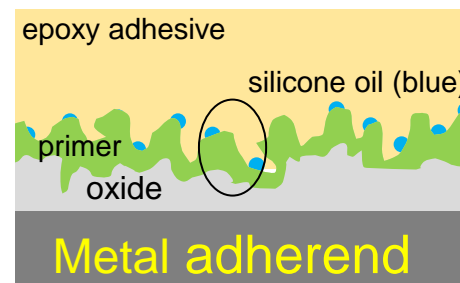


Gold plating deposit is rough and nodular

- The primed and gold plated aluminum surfaces exhibit a rough surface for bonding so that silicone may not inhibit mechanical interlocking



OR





Summary and Conclusions

- FT-IR/ATR can be used to create a calibration curve for non-curable silicone for each metal surface under investigation
- Silicone can be quantified from approximately 0.01 up to 32 $\mu\text{g}/\text{cm}^2$ on smooth gold surfaces or from approximately 0.04 up to 64 $\mu\text{g}/\text{cm}^2$ on rough aluminum
- The single-lap joint data indicate that primed and gold plated aluminum surfaces bonded with unfilled epoxy are insensitive to silicone contamination up to 64 and 32 $\mu\text{g}/\text{cm}^2$, respectively
- The features on the rough primer and gold plated surfaces may provide enough locations for physical dovetailing of the low viscosity, unfilled epoxy to allow a strong bond to form even in cases with silicone contamination clearly visible on the surface
- Future work will examine adhesion on smooth surfaces as well as with filled epoxies (e.g. thixotropic) to limit this mechanical interlocking