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Enhancing Interlaminar Bond Strength for High Performance Resin Systems and Liquid Photoimageable Soldermasks with an Organo-metallic Copper Surface Treatment Process

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Abstract

The technology shift toward higher performance (low Dk, low Df, faster signal speeds) resin materials for high reliability high layer count multlayer interconnect devices is moving rapidly. PWB fabricators are discovering that the bond strength between the copper circuitry and these resin systems is not as reliable with reduced oxide bonding treatments. It has been shown in the market place that reduced oxide processes are being replaced by new process developments for a variety of reasons that will be explained. In addition, increased use of ENIG (electroless nickel-immersion gold) and immersion tin processes is causing adhesion failures of some liquid photoimageable soldermasks. This paper will explore the mechanism of resin adhesion to copper surfaces and provide a discussion on the interaction of the key process parameters (etch rate, organic coating content, sulfuric acid concentration, copper loading in solution) on the process performance. Reduced oxide bonding technology will be the benchmark comparison for the performance of the alternative technology. Bond strengths for a variety of high performance resin systems will be measured. These materials will include high Tg epoxy FR-4, cyanate ester, BT, polyimide, PPE and PPO resins. In addition to measuring bond strengths, other methods including solder float and T-260 time to delamination will be utilized to compare results. Additional IPC recognized test methods would be employed to compare the performance and reliability of the organo-metallic process to reduced oxide. The paper will conclude with a discussion on improving soldermask adhesion with a modified organo-metallic surface treatment process.

Introduction

With continued emphasis on long term reliability and vastly improved electrical performance, manufacturers of high layer count multilayer printed wiring boards are beginning to abandon the reduced oxide bonding process in favor of alternative methods. One such method will be described here. This method (described by the authors as an organo-metallic adhesion promotion system) increases the bond strength of the resin to the copper by modifying the topography of the copper surface and simultaneously depositing an organic layer that acts as an adhesion promoter. The surface area or topography of the copper is enhanced by the selective micro etching along the grain boundaries of the copper. (This mechanism will be discussed further below) This organo-metallic process has found use due to the fact that higher performance resins and other advanced materials require higher pressures and temperatures for lamination. With reduced oxides, the needle-like structures composed of cupric oxide are very fragile. Typically, these higher pressures and temperatures cause these needles to fracture, reducing bond strengths. The structure of the oxide is shown in Figure 1 below.

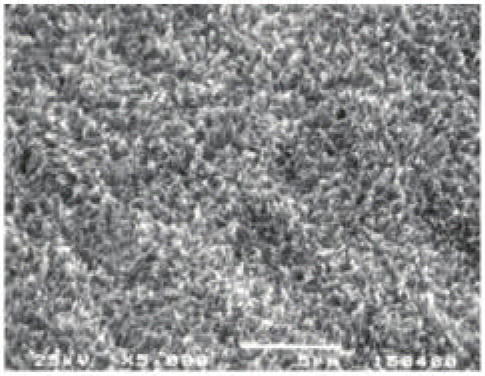


Figure 1 - SEM View of Reduced Oxide Coating

Contrast this with the structure shown in Figure 2. Here, one can see that the actual grain structure is formed by the selective micro etching along the grain boundaries of the copper. One can't see (from this SEM) the organic coating that is co-deposited on the surface However, analysis of the surface with various analytical techniques will reveal the presence of an organic material. The structure of the copper is one of copper metal, not a copper oxide crystal. The organic coating functions as a covalent bond enhancer with the functional resin system.

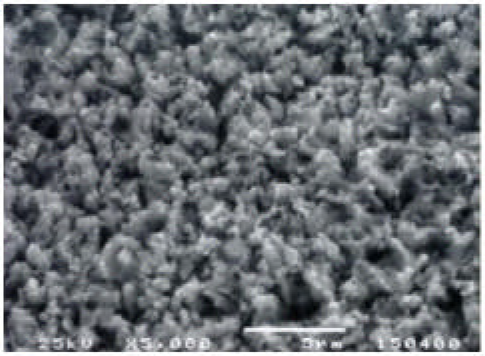


Figure 2 - SEM View of the Structure of the Organo-metallic Copper Crystal Structure

Theory of Bonding and Process Description

There are two main factors involved in enhancing the bonding strength of copper to the pre-preg for multilayer lamination of circuit boards. They are 1) the type and degree of roughness imparted to the copper surface and 2) the type and thickness of any coating that is applied to the copper surface.[1]

Roughness

Current oxide coating processes impart micro-roughness to the copper surface that greatly exceeds the degree of roughness that is obtained with normal copper micro-etchants. In order to match or exceed the bond strength that oxide processes impart to the copper, these micro-etchants would need to be reformulated to greatly increase the degree of roughness.[4] Not all forms of roughness are the same. For example, sanding the copper surface would impart a great deal of roughness to the surface but the bonding strength would still be very low due to the fact that this roughness would be macro-roughness rather than micro-roughness. Good copper adhesion starts with imparting a micro-roughened surface to the copper. This roughness can only be seen with a SEM at powers of about 2000X or higher. A power of 5000X is commonly used. With such a photograph of the surface we see that a typical oxide process roughens the copper on the order of 0.1 to 0.5 microns peak to peak. Also, the peak to valley distance (perpendicular to the copper plane) is greater than the peak-to-peak distance (parallel to the copper plane). The type of micro-roughness (different peak to peak and peak to valley distances) will influence the bonding characteristics of the copper to the pre-preg. Even shape (prism-like, jagged, round, bent etc.) can influence the bonding characteristics.[1]

Different pre-pregs will have different flow and wetting characteristics. It is possible that some pre-pregs will flow and wet out the entire micro-roughened surface from top to bottom. While other pre-pregs with low flow characteristics may not be able to flow all the way down to the bottom of the valley and may not completely wet out the micro-roughened copper. This leaves a micro-gap at the bottom of the valley where solution can leach into the coating and cause issues, maybe even pink ring (even though the peel strengths are high). So it is conceivable that some pre-pregs will like a certain type of micro-roughness, and other pre-pregs may do better with another type of micro-roughness.[2]

Coatings

Current oxide processes also forms a coating on the copper surface that exhibits different chemical and physical properties. For example, the wettability of the oxide surface is different than an equally roughened bare copper surface. The ability of the pre-preg to chemically and physically adhere to the surface is dependent on what that surface is, in addition to its surface area. The coating thickness and strength of the overall coating play a major role. For example, a very long oxide needle is fragile. Thus, an oxide coating that is too thick does not give good peel strengths even though the surface is very rough. The alternative process (organo-metallic) imparts a coating on the copper surface at the same time as etching/micro-roughening the surface. Unlike the inorganic oxide coating, the alternative coating is organic. (Often referred to as an organo-metallic, due to the nature of the organic coating forming on the copper) During the oxidation of the copper, a metal/organic coordinate is formed that is insoluble in the process solution. This coating is a vital part of the bonding mechanism. Tests have shown that copper surfaces with equal or even greater degree of micro-roughening, but which do not contain a metal/organic coating, do not provide good bonding characteristics, especially with respect to time to delamination. The organo metallic coating increases the bond strength, especially at high temperature stress conditions such as solder immersion. This is due to chemical interaction between the copper and the coating, (a coordination bond is formed), and the coating and the pre-preg, (a sharing of pi electrons occurs).[1]

Chemical Reaction

Organic metallic process is a peroxide-sulfuric based etching and coating solution that has been specially and uniquely formulated to impart micro-roughness to the copper surface that greatly exceeds normal etchants and at the same time forms a coating on the surface that promotes adhesion through chemical bonding. Peroxide etches copper by oxidizing Cu° to Cu^{2+}. The half-cell reactions are shown below:

$Cu^0 \rightarrow Cu^{2+} + 2e^-$ (-0.3419 volts)
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (+1.776 volts)

The net reaction is:
$H_2O_2 + 2H^+ + Cu^0 \rightarrow Cu^{2+} + 2H_2O$
(+1.4341 volts)

If sulfuric acid is used as the acid then we have:
$H_2O_2 + H_2SO_4 + Cu^0 \rightarrow CuSO_4 + 2H_2O$
(~+1.4341 volts)

This reaction consumes one mole of peroxide, one mole of sulfuric acid and one mole of copper metal and produces one mole of copper sulfate and two moles of water. The positive voltage indicates that this reaction is spontaneous and the relatively high voltage of this chemical system further indicates that virtually every molecular collision of peroxide with copper will result in a reaction (when the acid is in excess). This means that the number of collisions per second controls the reaction rate. So the higher the peroxide concentration, agitation, and temperature, the faster the reaction will go. The reaction above indicates that there is no gas produced by the reaction, yet when boards are etched with peroxide one can visually see gassing at the board surface. This means that the reaction is not 100% efficient and that some peroxide reacts at the surface by spontaneously breaking down.

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2\uparrow$$

Any mixture of peroxide and acid will etch copper. However, most printed circuit board applications use proprietary formulations in which special additives are added to this system to impart a better, more stable, and predictable etching solution. These additives do not directly partake in the etching reaction but act as catalysts to alter the reaction rate or change the type of roughening produced by the etch (discussed below). In the case of alternative process, an organic coating is deposited. Also, since peroxide is fairly unstable, stabilizers that inhibit the spontaneous decomposition of peroxide are a necessary ingredient in the formulation.

Function of Topography Modifier and Adhesion Promoter

The organo-metallic chemistry is function specific because it contains proprietary additives that adsorb onto the copper surface which influence the etch rate on a sub-micron scale. This causes the imparted roughness to be several times greater than without these additives. The additive adsorption on the surface causes the etch rate at the copper grain boundaries to be increased greatly over the etch rate away from these grain boundaries. This causes the resulting surface roughness to be much greater than a normal peroxide/sulfuric etchant. This type of influence on the etch rate is called topography modification. The additive is organic in nature. In addition to topography modification, the additive coordinates the copper ions as oxidation is occurring. This is a special, Cu^{1+}/organic coordinate that is insoluble in the solution and coats the surface. This special coordination only occurs when an additional additive is present which acts as a catalyst to the reaction. This catalyst for the Cu^{1+}/organic coating reaction is an additional additive that acts as a coating promoter. This coating is known to promote bonding to the pre-preg. For lack of a better term, one can refer to this as an adhesion promoter. The promoter causes the oxidation of copper to occur in two steps. With standard peroxide etch; the copper metal oxidizes from Cu° to Cu^{2+} in one step. That is, there is no relaxation step in the activation barrier of going from Cu° to Cu^{2+}. However, with the promoter present, the copper oxidation follows a two-step mechanism, Cu° to Cu^{1+} to Cu^{2+}. There is a dip in the activation barrier at Cu^{1+}. This two-step mechanism only occurs within certain concentration ranges of the promoter molecule. Outside these ranges (both low and high) the mechanism reverts back to a one step oxidation. With the two-step oxidation mechanism, the modifier is able to form an insoluble coordinate with the Cu^{1+} specie before it oxidizes to Cu^{2+}. The promoter thus creates an intermediate step. As stated earlier, the Cu^{1+}/organic coordinate is insoluble and coats the surface. Also, oxidation can continue. The Cu^{1+}/organic coordinate can be further oxidized to Cu^{2+} and organic. The organic is then free to search for more Cu^{1+} coming from the new surfaces being created by the etch.[1]

The topography modification/organic coating mechanism is depicted in Figure 3.

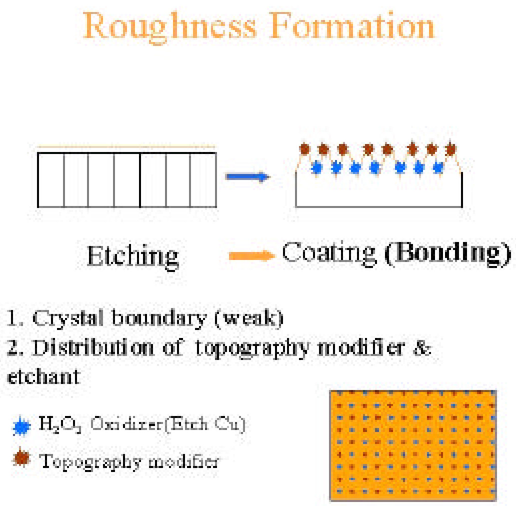


Figure 3 - Theory of Roughness Formation

Because the coating is formed during the etching of the copper surface, the coating has to fight for the surface as the surface itself is being etched away. The coating is dynamic in that as oxidation continues, the existing coating (the copper/organic coordinate) is dissolved and a new coating (with the freshly oxidized copper) is formed, replacing the old. The organic that was bound to the copper surface goes back into solution and seeks out new copper being oxidized and reforms the coating. Therefore, since the coating is constantly being destroyed and recreated, it is a dynamic coating. In this way only a relatively thin coating thickness can be accomplished. In other words, as copper is etched, a new surface of copper is exposed and the additives have to re-adsorb onto the new copper surface. This means that the coating thickness cannot build up indefinitely, but will be limited to a relatively thin layer. It is beneficial to avoid excessive coating thickness. [Similar to oxide where a lower weight gain provides an improved bond over the thicker, heavier oxide coatings][3]

The promoter also contains additives which help to maintain even adsorption of the topography modifier. If the modifier adsorbs very strongly and without something present to "tame" it, the coating may not be perfectly uniform.

The physical characteristics of the substrate are more important in the organo-metallic bonding process than in the reduced oxide process. There is a good reason for this. In the reduced oxide process a crystal of copper oxide is additively "grown" from the surface. This growth process is referred to as anodic oxidation of copper in an alkaline medium. The roughness seen on the SEM photo in Figure 1 is from this crystal growth. The copper oxide in the crystal is a product of copper metal being oxidized in an alkaline medium. These copper oxide crystals are loosely held and somewhat fragile.

In the organo-metallic process, the roughness seen on the SEM photo in Figure 2 is the substrate. The organo-metallic process subtractively "etches" the substrate. The roughness imparted into the substrate is a direct function of the grain structure of the substrate. In the oxide process the grain structure has nothing to do with growing the oxide crystal. These differences in the substrate characteristics manifest themselves as different thickness' of the organo-metallic coating deposited on the substrate and in different degrees of roughness. When comparing different manufacturers (i.e. Circuit Foil, Oak Mitsui or Gould) of the same foil type (HTE or RTF) one will likely see a difference in color hue (shade of red / brown) but not performance. In many cases these color differences are insignificant in terms of product integrity. However, the non-uniformity of the coating has more impact with organo-metallic coatings than those experienced with reduced oxide. ***This is why the operational parameters and proper concentrations of all active ingredients must be controlled within process specification.*** It is important that quantitative means of measuring these additives is available and user friendly to the fabricator.

Before entering a discussion on bond strengths of various resin materials, it is important to investigate the influence on bond strength of the key process parameters. Key process parameters including acid concentration, organic additives concentrations (both the topography modifier and adhesion promoter) are the key performance indicators for bond strength. Coating thickness/uniformity and the etch topography/profile are closely controlled by maintaining the proper concentration ranges for the sulfuric acid, topography modifier and adhesion promoter. The thinner, but more uniform organic coating with a sufficient surface roughness provides the optimum bond strength.

In the Figures 4-7 below, test panels made of FR-4 (140 Tg and 170 Tg) material) on one ounce copper were tested for peel strength to measure the bond integrity under various operating conditions. The performance ratings (1-10) indicate a rating schedule whereby the higher the number, the better the overall bond integrity. The performance rating scores were determined from a composite of recognized test methods including peel strength, solder shock, pink ring resistance and pressure cooker testing.

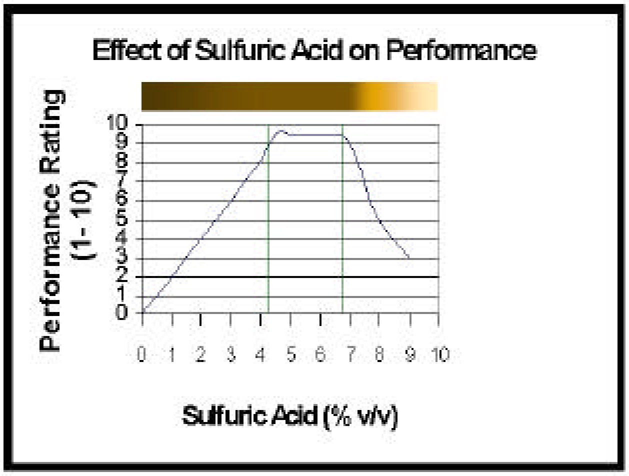


Figure 4 - Effect of Sulfuric Acid Concentration on Performance

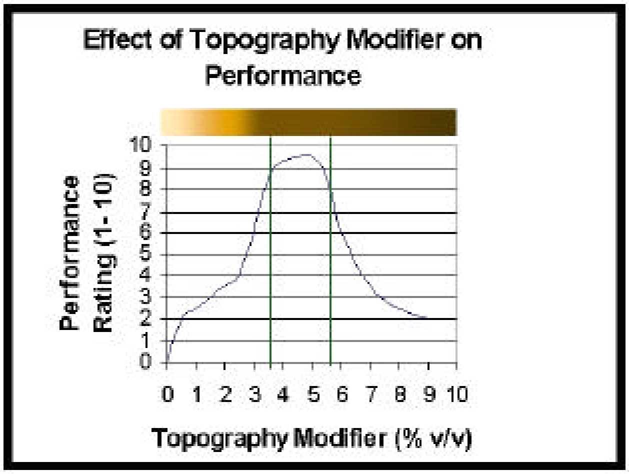


Figure 5 - Effect of Topography Modifier on Process Performance

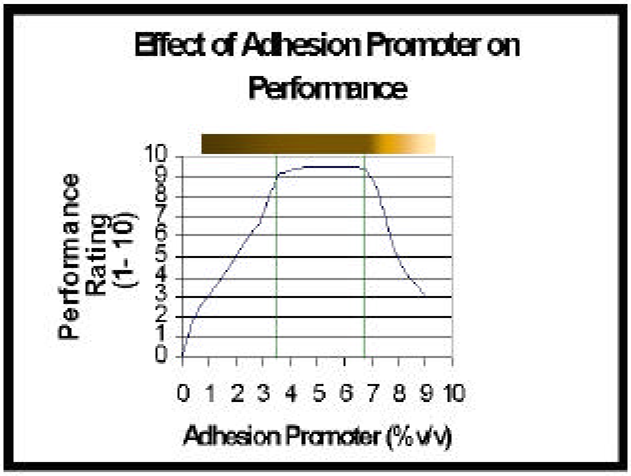


Figure 6 - Effect of Adhesion Promoter on Performance

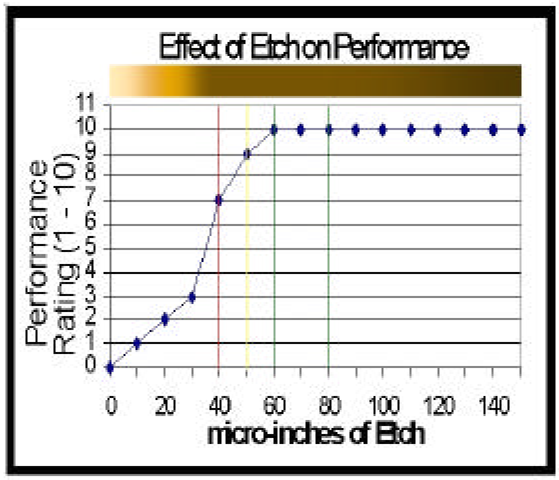


Figure 7 - Effect of Copper Etch Amount on Performance

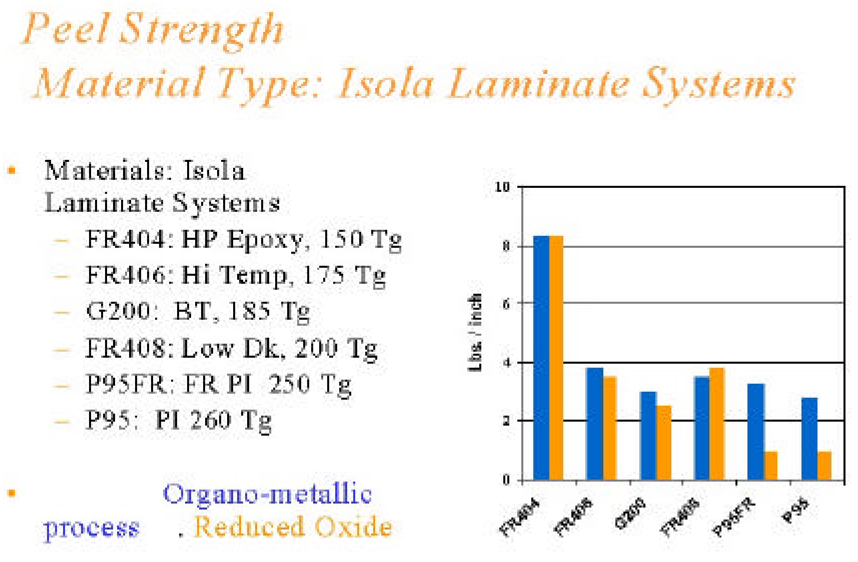
The above figure details the effect on the bond strength versus the amount of copper removed. It is obvious that with thin foils, the amount of copper removal be minimized without compromising bond strength.

Bond Strength to Pre-preg

The original premise to the process design was that the alternative technology has to provide optimum reliability in terms of bond strength for high performance resin and advanced materials. Typically, this included materials with Tg of 170 C and above, as well as polyimide, FR-5 and GETEK®.

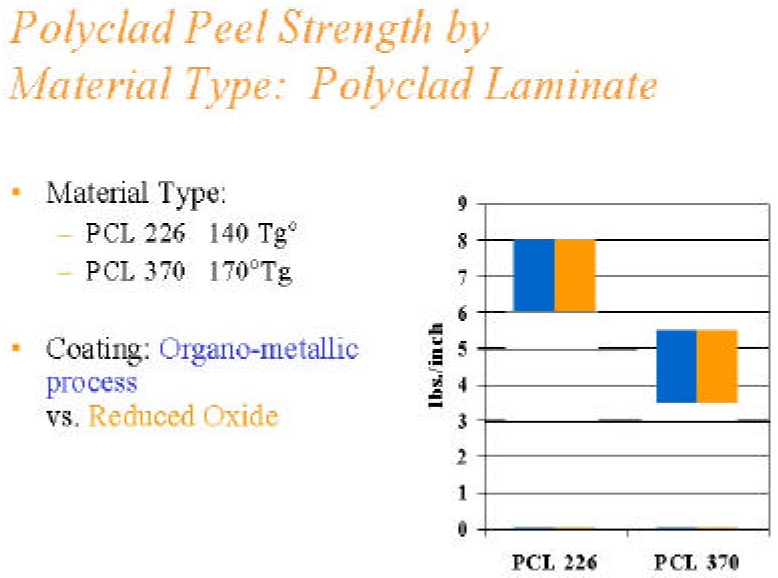
Peel strength testing data was supplemented with pressure cooker testing, thermal stress and time to delamination. An interesting upside to the alternative oxide process was overall improved reliability with the higher performance resin systems. This was attributed to the combination of a micro-roughened surface and an organic adhesion promoter that enhanced the resin adhesion for the higher Tg materials. Reduced oxide coatings, consisting of needle-like copper oxide crystals, easily fracture during the higher temperatures and pressure required during lamination.[5]

The following charts (Figures 8-10) show the peel strength data. To determine peel strength, standard HTE copper foils (1 ounce) were processed in the organo-metallic process and additional foils processed through reduced oxide as the control. The treated foils were laminated with the various resins under recommended parameters from the suppliers. The prepreg style chosen in each case was one sheet of 7628 and one sheet of 1080. The lighter weight was always laid up against the treated foil. Standard peel strengths were performed per IPC-TM-650 2.4.8 C condition A. The results are listed in Figures 8-10.


Peel Strength
Material Type: Isola Laminate Systems

- Materials: Isola Laminate Systems
  - FR404: HP Epoxy, 150 Tg
  - FR406: Hi Temp, 175 Tg
  - G200: BT, 185 Tg
  - FR408: Low Dk, 200 Tg
  - P95FR: FR PI 250 Tg
  - P95: PI 260 Tg
- Organo-metallic process . Reduced Oxide

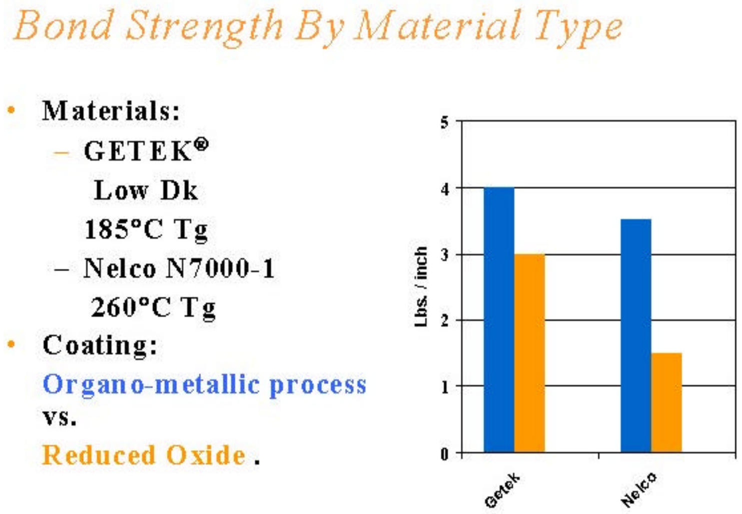
Figure 8 - Comparison of Peel Strengths for Various Resin Systems with Organo-metallic vs. Reduced Oxide



Polyclad Peel Strength by Material Type: Polyclad Laminate

- Material Type:
  - PCL 226 140 Tg°
  - PCL 370 170°Tg
- Coating: Organo-metallic process vs. Reduced Oxide

Figure 9 - Comparison of Peel Strengths from Another Material Supplier with Organo-metallic Process and vs. Reduced Oxide

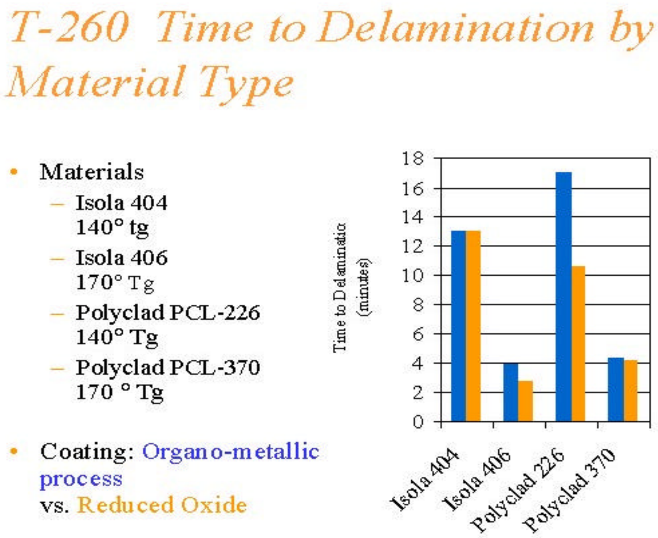


Bond Strength By Material Type

- **Materials:**
  - **GETEK®**
    Low Dk
    185°C Tg
  - **Nelco N7000-1**
    260°C Tg
- **Coating:**
  Organo-metallic process
  vs.
  Reduced Oxide .

Figure 10 - Peel Strength Data with Organo-metallic Process and Reduced Oxide for High Performance Materials

Bonding strength not withstanding, the multilayer pwbs fabricated with the organo-metallic bonding process must meet stringent performance requirements. The T-260 testing-time to delamination was already acknowledged as to its importance in qualifying alternative bonding processes. Other reliability metrics include IPC accredited methods including thermal stress, pressure cooker and pink ring resistance.



T-260 Time to Delamination by Material Type

- Materials
  - Isola 404
    140° tg
  - Isola 406
    170° Tg
  - Polyclad PCL-226
    140° Tg
  - Polyclad PCL-370
    170 ° Tg
- Coating: Organo-metallic process
  vs. Reduced Oxide

Figure 11 - Time to Delamination per IPC-TM-650. Comparison of Organo-metallic Process versus Reduced Oxide for the Materials Specified in Graph

Thermal stress requires floating mulitayer coupons on molten solder at 288 C for 10 seconds, and repeating for nine more cycles. There shall be no evidence of delamination.

The pressure cooker test (IPC-TM-650, method 2.6.16) is designed to measure the ability of the package to withstand a highly accelerated temperature and humidity stress test. No delamination can occur under the conditions of 30 minute dwell, at 15 psi pressure cook, followed by a 10 second float on molten solder. Solder temperature to be 260^0 C.

While the industry has enjoyed moderate success at minimizing the dreaded pink ring defect with reduced oxides, the desire has long to been to simplify the bonding treatment process. Secondly, improving bond strength on high performance and advanced resin materials is critical to the successful implementation of any interlayer treatment process. While the latter attribute is well documented, the ability of the oxide alternative bonding system to resist pink ring must be established. In all instances, where multilayer pwb test coupons (some fabricated with reduced oxide, others with alternative bonding treatment) were subjected a severe acid test, no pink ring was detected. The coupons were immersed in an aqueous solution of 17% hydrochloric acid for 15 minutes. After removal, the coupons were horizontally ground down to remove the outerlayer pad. Coupons were then inspected under 30X microscope. No pink ring was detected on the coupons fabricated with the organo-metallic bonding process. However, the reduced oxide bonding process showed pink ring.

(See Figures 12A and 12 B)

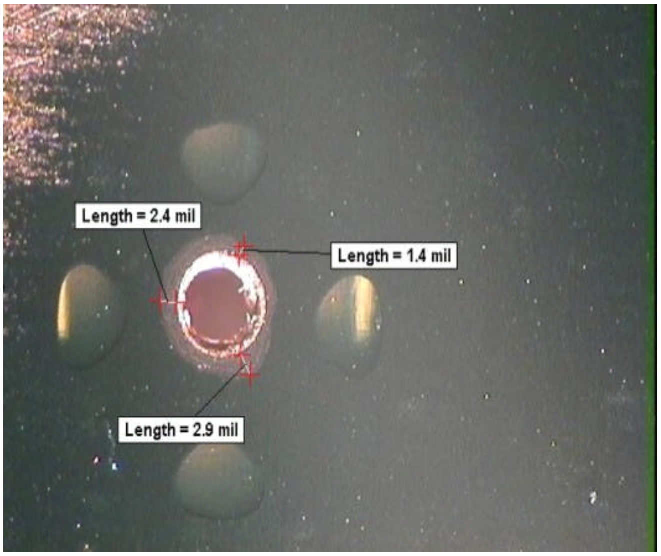


Figure 12A - Reduced Oxide Coupons Showing Pink Ring

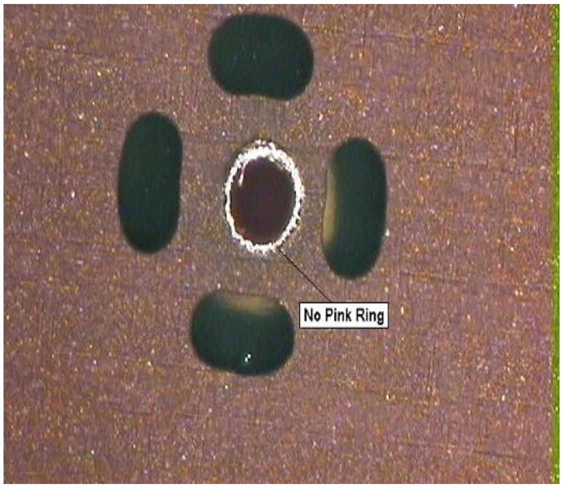


Figure 12B - Organo-metallic Process for MLB Coupons-no Pink Ring Found

Process Flow

The alternative bonding process is easily implemented as an immersion system or in horizontal conveyorized mode. Equipment considerations are minimal and capital expenditure is within the realm of the majority of pwb fabricators.

The recommended process flows and dwell times for the immersion (vertical) and horizontal (conveyorized) processes are listed below:

	Immersion	Horizontal
Acid Cleaner	180 sec	30 sec
Rinse	60 sec	45 sec
Pre-dip	60 sec	45 sec
Coating step	60 sec	40 sec
Rinse	60 sec	20 sec
Dry	300 sec	30 sec

One should note how quickly and efficiently the process flows. The organo-metallic coating (formed in the coating step above) is formed very quickly. The organo-metallic bonding process provides much greater through put than reduced oxide processes.

Process Control

The organo-metallic bonding process offers advantages over standard oxide processes in terms of consistency and ease of control. Replenishment of the organo-metallic bonding solution is usually done with a “feed and bleed” system. Typically components are pre-mixed in a side tank and then replenished based upon a panel counter, a copper sensor or a specific gravity controller.

Each of the control methods has its advantages and disadvantages. A panel counter is easy to use and involves little maintenance but it does not accurately track copper build up in the bath when panel size and % copper area vary widely. A copper sensor measures copper concentration by determining the amount of light that can pass through the solution. Due to the organo-metallic complex that is formed the etching solution may foul the light sensor resulting in the need for more frequent maintenance of the probe. The specific gravity controller measures the specific gravity of the solution, which is influenced by all of the components as well as copper concentration. If the bath components are controlled within a consistent range then specific gravity is a good indicator of copper concentration. If the bath components, especially sulfuric acid, are not controlled within the proper limits, then the specific gravity controller will not accurately control copper concentration. Despite the drawbacks of the control methods all three of the methods have been used successfully in field applications.

As an added benefit the concentration of all major components of the alternative bonding bath can be analyzed using simple analytical procedures. This minimizes performance problems by ensuring the bath components are properly balanced. Proper balance of the components is necessary so that appearance, bond strength and resistance to thermal excursions are all acceptable. This is especially critical when using high performance resin systems such as high T_g FR-4, polyimide and PPO.

Improving Soldermask Adhesion

The printed wiring board industry has experienced issues with liquid photoimageable solder masks under various conditions. LPI breakdown or lifting near the copper-mask interface typifies a common defect seen when fabricators institute electroless-nickel immersion gold (ENIG) as a final finish. The aggressive nature of the ENIG process is a particular nuisance for some aqueous based LPI's. Simply scrubbing the copper surface prior to soldermask application is often not an effective adhesion promotion mechanism for LPI and ENIG. (Please note not all LPI's exhibit this problem). A number of factors contribute to mask adhesion issues including acrylate content of the LPI, degree of cross-linking, mask thickness, and adhesion strength of the mask to the surface. Regardless, surface topography plays a unique role in enhancing the adhesion of the LPI. In Figure 13, the surface copper of the pwb was prepared with aluminum oxide.

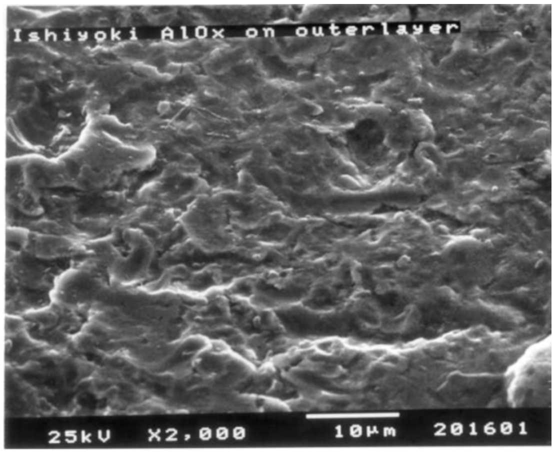


Figure 13 - Copper Surface Outerlayer Prepared with Aluminum Oxide Prior to LPI

Even though the surface roughness appears sufficient, the fabricator experienced issues with LPI breakdown after ENIG. Figure 14 shows the mask peeling from the surface due to marginal adhesion. Most likely, even with less than adequate surface preparation, most surface finishes would not have had such an adverse effect as ENIG.

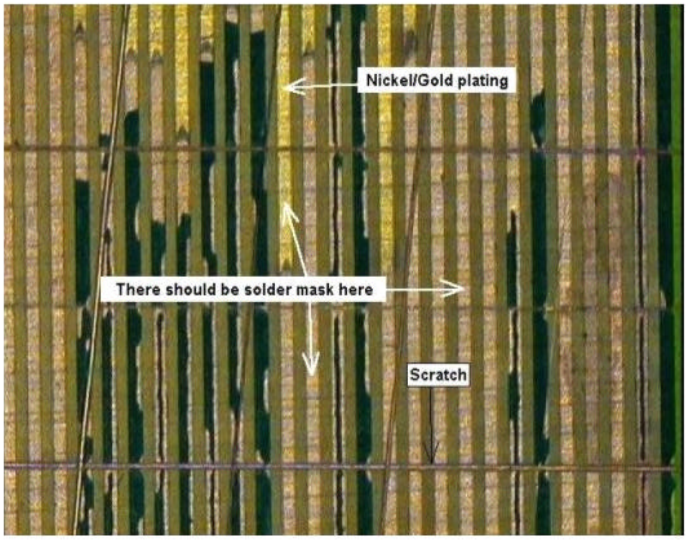


Figure 14 - Severe Peeling of LPI after ENIG. The Above Panel Treated with Aluminum Oxide (As shown in Figure 13) Mask Lifting Noted after Processing Through ENIG

While the above case is extreme, it nonetheless illustrates that marginal mask adhesion leads to yield loss for fabricators.

Surface preparation must be optimized to improve mask adhesion. One solution is to eliminate scrubbing (either pumice, AlOx) and utilize the oxide alternative (organo-metallic) adhesion promotion system. The surface topography that is achieved on plated copper outerlayers with this process is shown in Figure 15.

The topography represented in Figure 15 is remarkable simply because the copper surface is electrodeposited copper (from acid copper electroplating process). The electrodeposited copper is typically a fine-grained amorphous deposit (due to the use of organic grain refiners and brighteners) and is more resistant to etch attack as opposed to the foil (laminate) copper represented by a columnar grain structure.

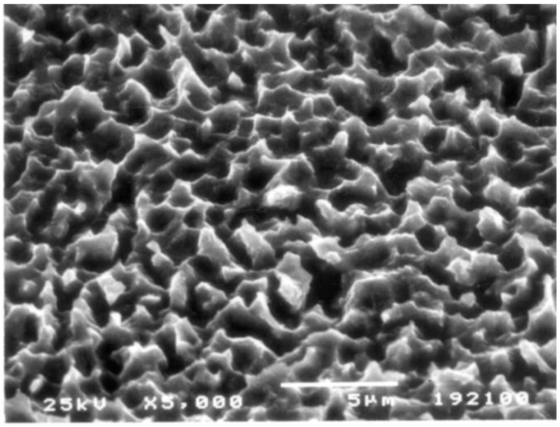


Figure 15 - Outerlayer Copper Surface Treated with Organo-metallic Copper Treatment Process

Performing the same tests as described above with an aluminum oxide treated surface, the oxide alternative process treated panels were coated with the same LPI and processed according to manufacturer's instructions. Panels were then processed through the same ENIG solution as the panel shown in Figure 14. The results are shown below in Figure 16.

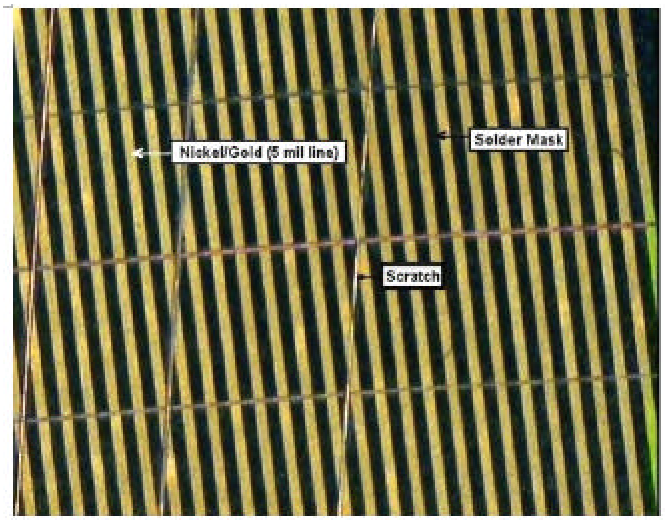


Figure 16-Excellent adhesion of the LPI after processing through ENIG

Basically, the process cycle that is used for treating interlayers is employed here with one possible additional step: A mild micro-etch is used to remove the organic coating. This step restores the surface to a matte copper appearance.

While the surface structure modification is a significant contributor to adhesion, a closer look at the sidewall of the copper trace provides additional insight. Note that there is sufficient topography on both the top of the trace as well as the sidewall. (Figure 17) It has been postulated that there is additional anchoring sites provided by the surface modification of the sidewall that would not be present with other surface preparation techniques.

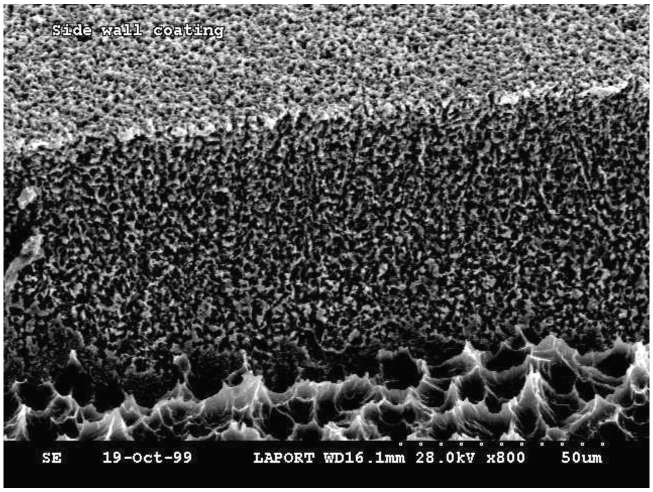


Figure 17 - Surface Preparation of Copper Surface Prior to Soldermask Application. Surface Treatment Process is a Modified Organo-metallic Surface Prep Process

Fabricators implementing the organo-metallic copper treatment process earned immediate improvements in yields and made major reductions in reworking LPI processed pwbs.

Summary

The organo-metallic adhesion promotion system offers many benefits to the fabricator. By improving the speed at which the coating is formed on copper surfaces, productivity in the interlayer fabrication area has increased several fold. The process speed and the relative simplicity of this technology (as compared to reduced oxide) allows for easy adaptation to either vertical (immersion) or horizontal conveyorized modes. Capital spending outlays to implement the process is significantly less than reduced oxide, and return on invested capital can be realized in a matter of a few short months.

Productivity gains aside, the most important aspects of any technology are its process capability and the long-term reliability of products fabricated with the process. The organic metallic process described herein details the numerous metrics employed to measure process capability and reliability. Due to the nature of the surface topography and the ability of the organic coating to covalently bond with resin systems, the copper foil to resin bond is by all measures more reliable than the bond formed by reduced oxide. Several reasons were cited for this including the fragile nature of oxide crystal (from the reduced oxide) and the lack of a covalent bond forming mechanism.

It has been shown that the organo-metallic process can be “formulated” to act as an adhesion promoter for liquid photoimageable soldermasks. The results show that issues with LPI peeling or blistering during ENIG processing are virtually eliminated.

There are many more applications for the organo-metallic process. These other applications, including primary imaging and sequential build, will be the topic of another paper.

References

1. Electrochemicals Product Technology Bulletin
2. Electrochemicals U.S. Patent Pending
3. “What’s Happening with Multilayer Bonders,” K.H. Dietz, Circuitree Magazine, March 1998
4. U.S. Patent # 5,691,130
5. U.S. Patent # 6,020,029
6. IPC Test Methods Manual TM-650

Enhancing Interlaminar Bond Strength for High Performance Resin Systems and Liquid Photoimageable Soldermasks with an Organo-metallic Copper Surface Treatment Process

Michael Carano

Electrochemicals, Inc.

Agenda

- Introduction
- Conventional Bonding Process
- Process Development-Organo-metallic process
- Performance Criteria
- Process variables
- Process for LPI adhesion

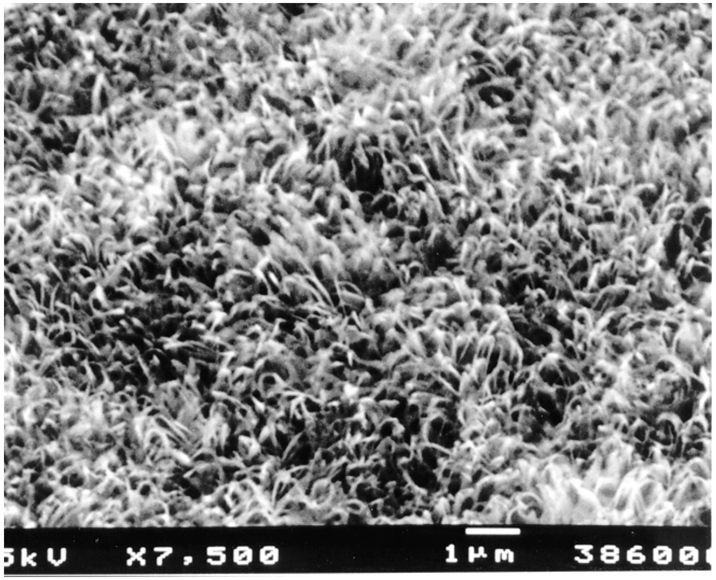
Introduction

- Technology step change to higher performance resin systems
- Increased reliability requirements
- Need for conveyorized processing and overall cost reductions

Conventional Bonding Process

- Long time industry workhorse based on anodic oxidation of copper
- Grow copper crystals on surface
- Rely on prepreg flow to encapsulate crystals
- Difficult and expensive to conveyorize

Innerlayer Bonding



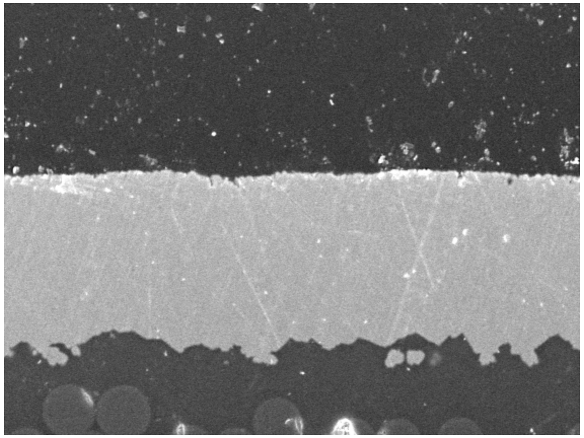
- Conventional oxide has reached limitations
- More brittle high Tg resins don’t work well
- Crystal structure of the black oxide leads to high resistance shorts on fine lines
- Not effective against pink ring unless post treatment used

Needs Assessment For an Alternative to Conventional Oxide

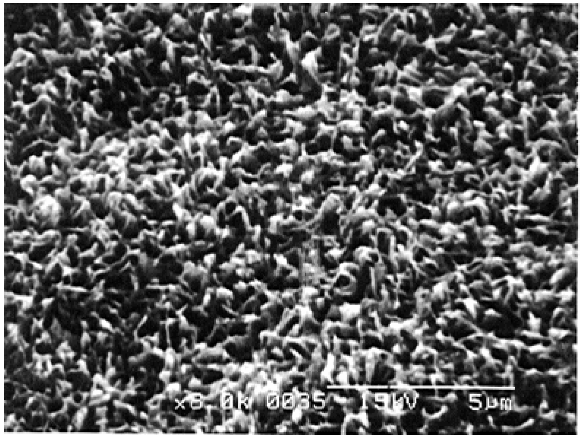
- Improved acid resistance
- Longer hold times
- Reduced cycle time
- Reduced use of resources
- Ideal for horizontal processing
- Thin core processing
- Reduced incidence of wedge voids
- Lower cost
- High loading/lower copper removal
- Reliability equal to or better

Surface Topography Comparison

REDUCED OXIDE

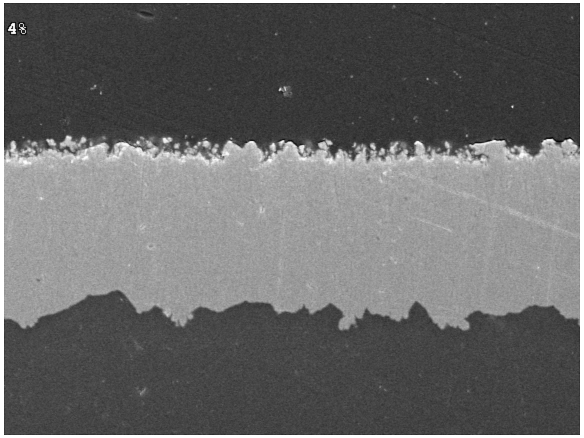


Side view

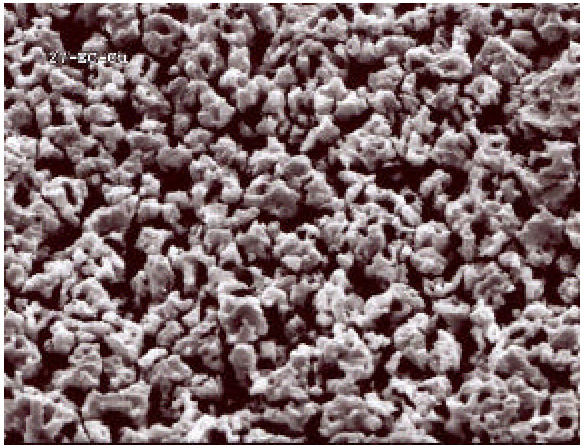


Top view

Alternative Process

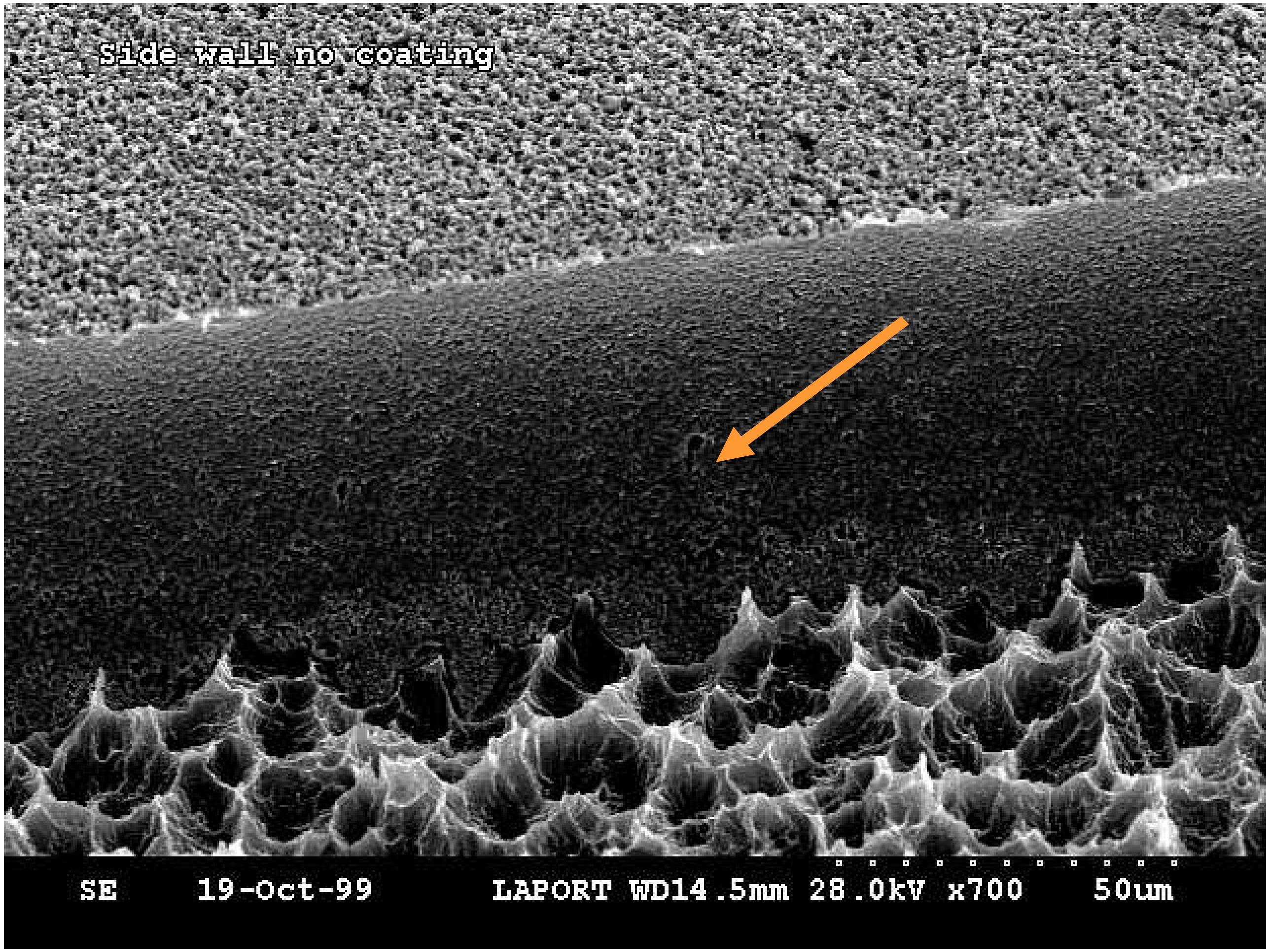


Side view

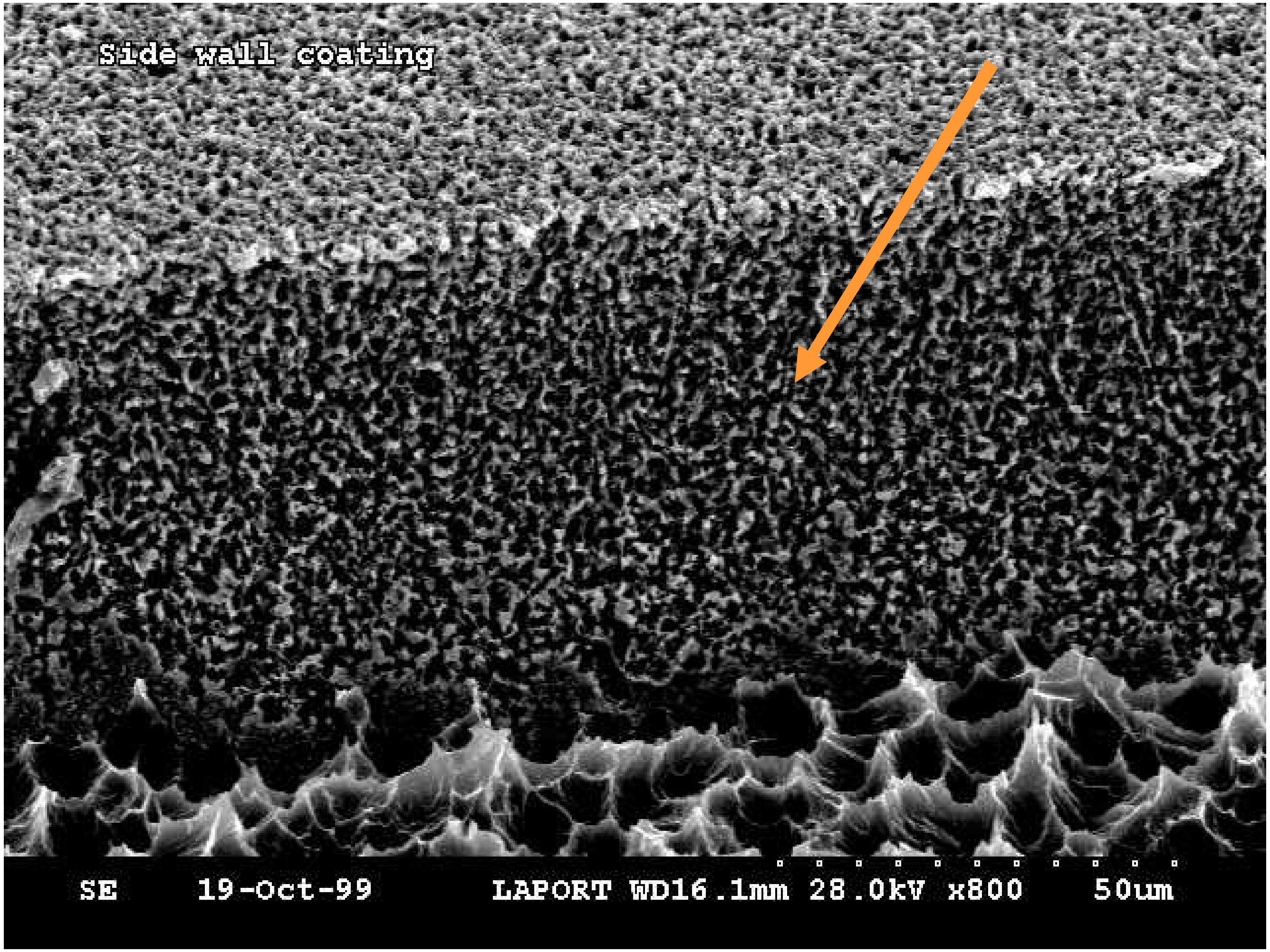


Top view

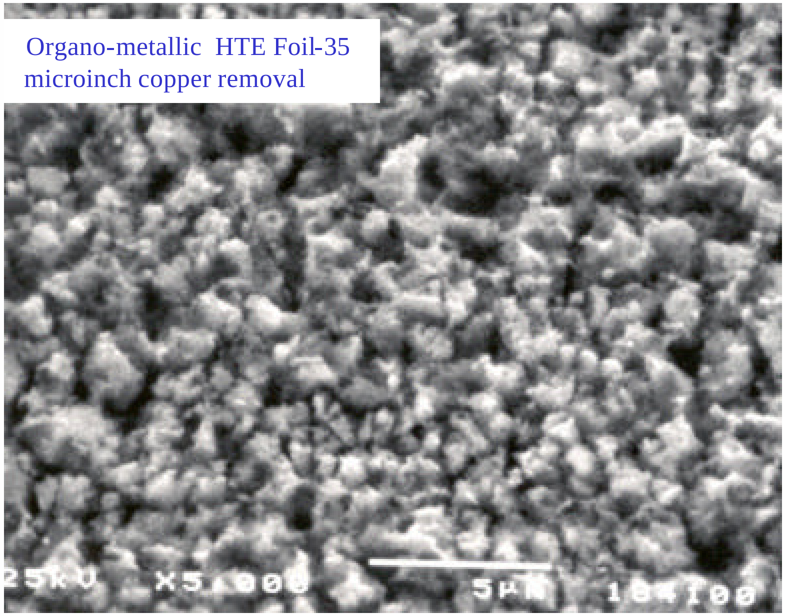
Possible Resin Flow Encapsulation Issues with Oxide



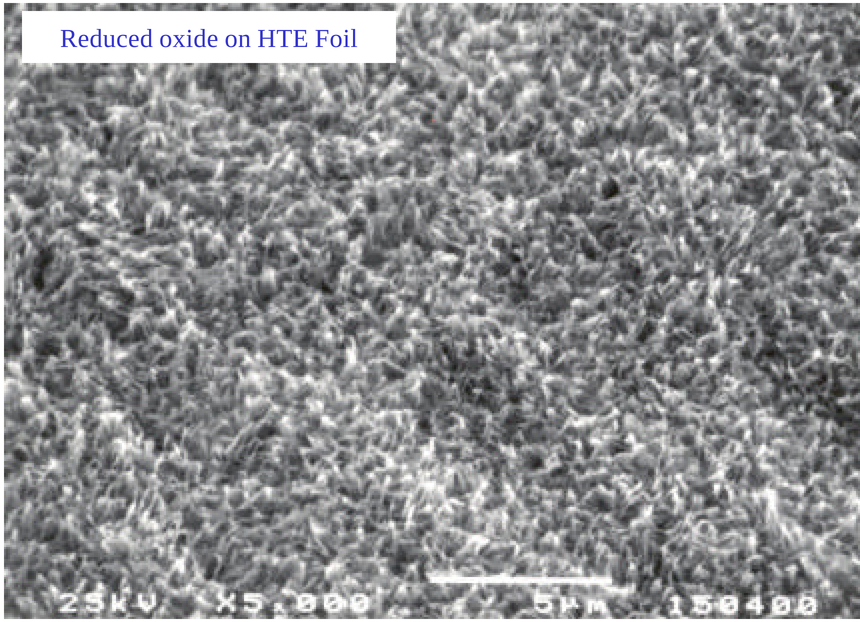
Organo-metallic surface treatment



Surface Coating Comparison



Organo-metallic HTE Foil-35 microinch copper removal



Reduced oxide on HTE Foil

Technical Background

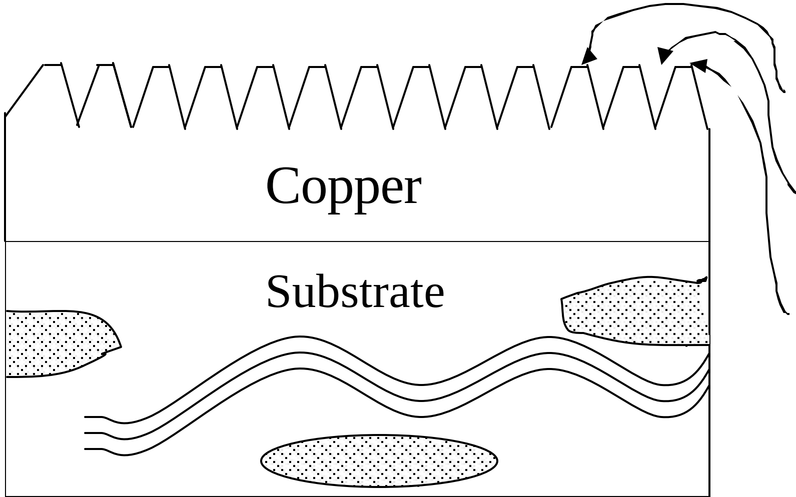
Topography and Coating Mechanism from a peroxide/sulfuric acid micro etchant

Formulation

- Peroxide/Sulfuric based etch and coating solution
- Specific organic additive used to modify the topography
- Another organic additive used as an adhesion promoter and coverage (uniformity enhancer)
- Adhesion promoter component enhances bonding by allowing the modifier to form an insoluble coating on the surface

Etching and Coating Mechanism

- Peroxide/Sulfuric etch characteristics modified by additives
- Surface topography has greater surface area:
  - More peaks / valleys
  - Sub-micron peak to peak
- Organic components facilitate differential etching and uniformity
- Inorganic components control copper dissolution and organic deposition
- Etch rate (total grams copper etched per minute) is unchanged

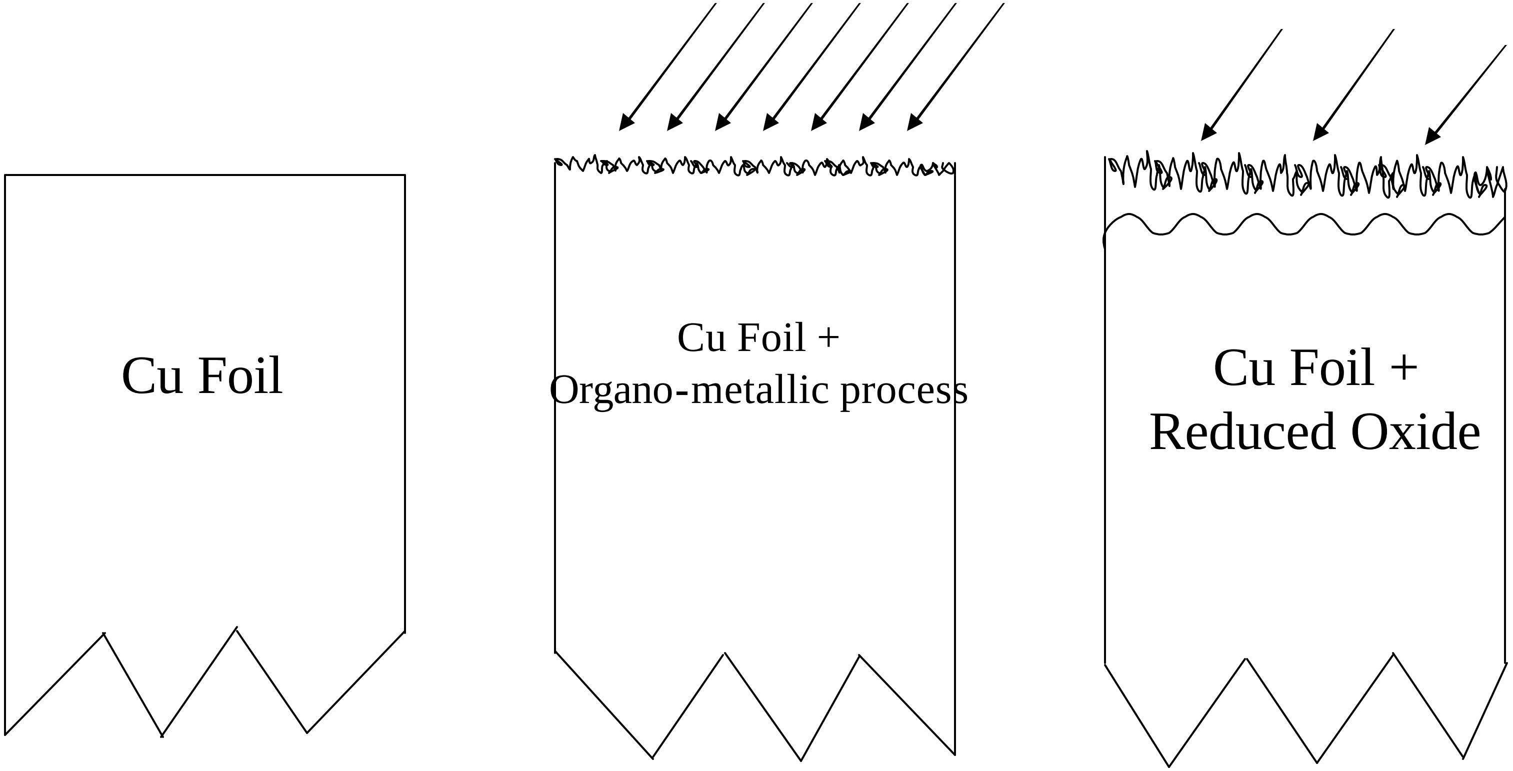


Adsorption of modifier onto surface in pre-dip

Micro-etching in etch solution

Further adsorption of organics onto surface in etch solution

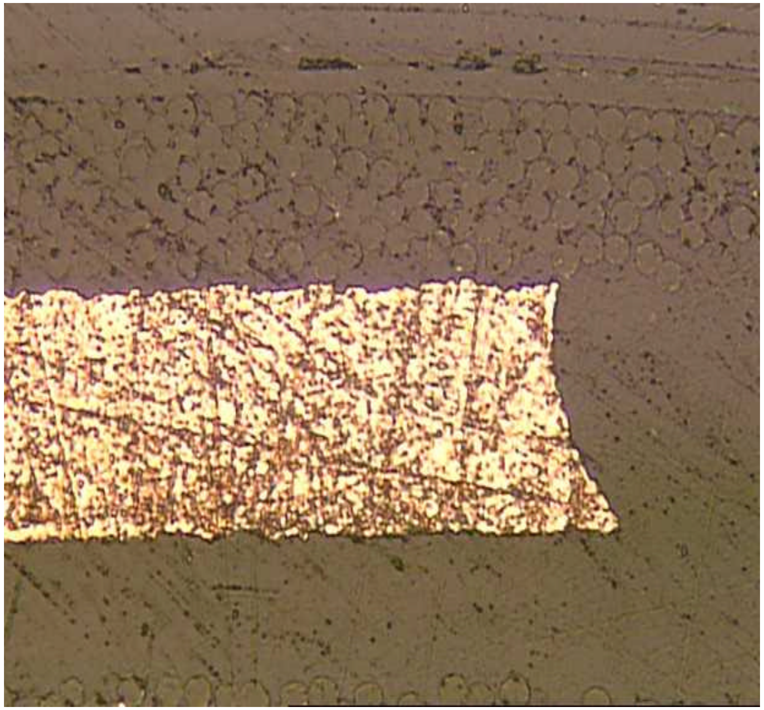
Resin Bonding Mechanism Comparison



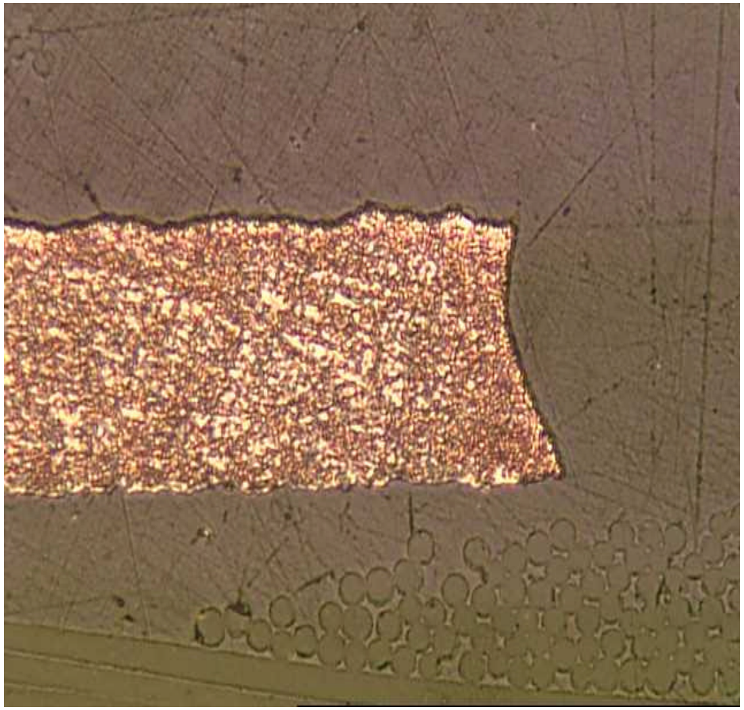
- Oxide coatings bond by resin wet-out and encapsulation of surface topography - dependant on the resin flow
- Organo-metallic component of etching solution facilitates resin wetout of surface; chemical bonding occurs in addition to mechanical

Topography Encapsulation

Organo-metallic on HTE

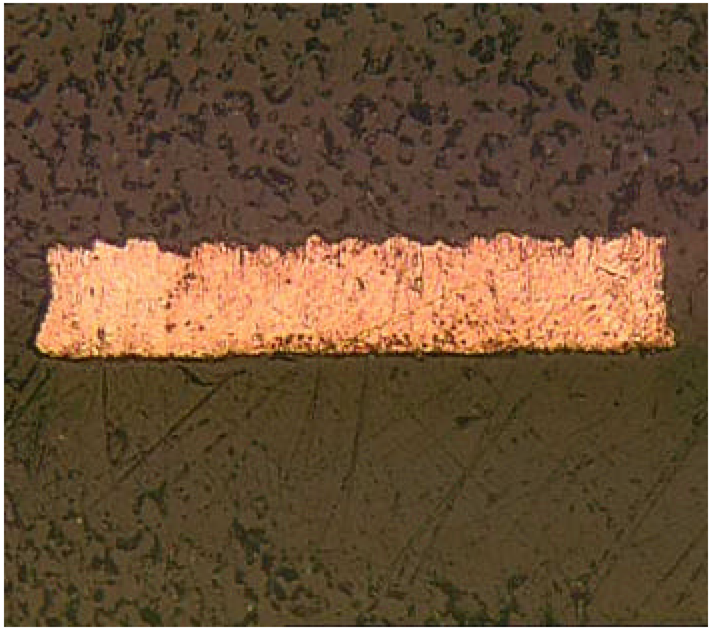


Reduced Oxide on HTE

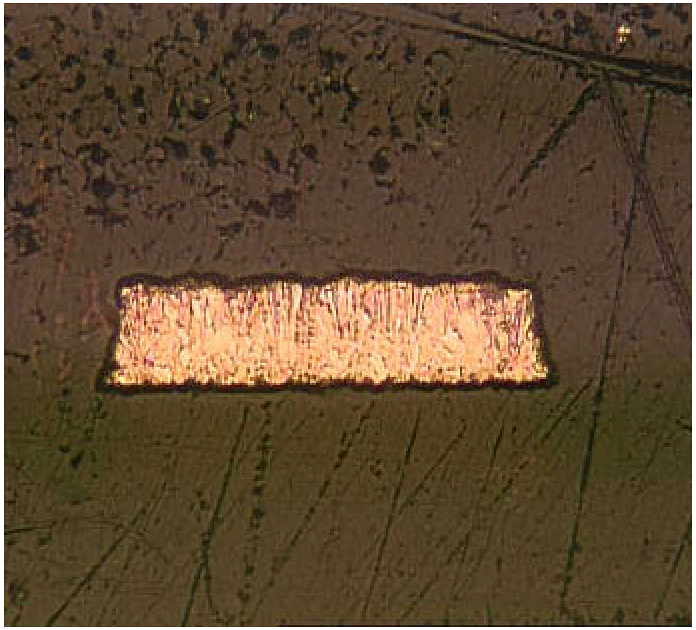


Topography Encapsulation

Organano-metallic on RTF



Reduced Oxide on RTF



Coating Composition Study
FR4 (Tg = 140°C)

Area Comment	Organic Content (Atomic %)	Oxygen (Atomic %)	Copper (Atomic %)	Peel (Lbs./in)	T-260 Time to Delam
Organo-metallic coating	**13**	11	15	7.1	> 10 min.
Organo-metallic with organic removed	2.3	17	61	7.3	< 3 min.
Reduced Oxide	0.5	35.7	49.3	6.0	> 10 min.

Coating Study

Conclusion

- Adhesion is a function of both the degree of micro-roughening and coating characteristics.

Process Optimization

Evaluate key process parameters to determine their influence on appearance and overall performance

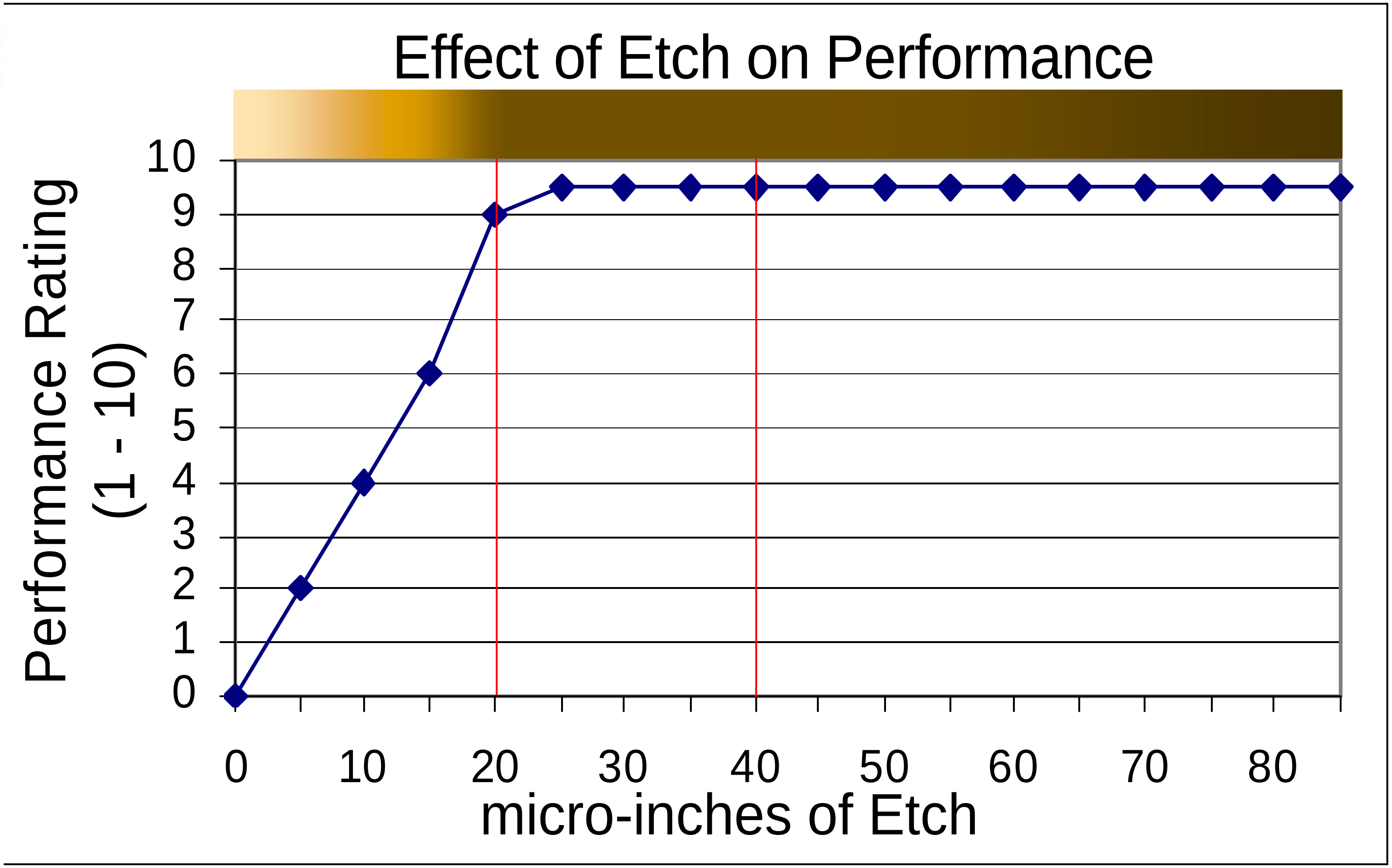
- Temperature
- Sulfuric Concentration
- Additive Concentration
- HTE and RTF

- Color
- Peels
- MLB Integrity

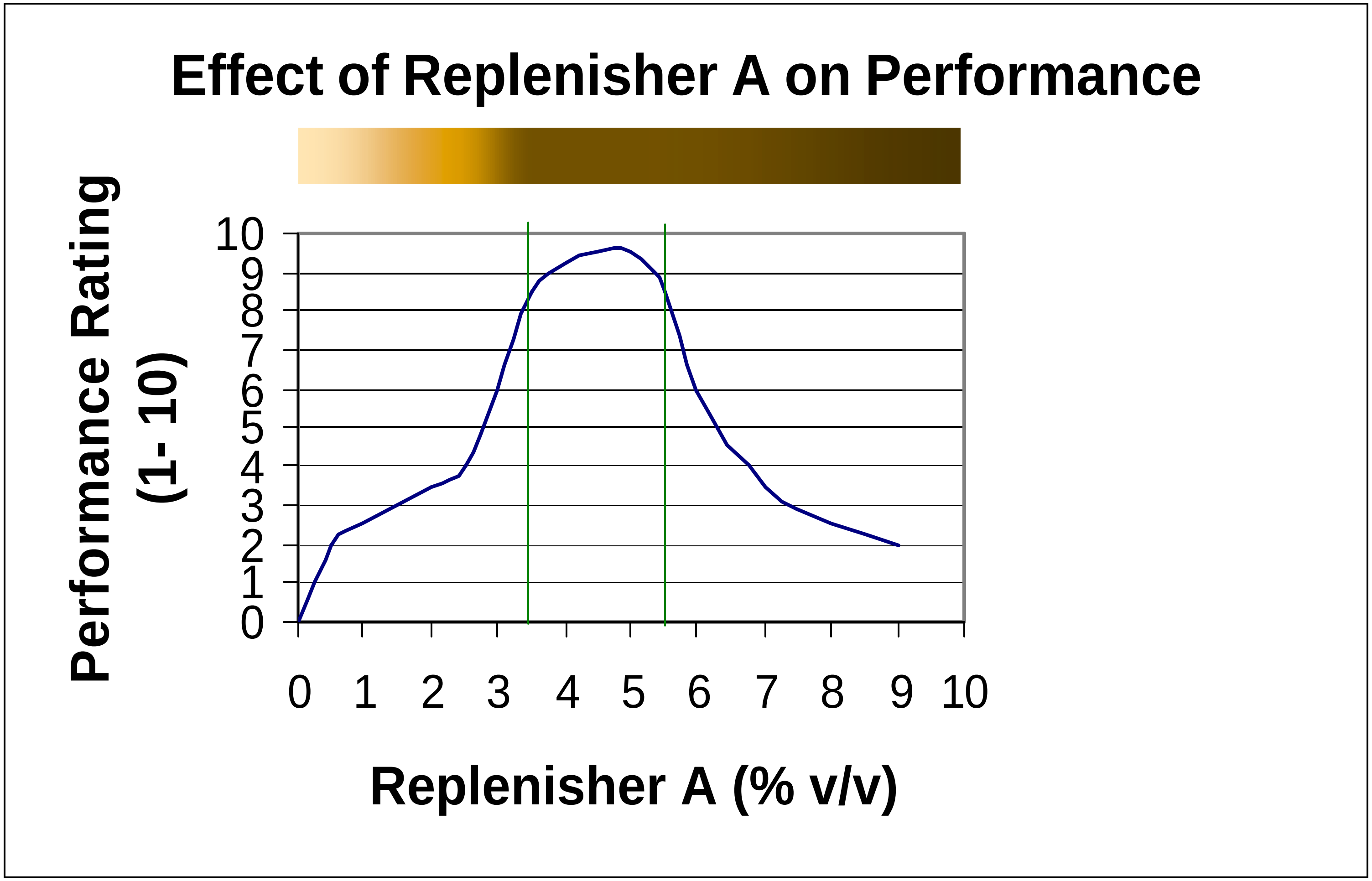
MLB Integrity –composite of tests for measuring coating performance

Test Method	**Acceptance Criteria**
Thermal Stress per IPC-TM-650 method 2.6.8 Solder float @ 288°C for 10 seconds (5 times)	No blisters or delamination
Pink Ring per IPC-TM-650 method 2.1.1 Method used: Standard PCB Process	< 3 mils.
Pressure Vessel per IPC-TM-650 method 2.6.16 15 psi pressure for 120 min. followed by vertical solder dip for 60 sec. at 260°C	No blisters or delamination associated with coating
Delamination time (T-260) method 2.4.24.1 10°C per minute to 260°C isothermal until failure	Time in minutes to delam
Peel strength per IPC-TM-650 method 2.4.8C, Condition A	Record Peel Strength Lbs./in

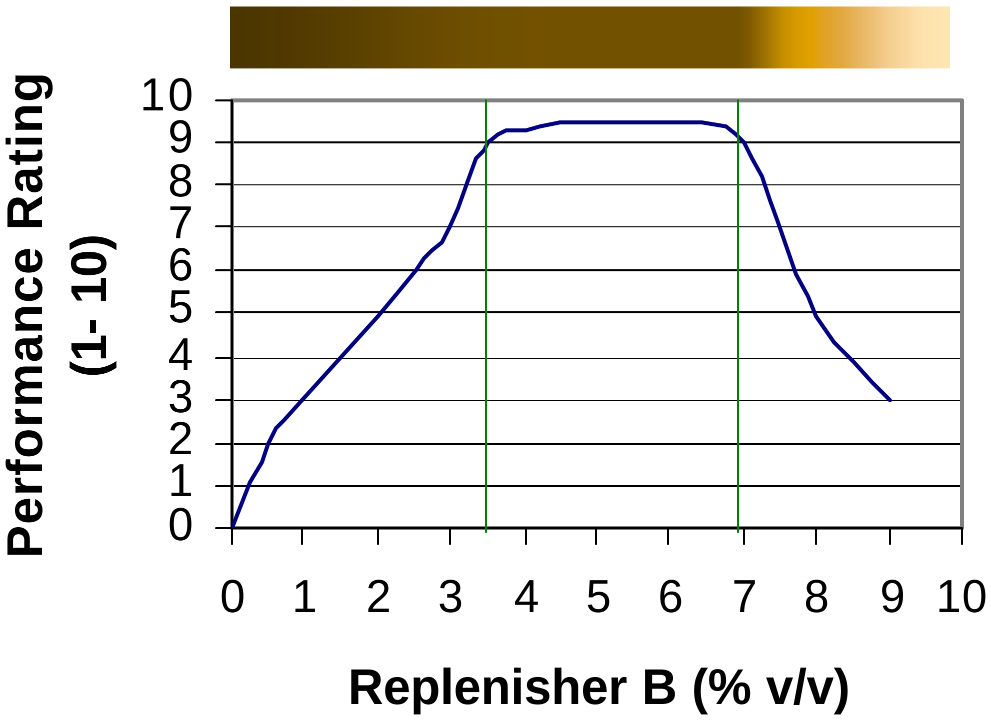
Process Optimization



Process Optimization-topography modification

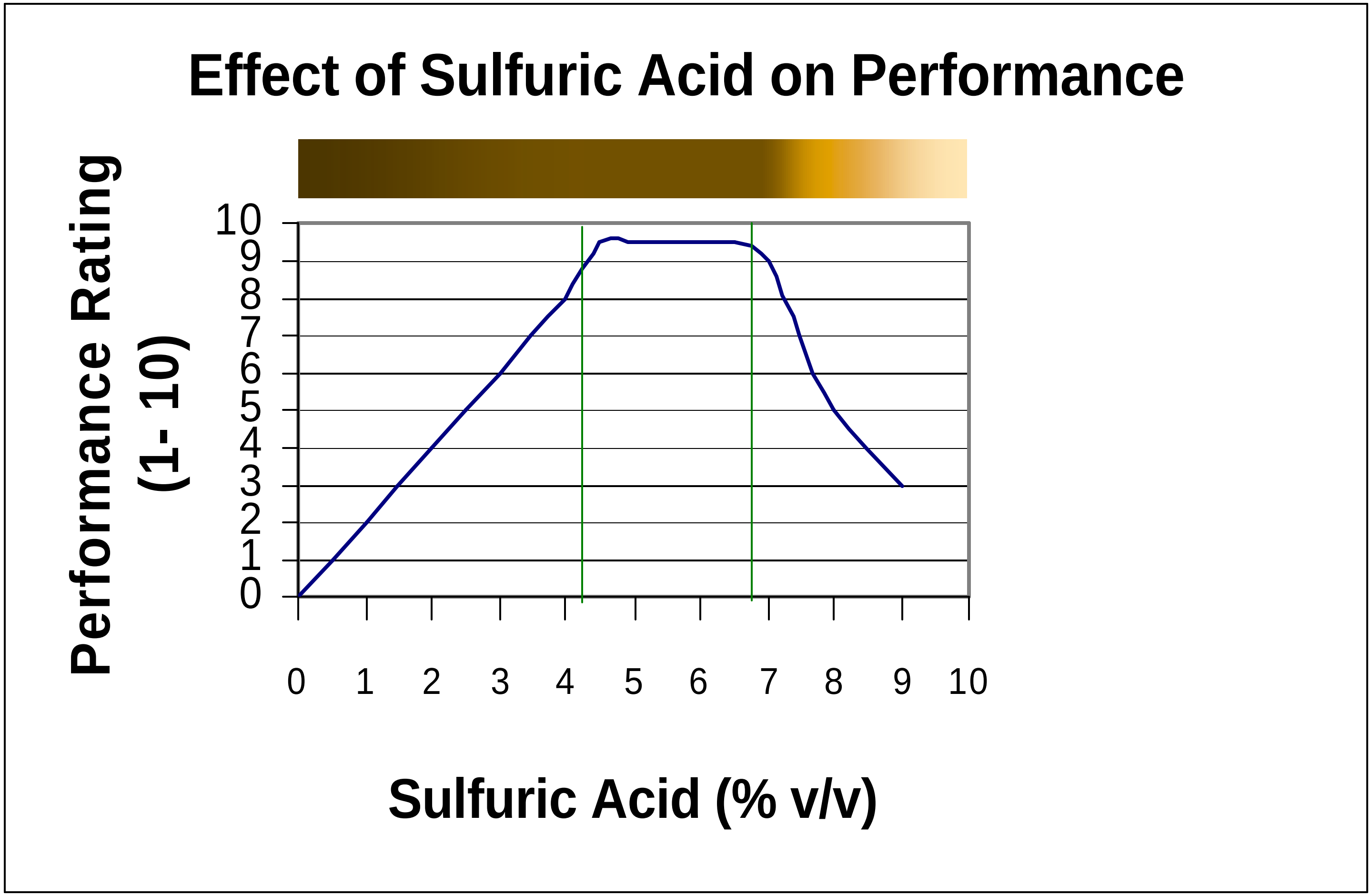


Process Optimization-Adhesion Promoter



Effect of Replenisher B on Performance

Process Optimization

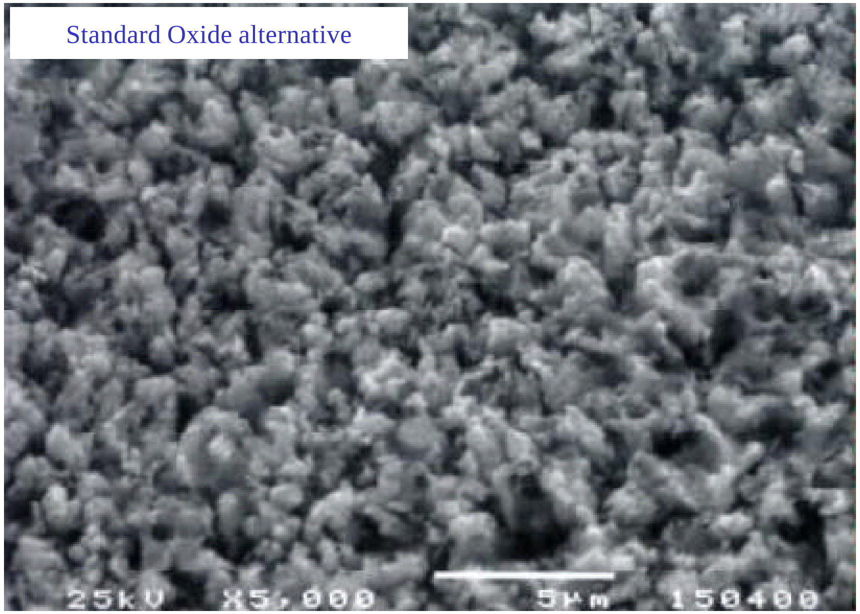


Overall Process Development Goal

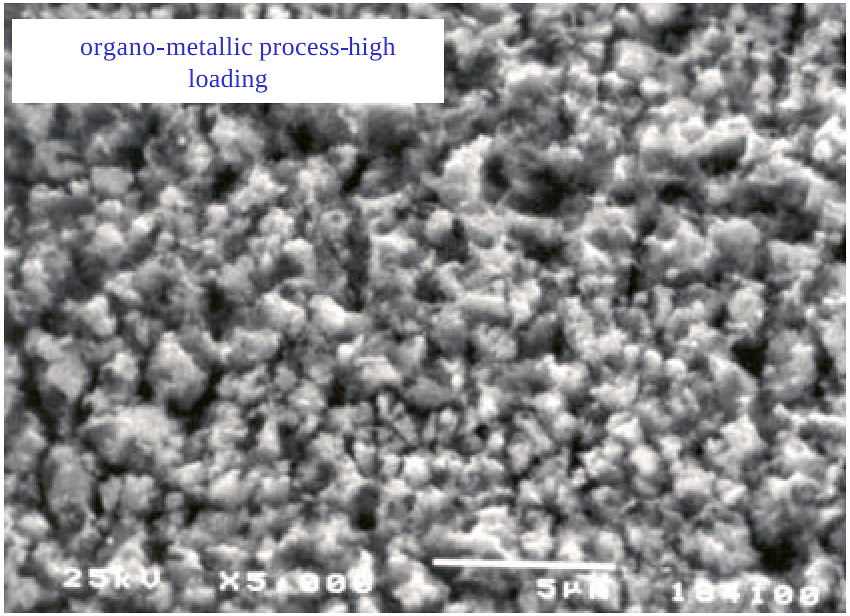
- Reduced copper removal-for improved signal integrity and impedance performance
- High copper loading without compromising MLB integrity
- High bond strengths and MLB integrity with a variety of high performance materials

High Loading Objective

Optimized Bonding & Topography



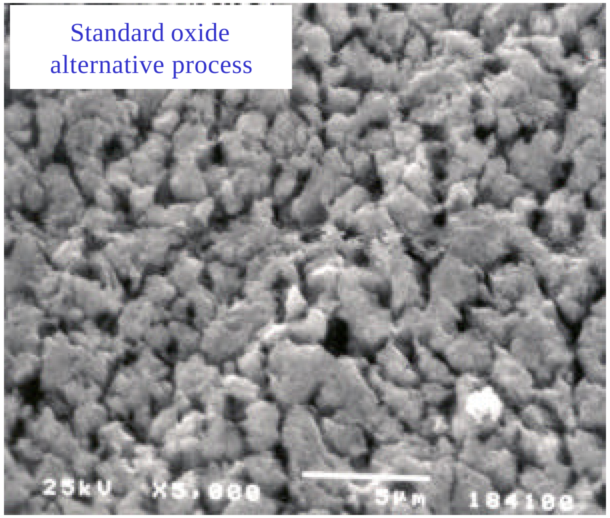
Standard Process Chemistry
20 g/l Cu - 70 µ



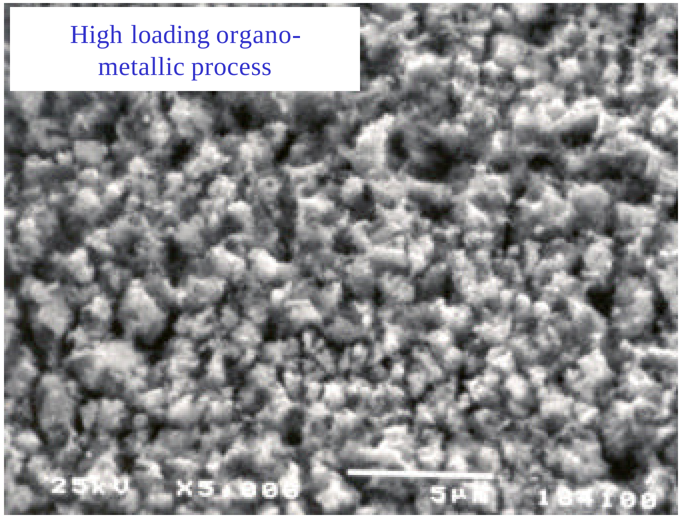
High Loading Process
40 g/l Cu - 30 µ

Organo-metallic process-high copper loading

Uniform Appearance & Topography-HTE


Standard oxide alternative process

Standard Process Chemistry
40 g/l Cu - 30 µ”


High loading organo-metallic process

High Loading Process
40 g/l Cu - 30 µ”

Performance Data

Peel Strength data from
laminate suppliers

Organo-metallic process- Performance

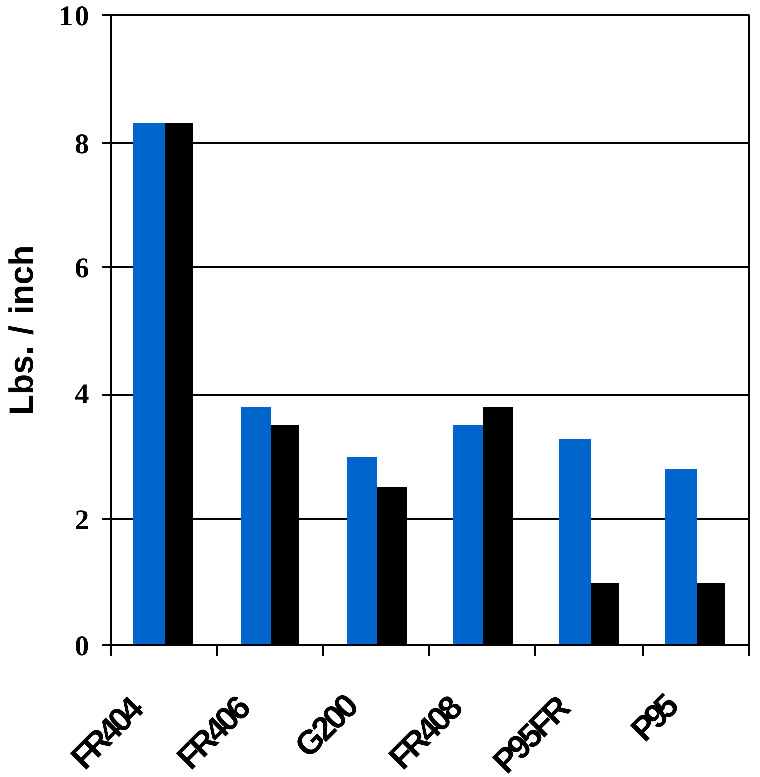
Copper Types and Materials

- Copper:
  - HTE Foil
  - RT Foil (Reverse Treat)
  - RA Foil (Rolled and Annealed)
  - Electroplated Copper
- Materials:
  - FR4: Tetrafunctional, Multifunctional, High Temperature, Low Dk
  - Polyimide
  - Low Loss / Thermoplastics
  - BT, Cyanate Ester

Organo-metallic- Peel Strength Material Type: Isola Laminate Systems

- Materials: Isola Laminate Systems
  - FR404: HP Epoxy, 150 Tg
  - FR406: Hi Temp, 175 Tg
  - G200: BT, 185 Tg
  - FR408: Low Dk, 200 Tg
  - P95FR: FR PI 250 Tg
  - P95: PI 260 Tg

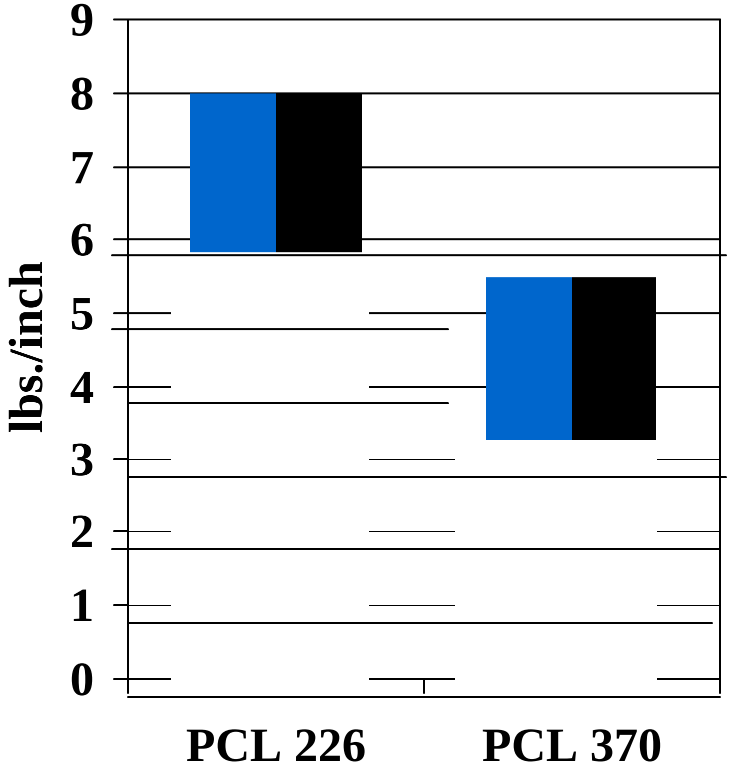
- Coating: Organo-metallic vs. Reduced Oxide



Polyclad Peel Strength by Material Type: Polyclad Laminate

- Material Type:
  - PCL 226 Tg 140°
  - PCL 370 Tg 170°

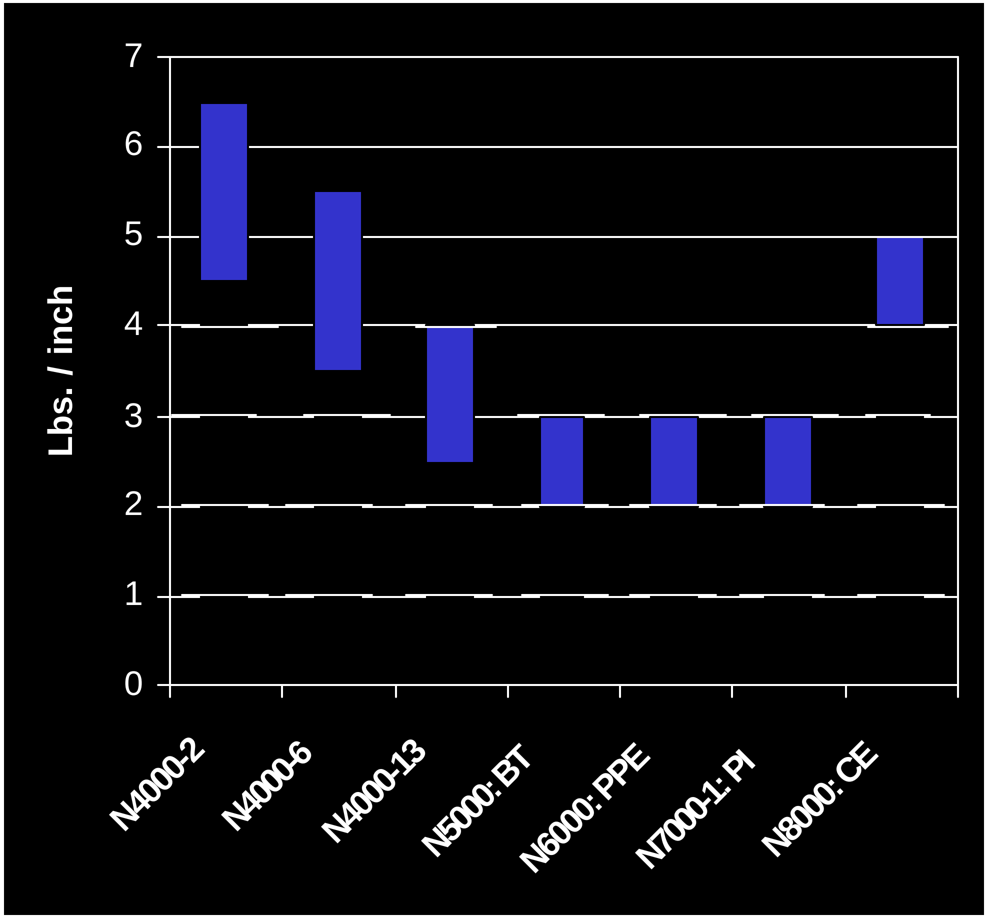
- Coating: Organo-metallic vs. Reduced Oxide



Organo metallic Process- Peel Strength
Material Type: Nelco / Neltec Laminate

Materials: Nelco

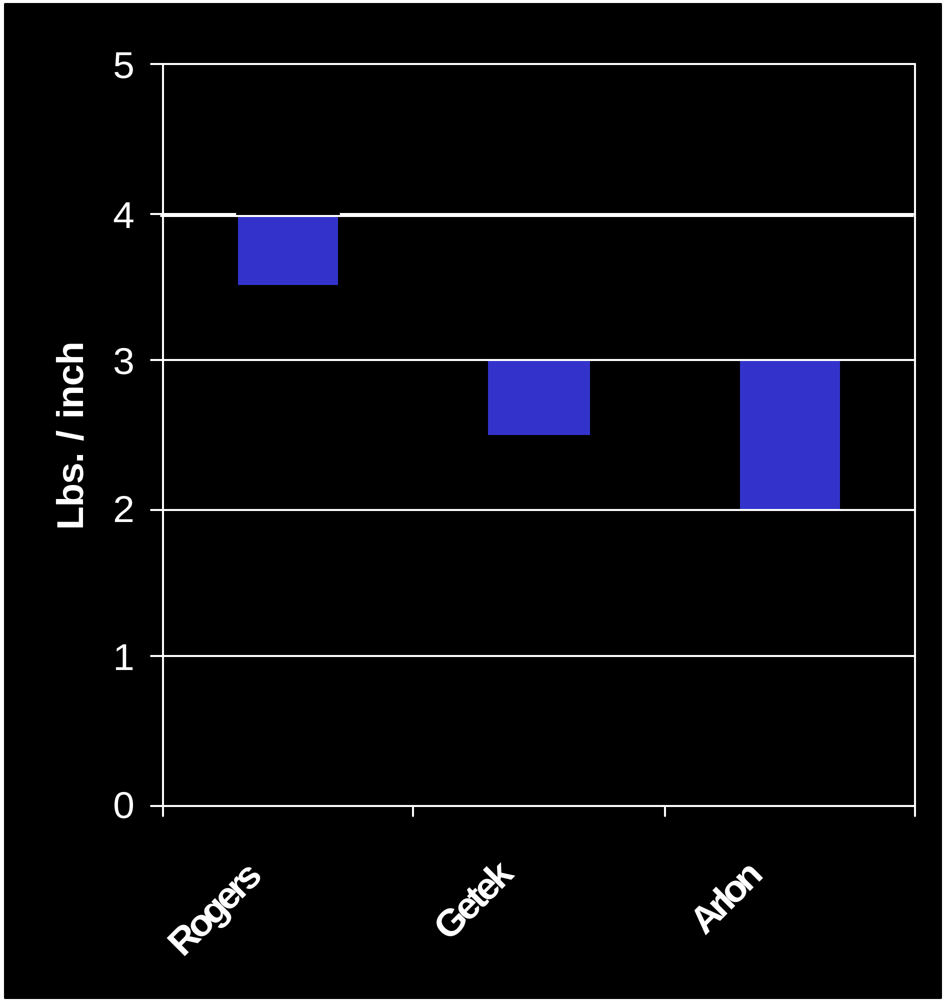
- N4000-2: 140 Tg
- N4000-6: 180 Tg
- N4000-13: Low Dk, 200 Tg
- N5000: BT, 185 Tg
- N6000: PPE, 200 Tg
- N7000-1: PIL, 260 Tg
- N8000: CE, 250 Tg



Organo-metallic process-Peel Strength By Material Type

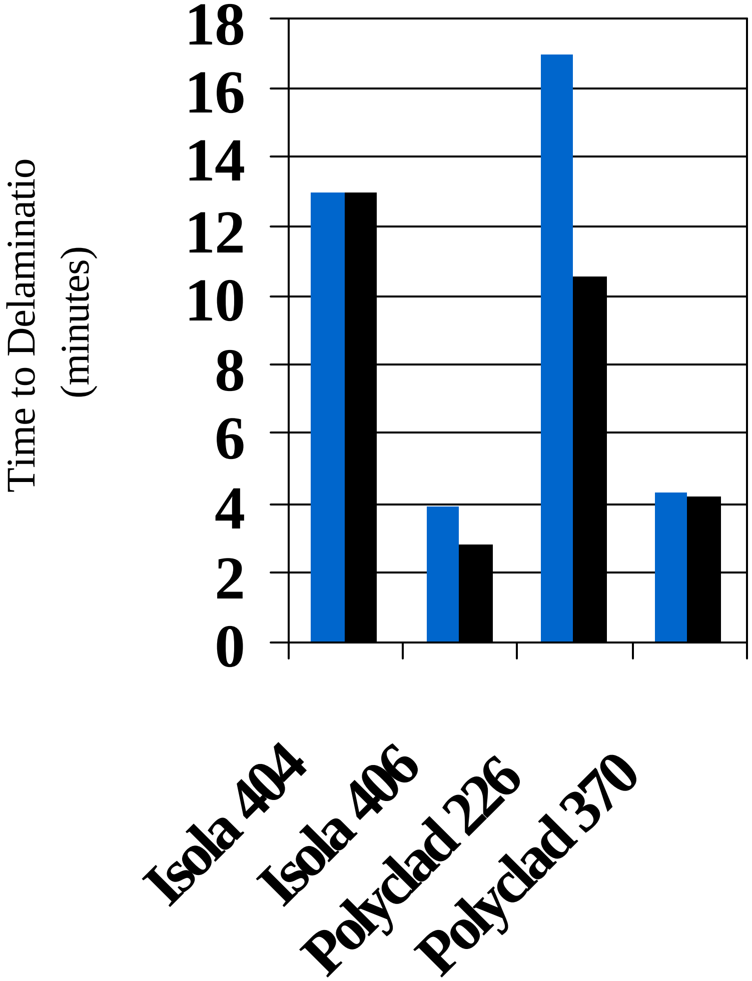
Materials:

- Rogers RO4000
  Ceramic Thermoset
  280 Tg
- GETEK®
  Low Dk
  185 Tg
- Arlon 85NT
  Polyimide/Thermount
  250 Tg



T-260 by Material Type

- Materials
  - Isola 404
    Tg 140°
  - Isola 406
    Tg 170°
  - Polyclad PCL-226
    Tg 140°
  - Polyclad PCL-370
    Tg 170 °
- Coating: Organo-metallic vs. Reduced Oxide



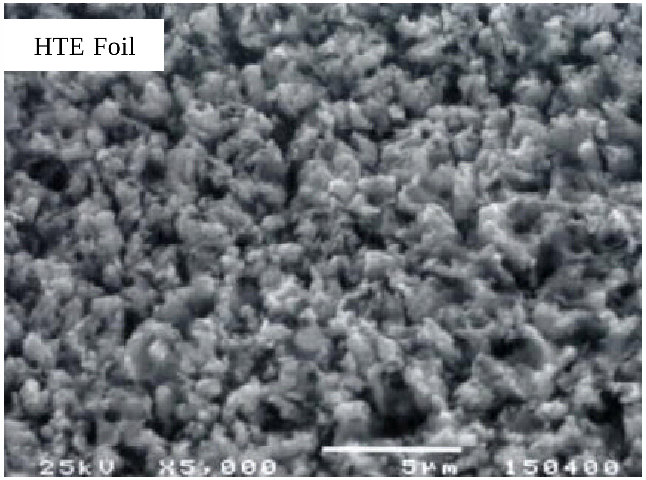
GETEK® Tg = 185° C-performance results

	Specimen	**Test Condition**	**Organo-metallic**	**Double Treat**
Thermal Stress	4-layer MLB	Solder float @ 260°C (500°F)	32 min.	32 min.
Time to Delamination	4-layer MLB	Solder float @ 288°C (550°F)	8 min.	8 min.
Pressure Cooker	4-layer MLB	30 min. 15 psi 5 min. @ 260°C (500°F)	Pass	Pass
		60 min. 15 psi 5 min. @ 260° (500°F)	Pass	Pass
		120 min. 15 psi 10 sec. @ 260°C (500°F)	Pass	Fail
Acid Resistance	4-layer MLB	Immersion 10% H_2SO_4 24 hours	No Pink Ring	No Pink Ring
Pink Ring Resistance	4-layer MLB	Typical PCB process exposure	No Pink Ring	No Pink Ring

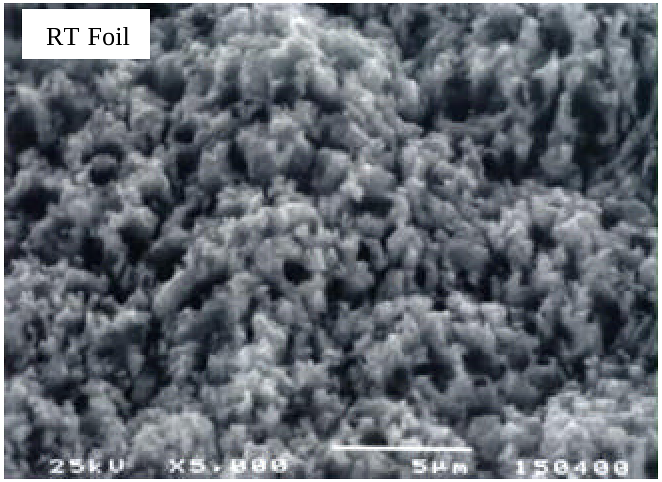
Polyimide Laminate Tg = 260° C Performance results

	Specimen	**Test Condition**	**Organo-metallic**	**Reduced Oxide**
Thermal Stress	4-layer MLB	IPC-TM-650 Method 2.6.8 5 x 10 @ 288°C (550°F)	No Delam	No Delam
Time to Delamination	4-layer MLB	Solder float @ 288°C (550°F)	> 4 min.	> 4 min.
Peel Strength	1 oz. foil	IPC-TM-650, Method 2.4.8	See Chart	See Chart
Pressure Cooker	4-layer MLB	Exceeds IPC-TM-650 Method 2.6.16 120 min. 15 psi 60 seconds @ 260°C (500°F)	No delam	No Delam
Acid Resistance	4-layer MLB	Immersion 20% HCl, 49°C (120°F), 30 minutes	No Pink Ring	No Pink Ring
Pink Ring Resistance	4-layer MLB	Typical PCB process exposure	No Pink Ring	No Pink Ring

Coating Topography by Foil Type

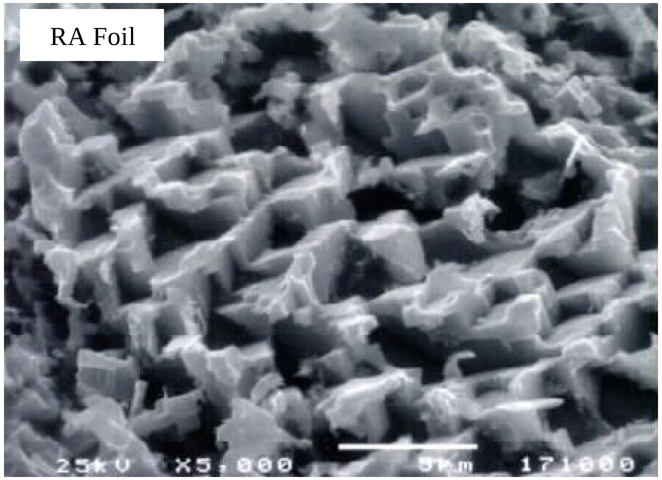


HTE Foil



RT Foil

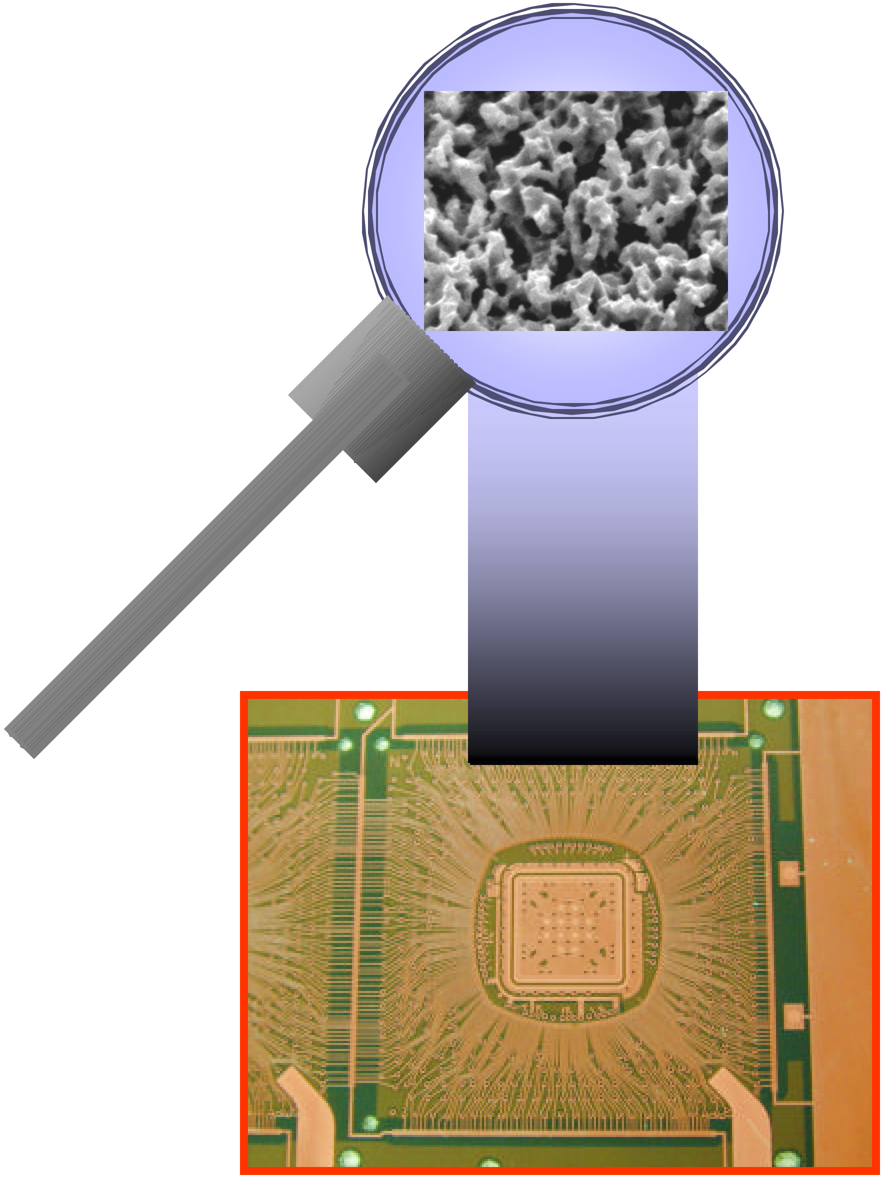
Plated Copper



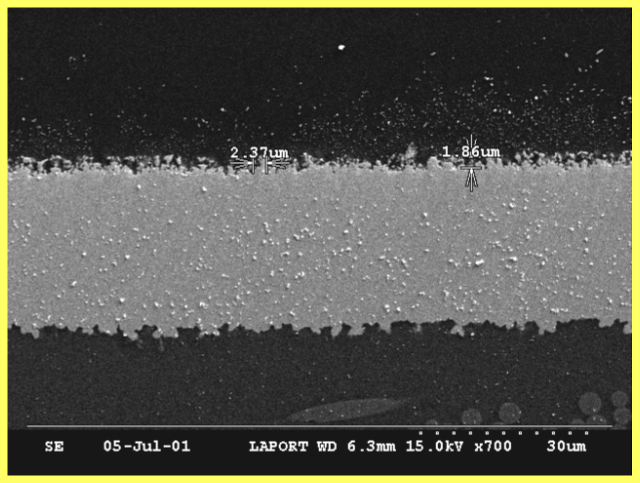
RA Foil

Modified Organo-metallic process

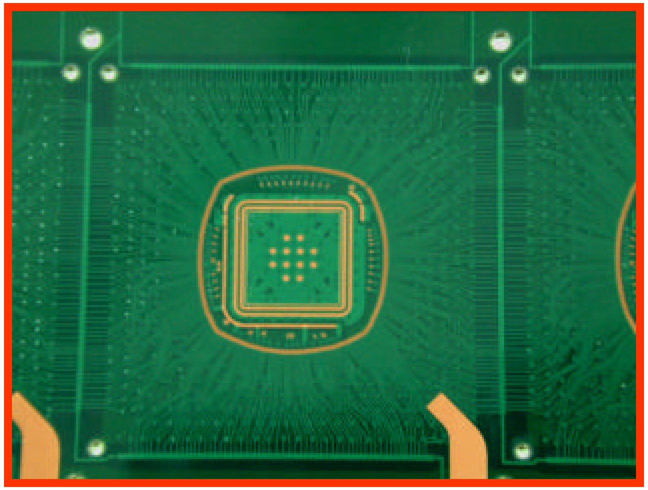
Designed to improve yields for fine line imaging and LPI adhesion



Copper surface after treatment



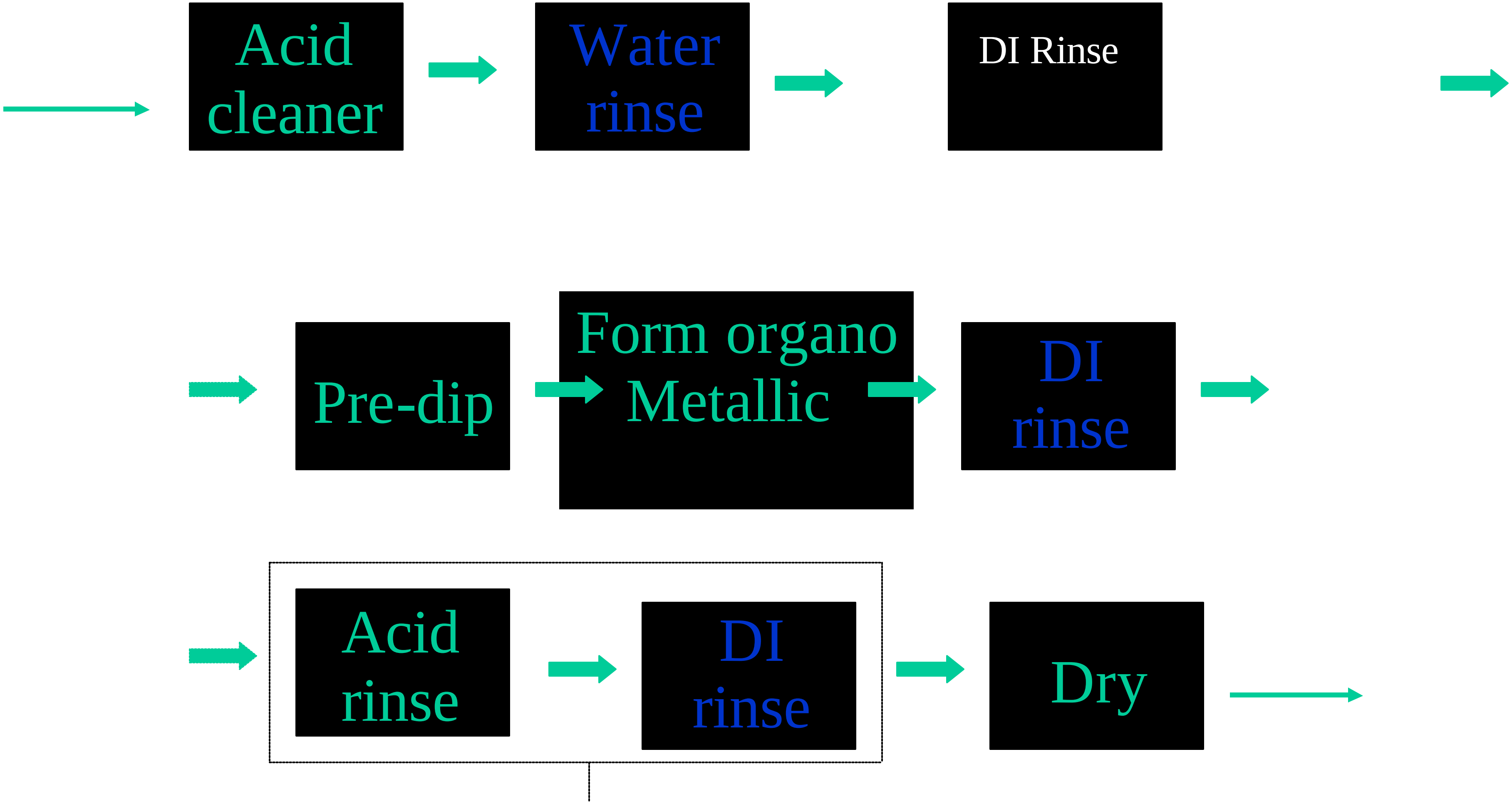
Side view of modified organo-metallic process



After solder mask

Organo-metallic Process Chart--two step

(for Outer-layer Dry Film or LPI Pretreatment)



Acid cleaner

Water rinse

DI Rinse

Pre-dip

Form organo Metallic

DI rinse

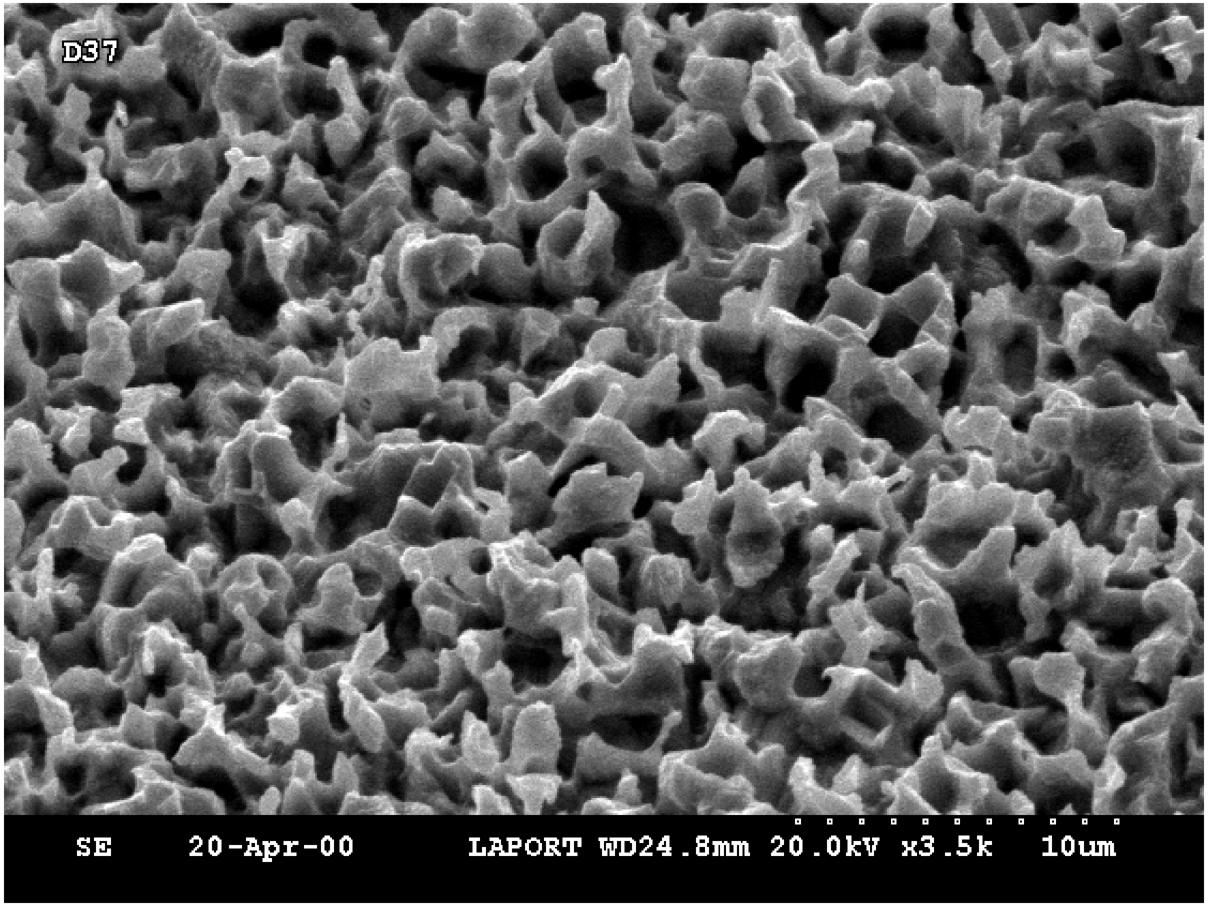
Acid rinse

DI rinse

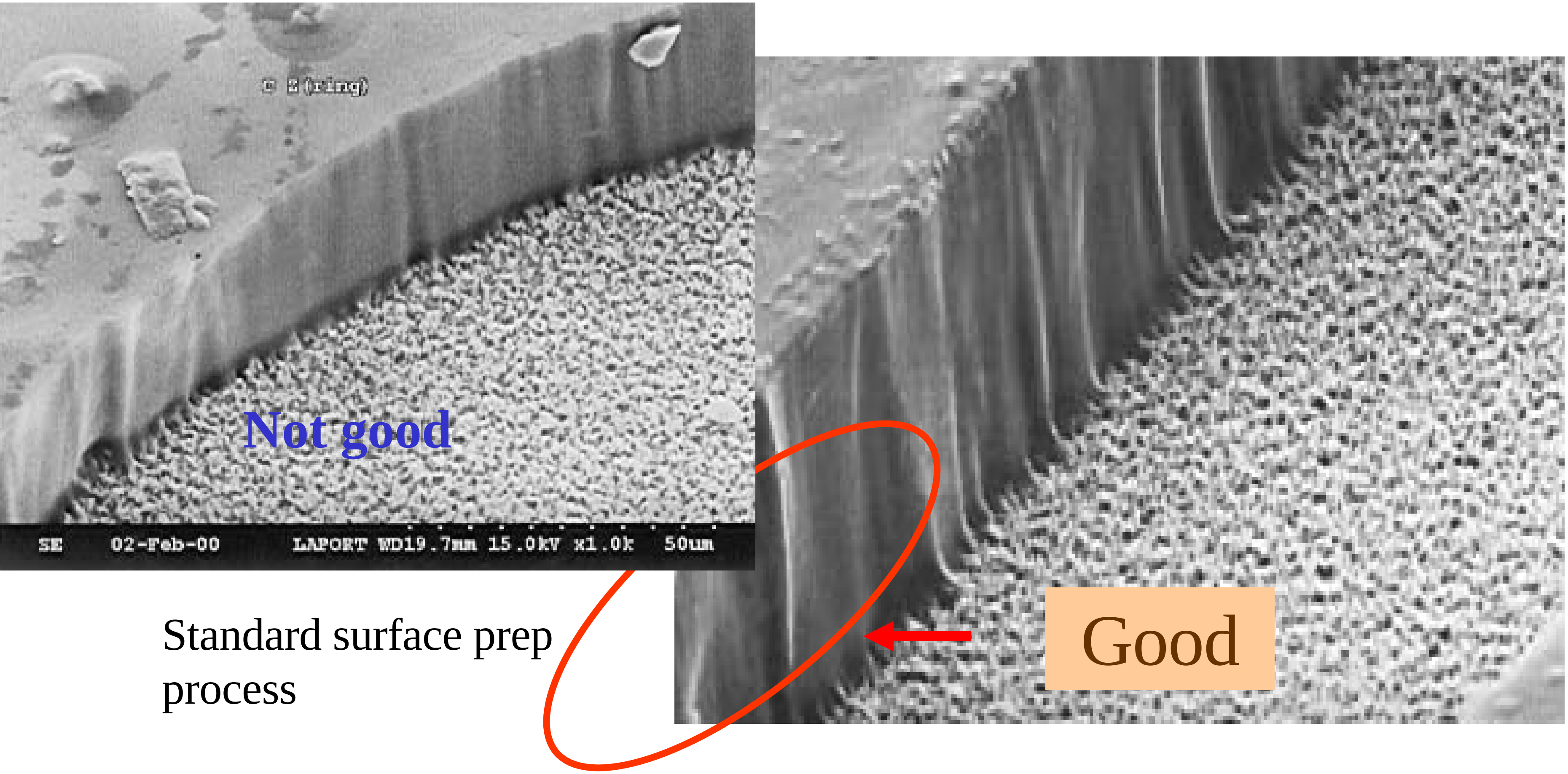
Dry

Remove Coating & Adjust Color

Modified Organo-metallic process



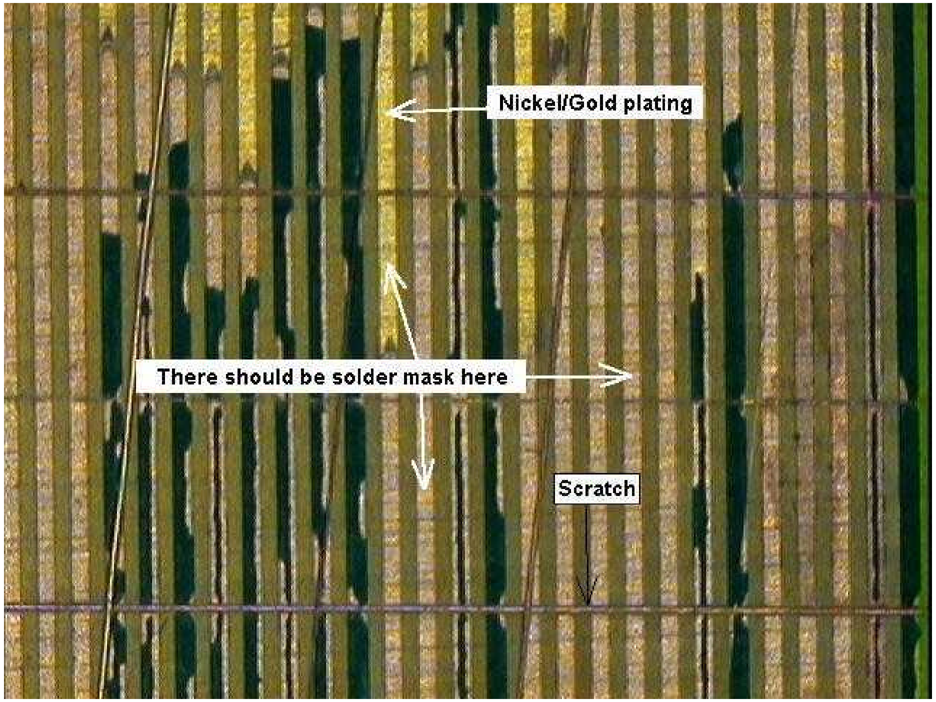
Organo-metallic process-modified for primary image or LPI adhesion



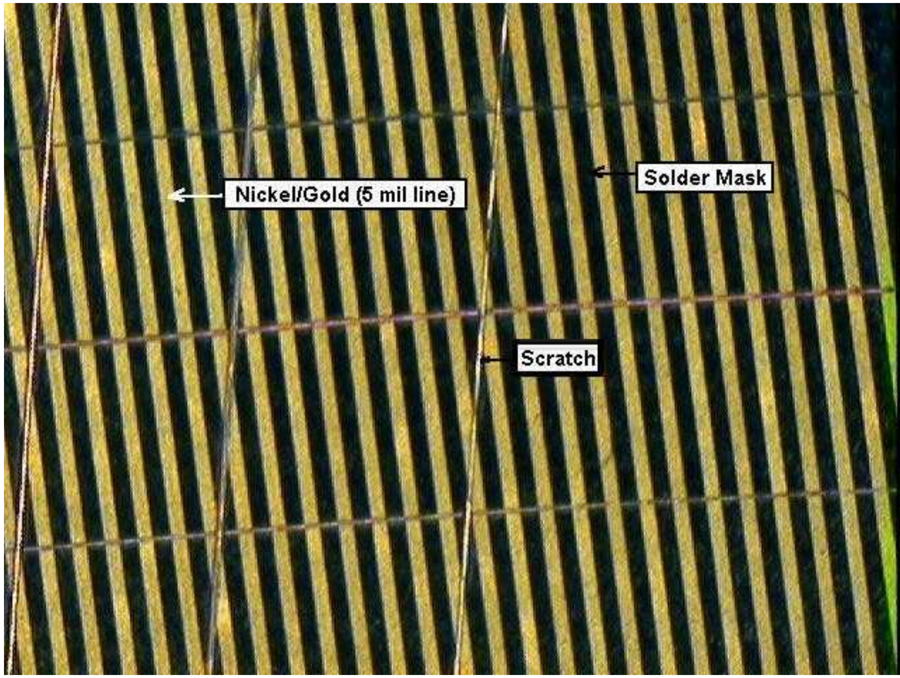
Standard surface prep process

Modified organo-metallic process

ENIG Processed PWB’s

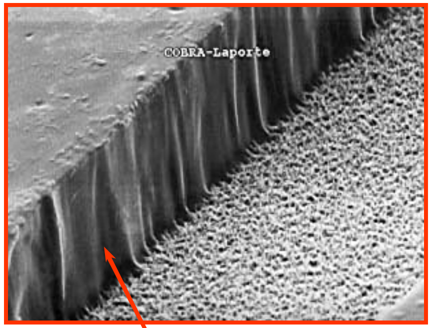


Pumice scrubbed surface with LPI
And processed through ENIG



Surface prepared with modified organo
metallic process prior to LPI and ENIG

Resist yields with different surface treatments



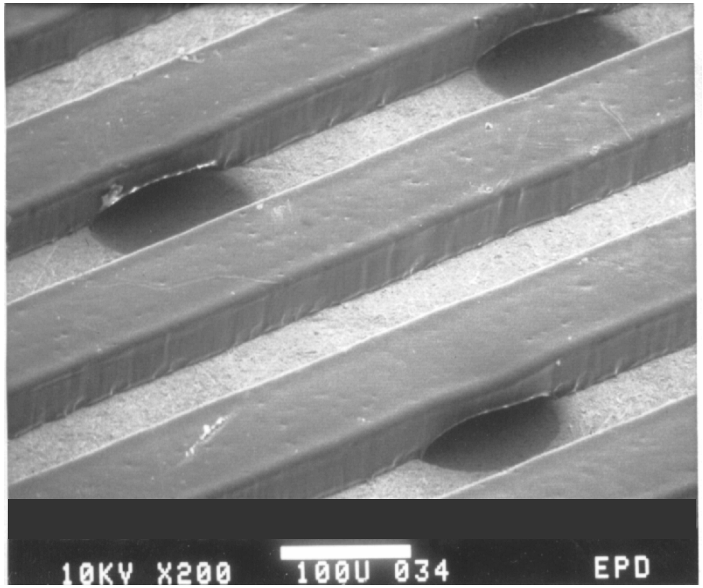
Organo-metallic for Dry Film **pretreatment** :

Item \ Pretreatment	scrubbing	SPS	pumice	Modified organo metallic
lines/spaces ? 4/4	?100 %	?100 %	?100 %	?100 %
lines/spaces = 3/3	<90%	<90%	<95%	>99%
lines/spaces = 2/2	---	---	---	>99%

Feature :

1. Excellent performance for HDI very fine line (<50µin, 2mil)
2. Higher yield than mechanical pretreatment system
3. Thin anti-tarnish film avoid oxidization. (Holding time : 2~3 days)

Photoresist Conformation To Copper Surface-Dry Film



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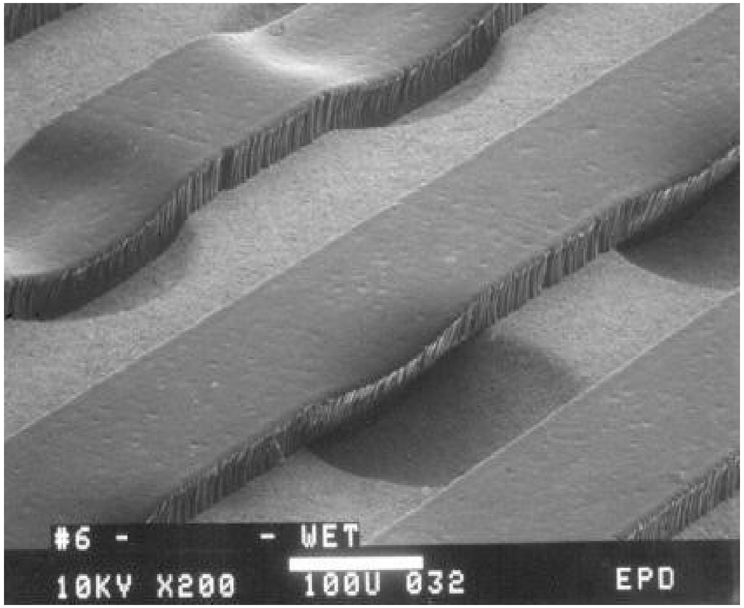
Test panel-pumice scrub



Organo-metallic modified treatment

Summary

- New conversion coating developed as an alternative to reduced oxide
- Less hazardous process solutions
- Horizontal and Vertical Processes
- Fewer process steps, shorter cycle time
- Reduced rinse water consumption
- Bond strength equal to or better than conventional oxide systems
- Pink Ring Resistant
- Robust handling characteristics
- Process designed for reduced copper removal an higher solution loading