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Oxide Alternative Process Development for High Frequency Bonding Applications

Neal Wood, Patrick Brooks, Thomas Thomas, Thomas Huelsmann, Tatjana Koenigsmann, Andry Liong, Wonjin Cho, Carrick Chan
Atotech Deutschland GmbH, Berlin

Abstract

The demand for smaller, faster and smarter electronic devices that can communicate to each other via wireless networks is stretching current communication systems to their limits. This rapid paced evolution is the driving force for the development of the next generation of network systems, the so-called 5G, to give the increased speed of communication and data capacity required.

One of the key factors, which will influence the development in 5G, is the range of frequencies at which data is transferred. Current 4G systems operate in relatively low frequencies of <6GHz. With the introduction of 5G systems, the requirement will be to run at much higher frequency band width; typical range will be from 6 up to >100GHz to enable faster mobile broadband, with low latency (the time taken for devices to respond to each other or a signal from another device) and the "internet of things" where compatible devices "talk to each other".

With this transition to higher frequencies, the path of the electrical signal moves towards the edge of the copper traces into the so-called "skin" or the extreme outer edges of the copper trace. If this "skin" has been heavily roughened or etched, such as is the case in conventional multi-layer bonding enhancement processes, then there is an unacceptably high loss of the electrical signal.

To overcome this high signal loss material suppliers have been developing reliable high-speed dielectrics with low dissipation factors and dielectric constants. In combination with this, the contribution to signal loss from the bonding enhancement chemistry is under great scrutiny. Here, the challenge is to provide the most functionally reliable bonding process with the minimal surface roughening; but as the widely used Oxide Replacement bonding enhancement systems rely heavily upon surface roughening to give good bond strength this creates something of a challenge.

This paper highlights the challenges, developments and modifications made with conventional Sulphuric-Peroxide based Oxide Replacement bonding enhancement system to meet the low signal loss requirements for High Frequency applications, whilst maintaining the highest functional performance and bonding integrity needed for manufacture of reliable multi-layer PCB's.

Background – The Evolution of Oxide Replacement Systems.

In the late 1990's the manufacture process used in fabrication of multi-layer circuits went through something of a revolution. Up until this time, the bonding enhancement chemistry used almost exclusively was a Reduced Black Oxide (RBO). In this RBO process, the surface of the copper trace undergoes a controlled oxidation to form a dense needle like structure having a huge increase in surface area, in what should be considered as an "additive process"; after chemical reduction of this oxide coating the resulting structure offers an optimum structure for bonding. In this additive process, the bond strength and thermal reliability are purely due to the high degree of "mechanical roughness."

Although the RBO process offered a reliable, production proven process, a number of technical and commercial challenges opened the way for the introduction of an alternative manufacture processes. Oxide Replacement (OR) bonding systems are most typically etching solutions based upon a blend of Sulphuric Acid and Hydrogen Peroxide. If a "base etchant" of Sulphuric Acid and Hydrogen Peroxide is used, a very flat, smooth copper structure is formed. To change from this flat structure to one more suited to bonding enhancement applications, it is possible to have a profound effect upon the etched structure by the addition of certain "etch modifying agents", most common of which are organic materials such as triazole type compounds.

The addition of such etch modifying compounds has a number of possible mechanisms by which it can influence the bonding properties. The first two possibilities also result in "mechanical bonding", as previously discussed for RBO, with two levels of surface roughening; first is the increased attack upon copper grain boundaries (often referred to as intergranular etching [IGE]), with the second order of roughening being in the attack at the copper crystal surface itself. In this case, the adhesive properties attributed to the system are purely through the mechanical roughening. In the final mechanism suggested, in some specific cases the materials used as etch modifiers can result in the formation of a Copper-organometallic species that has some ability to form a chemical bond with the resin systems of the pre-preg materials used. In the ideal, case where a synergy of mechanical and chemical bonding occurs, the best possible bond strength and thermal reliability results.

Challenges faced with High Frequency Applications

Following the introduction of Sulphuric-Peroxide based OR systems many generations of process followed. One of the most common changes with this ongoing process development has been to change the etch modifying additive chemistry, most commonly to give a higher degree of mechanical roughness for a lower amount of copper removal, which will therefore enhance the bonding performance in multi-layer fabrication.

However, with the growing relevance of High Frequency circuit requirements, in what is often more recently referred to as 5G applications, this approach to provide a bonding system reliant upon the highest possible surface roughening is directly opposed to the signal integrity demands of the electronic design. As the frequency of the electrical signal is increased, the path travelled within the copper trace changes and the electronic flow moves towards the outer most layer of the copper surface. In this so-called “skin effect”, as the frequency increases, the path continues to migrate to outer edges of the trace. Typical relationship between Frequency and skin depth is shown here in Table One:

Table One: Range of Skin Depth for given Frequency

Frequency (GHz)	1	10	50	77	110
Skin Depth (µm)	2.00	0.67	0.30	0.24	0.20

To overcome the skin, effect the “ideal” design of copper trace for high frequency application would be a perfectly smooth, flat surface. However, this is a direct contradiction to the approach taken with the most commonly used Sulphuric-Peroxide OR systems, where the best bond integrity is found with highest roughening.

Herein lies the challenge with the development of Bonding Enhancement chemistry suitable for 5G Applications. The ultimate goal would be a non-etching, none roughening process capable of providing the same high bonding strength as a highly roughening OR system. To achieve such a target the bonding system must effectively use only pure chemical means to provide adhesion between the copper substrate and dielectric material. To meet industry requirements, any such system would also need to be fully independent of the resin system to which it must bond the copper surface. Essentially, it must act as a “universal glue” which is capable of forming strong chemical bonds between copper and the polymeric backbone of any dielectric material.

In this paper, the changes made to a market leading OR process to meet these challenges are discussed.

Relationship between Signal Integrity and Surface Roughness.

In the continuing process development of Sulphuric-Peroxide OR Systems, certain process performance parameters are routinely measured. For example, peel strength and thermal reliability in terms of measuring the number of Solder Dip or Reflow cycles passed before delamination are commonly measured as a guide to process performance. However, for high frequency applications what process parameters should be most closely monitored?

As the impact of surface roughness is considered critical in terms of the skin effect, initial DOE’s focused upon the relationship between Signal Integrity (SI) data and Surface Roughness Data, where the roughness measurements were taken using Atomic Force Microscopy, with a 10-µm x 10-µm sample size.

In this test matrix concentrations of one of the key Etch Modifying agents were varied to achieve a range of roughness values within the etched copper structure. Figure One shows the Scatterplot Matrix used to analyze the relationship between Signal Integrity (SI and) Sa (mean surface roughness), Sz (the maximum peak to trough height in the etched copper deposit) and RSAI (Relative Surface Area Increase). Analysis of this data shows the greatest correlation between RSAI and SI. To emphasis this relationship between RSAI and SI, Figure Two shows the Bivariate Plot for SI vs RSAI, which shows a relatively strong linear relationship.

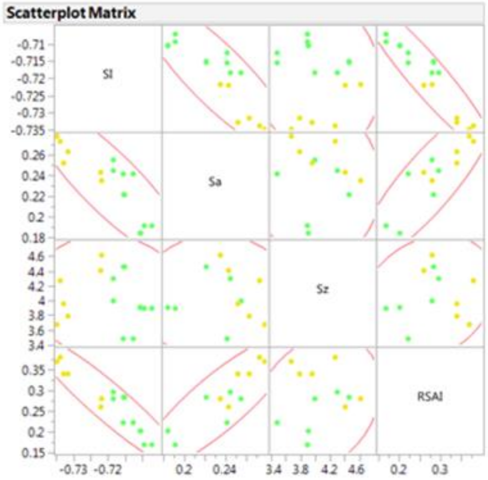
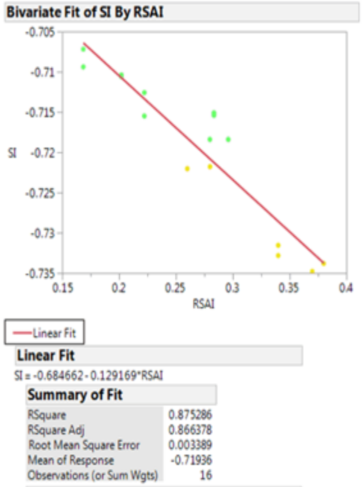


Figure One:
Relationship between roughness and SI



Linear Fit

SI = -0.684662 - 0.129169*RSAI

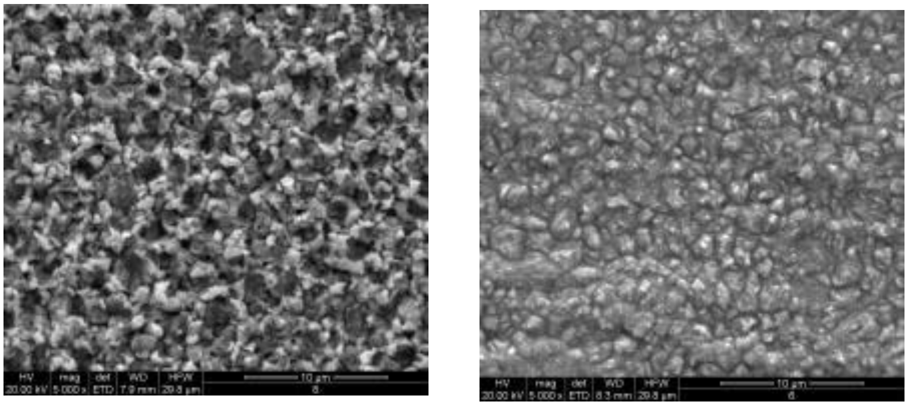
Summary of Fit

RSquare	0.875286
RSquare Adj	0.866378
Root Mean Square Error	0.003389
Mean of Response	-0.71936
Observations (or Sum Wgts)	16

Figure Two:
Bivariate Plot showing SI .vs. RSAI

Performance Comparison between Standard OR and First-Generation High Frequency OR.

Having identified the relationship between SI and RSAI it is now possible to optimize the formulation of the first-generation Oxide Replacement Process, specifically designed for High Frequency Applications (HF OR #1). Figure Three shows the structure for the two processes by SEM. The standard OR appears to have a significantly rougher surface than HF OR #1:



Standard OR SEM x 5K
(HVLP Copper)

HF OR #1 x 5K
(HVLP Copper)

Figure Three: Comparison of structure by SEM for Standard Oxide Replacement and First-Generation Oxide Replacement for High Frequency

The observation that the standard process has a much rougher surface than the modified High Frequency solution is confirmed by surface area measurement data as shown in Figure Four. Here, the Anova Plot clearly shows a significantly rougher surface for the Standard OR process compared with the modified High Frequency OR #1. Figure Five shows the Anova plot comparing SI data for the two systems; as with the Bivariate Fit in Figure Two, Figure Five confirms that the lower RSAI found with the modified system results in the desired improvement in SI performance.

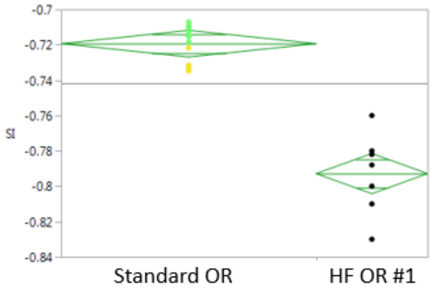


Figure Four:
Comparison of SI

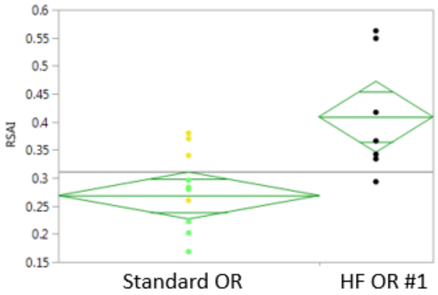


Figure Five:
Comparison of RSAI

Peel Strength and Thermal Reliability

Having identified the relationship between reduced surface roughening (lower RSAI) and an improved SI performance, the impact upon Peel Strength (Bond Strength) is investigated in a full loading test of the two standard OR system and the first-generation HF OR #1. Oxide Replacement systems rely heavily upon surface roughening, though not wholly upon the mechanical roughness, as previously explained, due to the contribution towards bond strength from the Chemical Bond formed between the organometallic coating and the pre-preg materials used, therefore there is a concern that there will be a negative impact upon bond strength and thermal reliability due to the lower surface roughness.

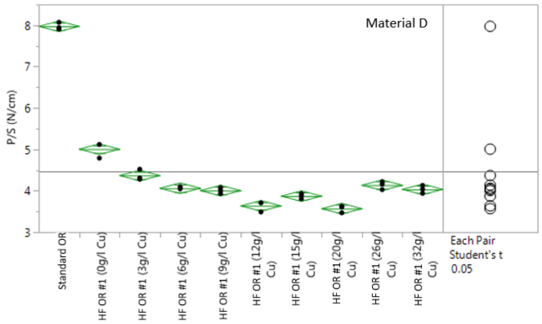


Figure Six:
Peel Strength with Material D

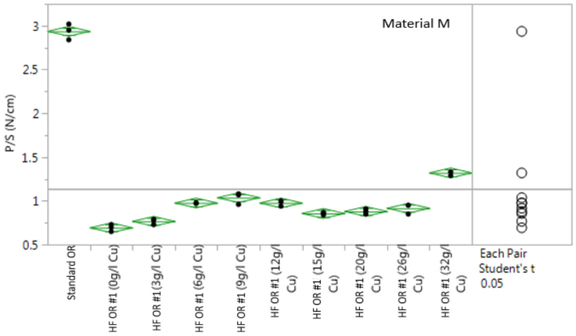
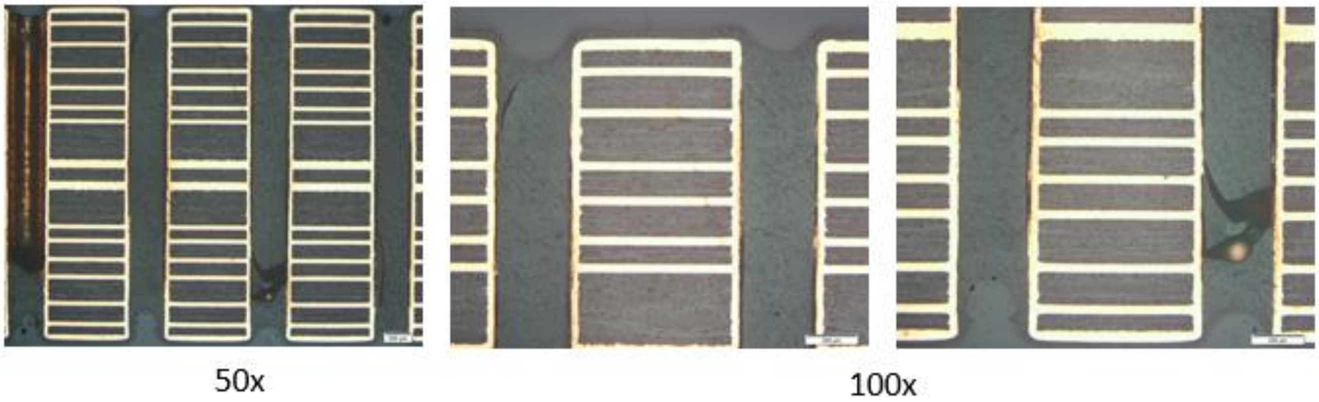


Figure Seven:
Peel Strength with Material M

Figure 6 and 7 show the peel strength data across a full copper loading range for HF OR #1, where the peel strength found with the original OR process is provided as a reference. Clearly, the reduced roughness has a strong negative effect upon the peel strength as a significant fall in peel is observed. However, while it is appreciated that a low peel strength is far from desired this does by no means indicate that a poor thermal reliability will also be observed.

Thermal reliability results for the same system demonstrate excellent results. Figure 8 shows cross section results after Solder Dip test, where high layer count server type panels were prepared with a single press application using a range of high frequency PCB laminates, pass 15 cycles with no delamination in any case. In the example shown, this far exceeds the target OEM specification of five cycles without delamination. Similar excellent performance is also observed with iR Reflow Test with 15 Cycles at a peak temperature of 260°C.



Thermal Stress Test: IPC TM 650 2.4.13
Test Condition:
- Temperature: 288°C ±5°C
- Contact Time: 10±1 Seconds
- Cycles: 3,5,8,12,15 cycles

Test Criteria: No Delamination after thermal stress test

Materials:
HVLP Cu with M (24 Layers TV)
HVLP Cu with D (32L TV)
HVLP Cu with T (32L TV)

Figure Eight: Cross section analysis of High Layer Count, single stack test coupon after 15 x Solder Dip Test

Performance with the First-Generation High Frequency Oxide Replacement shows excellent performance, though the low peel strength results inevitably raise some concerns. Therefore, the aim with second phase of process development is to enhance the process performance further still in terms of peel strength whilst maintaining the excellent SI performance of the first-generation process. To meet this objective, two directions of process development are taken.

Second Generation High Frequency OR

To improve upon the performance of HF OR #1, a further optimization of the Organic Etch Modifying additives used in the first generation is undertaken. Here, it is vital that the benefits of the first generation over the standard OR process are not lost; this means that any changes made to improve peel strength (and ultimately the thermal reliability) have no negative effect upon the roughness of the etched copper deposit and therefore the Signal Integrity.

The original, or standard OR system contains a blend of multiple organic etch modifiers. In the first stage of process development, the concept was to keep concentration of all these etch modifying agents to an absolute minimum to minimize the roughness of the etched copper structure. However, by reducing concentration of all such components also has a negative effect in terms of reducing the amount of organometallic coating. By making changes to reduce the thickness of the organometallic coating in theory this would also reduce the ability of the coating to form chemical bonds with the dielectric resin system.

Here, the concentration of one of these organic etch modifiers is increased in an attempt to gain higher peel strength performance. Figure 9 shows that by increasing the concentration of this specific etch modifying compound three benefits are found when compared with the first-generation high frequency product. Both peel strength and number of reflow cycles until delamination are increased, while at the same time there is a corresponding small but significant reduction in RSAI. By reducing the surface area increase, this change also results in a desirable improvement in signal loss performance.

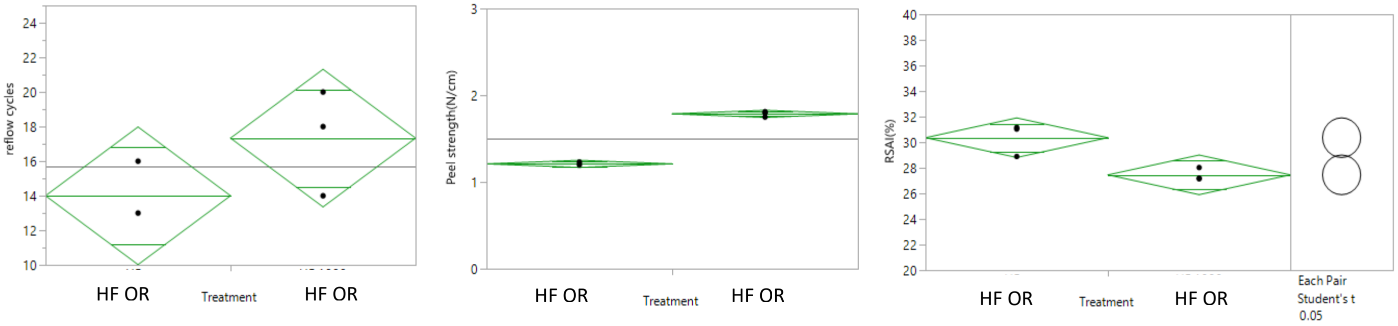


Figure Nine: Comparison between First and Second Generation High Frequency Oxide Replacement Processes

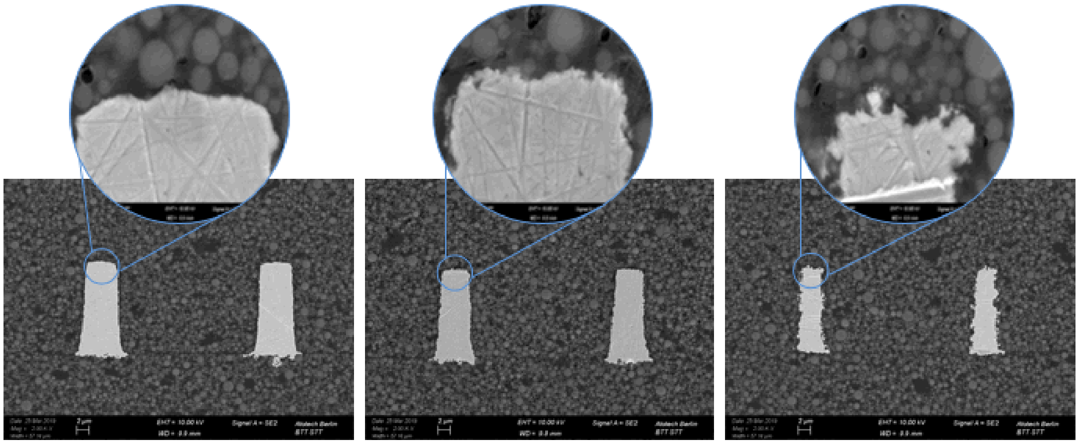
Second Generation High Frequency OR with additional Post Dip

Having optimized further still the concentrations of etch modifying agents in the work leading to the second generation of High Frequency Oxide Replacement systems (HF OR #2), the next challenge is how to improve the performance further still? To this point, the task to improve signal integrity performance has focused upon the reduction in surface roughening, which has so far been demonstrated to give an improvement in insertion loss performance, but pose challenges in terms of bond strength due to the part reliance upon mechanical adhesion due to surface roughness.

For the next step forward in development of Oxide Alternatives for High frequency applications, the target is to achieve acceptable bonding performance but with a reduced copper etch depth. By reducing the etch depth, the effective line width and track height reduction will also be reduced, a change which will also result in improved SI performance.

The typical etch depth with Oxide Replacement solutions is however, set in the range 0.8 to 1.2-microns of copper removal for good reason. This is the etch depth required to achieve acceptable bonding performance. So the challenge now is how to improve the bonding performance of HF OR #2, with the modified etch system to provide lower surface roughness and acceptable adhesion, and at a lower etch depth? The solution to this challenge comes in the form of a novel post dip solution, based upon an adhesive organo-Silane coating. The benefit of such a system is that the organo-Silane coating can offer a degree of chemical bonding, therefore increasing bond strength at the new, lower etch depth.

First, the improvements in line width and track height reduction of such a system are shown here in Figure Ten:



As Received – no etching

Oxide Replacement HF OR #2
Etch depth 0.3-microns

Oxide Replacement HF OR #2
Etch depth 1.0-microns

Figure Ten: Comparison between Line Width and Track Height reduction for HF OR #2 at differing etch depths (For 14-micron width feature size)

Analysis of line width reduction (made at both top and bottom of the copper trace) and track height is shown here in Figure Eleven:

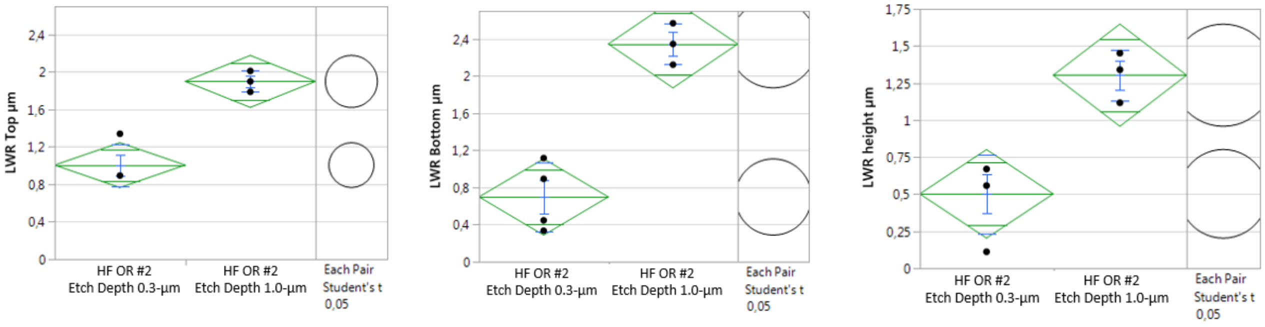


Figure Eleven: Analysis of Line Width and Track Height Reduction for HF OR #2 at differing etch depths (For 14-micron width feature size)

Now having established the benefits of using HF OR #2 at a lower etch depth, the performance in combination with the application of the adhesive-Silane coating need to be shown.

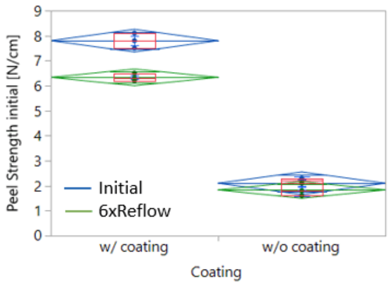


Figure Twelve:
Peel Strength Data with and without application of Silane Coating, before and after reflow

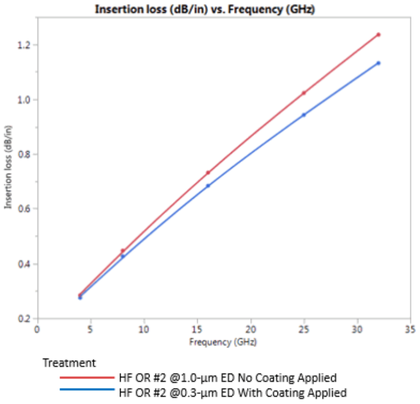


Figure Thirteen:
SI Data with and without application of Silane Coating, at different Etch Depths

Figure Twelve shows a comparison between the peel strength results obtained with and without the application of the adhesive Silane coating. Results are shown for initial peel strength and after six reflow cycles. It can clearly be shown that the system where the Coating is applied has a significantly higher bond strength.

Finally, Figure Thirteen shows Signal loss data for the high and low copper etch depths with the HF OR #2 base system, where the adhesive Silane coating has also been applied to the lower etch depth case. By using the same etching process, albeit at a lower copper removal, it can be shown that an improved performance in terms of reduced SI loss is seen across a range of frequencies under test.

There is however, one significant negative side to this approach with low etch depth and application of an adhesive post dip coating. The proposed process sequence will not fit into conventional Oxide Replacement equipment. Therefore, expenditure will be required for new process equipment so this type of change may not be universally applicable.

Summary

There is a high demand for bonding enhancement systems compatible with the needs of high frequency applications. The challenge in the development of Bonding Enhancement chemistry is to provide a system that does wholly not rely on high surface roughening to provide bond strength and good thermal reliability. Essential the ultimate goal is for a non-etching, non-roughening system that would purely rely upon chemical bonding between the copper traces and polymers in the dielectric system.

Currently no such system is known and while the search for such a process continues, modifications to the current Sulphuric-Peroxide based Oxide Alternative system widely used in multi-layer circuit manufacture can help meet the near-term requirements for high frequency production.

By making changes to the etch modifier compounds used in Oxide Alternatives, it is possible to somewhat reduce the surface roughening whilst maintaining the desired bond strength and thermal properties of the board. This is achieved by a synergy of mechanical and chemical bonding, which can also be further enhanced by the application of an adhesive post dip coating based upon an organo-Silane chemistry.