

Process Improvement Strategies for Weak Microvia Interfaces

William Bowerman, Jordan Kologe, Rich Bellemare and Warren Kenzie
MacDermid Alpha Electronics Solutions
Waterbury, Connecticut, USA
William.Bowerman@MacDermidAlpha.com

Abstract

The industry has been openly discussing the concern about weak microvia interfaces after IR reflow and the potential for an undetected open or latent defect that can escape after expensive components have been soldered to the board. A specific concern is for the reliability of stacked microvia designs on very complex panels that are often built in low volumes. This type of build is typical of American and European OEMs who are using large and expensive BGA components in mission critical electronics. Due to the limited number of units made, this board segment of the industry is more vulnerable to weak interface failure than the HDI boards for mobile devices that are made with high levels of automation in mass production by fabricators in Asia. Further complicating the board design impact, the metallization process that is used can have very different reliability performance from different lines in different regions.

The goal for the metallization process is to form a continuous metallurgical structure to withstand the thermo-mechanical stress of IR reflow during assembly. The best condition consists of epitaxial growth of a thin electroless copper deposit on the target pad with a grain structure that recrystallizes with temperature and becomes indistinguishable from the target pad and electrolytic copper structures. There are multiple factors that influence the ability to form this recrystallized structure, which in turn affects the strength of the microvia interface. These include the circuit design, laminate material selection, type and settings of laser via formation, post-laser conditioning of the target pad copper, the desmear and electroless copper process processes, and the electrolytic copper via fill plating processes.

Through extensive auditing as a supplier of primary metallization and electrolytic copper via fill chemistries, and cooperative work with PCB fabricator customers to improve microvia reliability, a wide range of studies were conducted. Presented in this paper are potential areas of concern for microvia reliability with a specific focus on metallization processes and the factors stated above as well as testing on improvements. The approach taken includes low level DOE testing for process improvement as measured by a test panel using IPC TM-650 2.6.26A and TM-650 2.6.27, otherwise known as IST and simulated IR reflow testing. Experience in failure analysis techniques, limitations on some commonly utilized inspection methods, and a review of overall best practices for plating are also discussed.

Testing was augmented with SEM, FIB, and broad-beam Ion Milling techniques to evaluate various the various structures. Current induced or air to air thermal cycling were utilized to determine the level of microvia survivability and judge process improvements.

Introduction

The goal of the electroless copper seed layer for primary metallization is to render the entire microvia surface conductive for electrolytic copper filling and to ultimately form a continuous metallurgical structure between the via target pad and the electrolytic copper plated with the via filling process. A well-formed microvia interface is thought to have the best resistance against interfacial separation caused by the thermal mechanical stress induced by reflow temperatures. Testing and screening for separation has been performed by Simulated IR Reflow in an air to air environment and by Current Induced Thermal Cycling above the T_g of the laminate where CTE mismatch is at its greatest.^{1,2} Both methods are useful for studying the robustness of the manufacturing process of HDI interconnects. Much of the North American and European HDI market is focused on aerospace, defense, and telecommunications electronics which design complex conventional HDI boards. To define conventional HDI, this paper will assume a core multilayer with 1 to several layers of HDI that can be stacked or staggered over buried vias. Stacked via structures that are greater than 2 layers have proven to be one of the greatest challenges to microvia reliability.

Other aspects critical to the survivability of the microvia interface through reflow not discussed in this paper include overall panel design, materials, lay-up, cure, via size and depth. Other authors have made contributions to understanding these topics.³ The focus of this paper is to offer some insight into the variety of conditions observed and best practices for metallization of microvias.

Via Formation and Target Pad Preparation

The importance of proper via formation and target pad copper preparation is critical to the interfacial bond. Laser via formation can have dramatic effects on the condition of the target pad. It can damage the target pad copper, leaving the surface coated with overly rough, loosely adherent and porous recast copper, or with a thin resinous layer of dielectric. Via formation is typically accomplished with two types of lasers: UV and CO₂.

UV Nd:YAG lasers remove both copper and resin/glass material by high resolution photon ablation. The via is formed by the UV laser beam of ~ 20 μm (0.0009”) in diameter and smaller than the finished via. The laser beam has a short

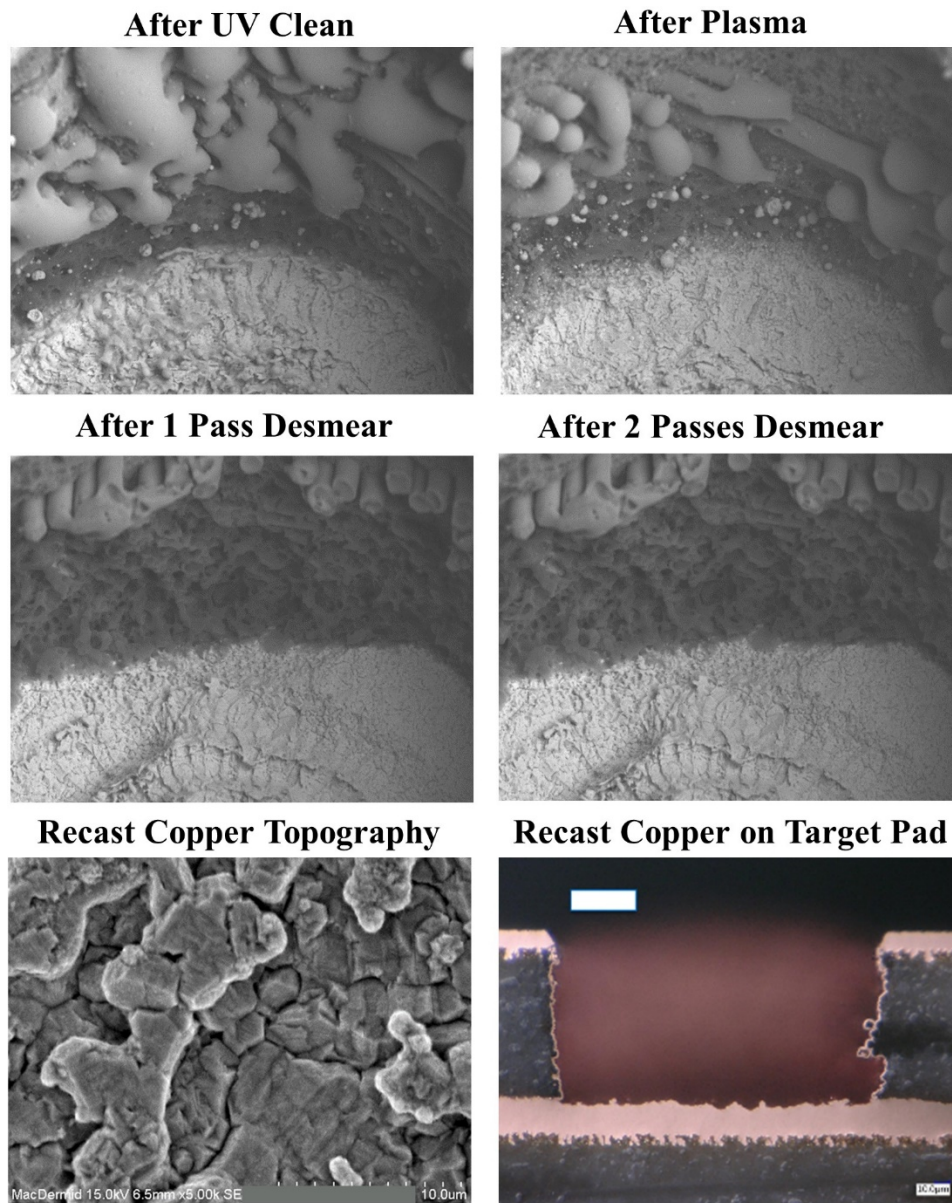


Figure 1 – UV drilled microvias shown after defocused laser clean, plasma clean, and 1x-2x desmear, recast copper macro-rough topography on un-plated target pad.

wavelength of 1,064 nm with a short pulse duration of ~120 ns and a pulse rate of 10 KHz. The tool has several options to control the path of the laser spot to form the required diameter microvia. The energy of the laser must be matched to the thickness of the copper and dielectric material as the UV laser does not inherently stop at the target pad during the drilling process. If the energy is too strong, the target copper can be plowed becoming overly rough with the ablated copper recondensing on the surface creating what is known as recast copper. This recast copper is loosely adherent with an amorphous structure that will weaken the microvia target pad interface. The recast copper can cause a porous electroless copper deposition susceptible to hydrogen gas entrapment. The UV laser can be programmed with a defocused beam as a cleaning step to remove remaining resinous debris and maintain a smoother copper topography. Figure 1 shows progressive photos of a UV lasered microvia after UV cleaning, plasma cleaning, and one to two chemical desmear passes as well as the topography of recast copper from a top-down and cross-sectional view.

CO₂ lasers remove resin/glass by low resolution thermal ablation. The CO₂ laser has a long wavelength of 10,600 nm, with a pulse duration of μ s and a larger beam diameter of 40 – 75 μ m that can be reduced to a focal point by lenses and apertures. The CO₂ beam reflects off copper. In the past, a conformal mask or capture pad was etched followed by the CO₂ laser to remove resin/glass in the dielectric. Today, with the use of thinner copper foils and Laser Direct Drill (LDD) oxide coatings, the energy of the CO₂ laser can be absorbed by the copper and the beam can machine through the capture pad copper. While the CO₂ beam will inherently stop at the target pad copper, one drawback is that as the CO₂ beams nears the target pad, ~ 0.1 μ m (4 μ "') from the surface, the energy is absorbed by the underlying copper and a thin resinous layer is left at the bottom of the microvia.⁴ This thin layer is removed by either plasma, chemical desmear or a combination of both.

Combination UV-CO₂ lasers have rapidly become the tool of choice in North America and Europe for HDI via formation. The UV laser beam first removes the copper from the capture pad, as well as some of the resin/glass below, defining the opening. The CO₂ laser beam then removes the remaining resin/glass material down to the target pad. Both the UV and CO₂ lasers create heat that melt the glass and leave carbonized debris on the side walls. The UV beam is again used but defocused, providing an optional cleaning step to remove the residual film without damaging the target pad. Figure 2 shows the appearance of a microvia drilled with a combination UV-CO₂ laser after laser, plasma, and desmear passes.

Recently, pico lasers have also been introduced for via laser formation. The pulse duration for these lasers is in picoseconds, which significantly reduces the amount of heat damage to the resin/glass and copper. The result is little to no heat affected zone in the via wall or the target pad. Pico lasers are also known as green or cold lasers.

Based on the laser tool used and the condition of the microvia wall and target pad, the fabricator may incorporate several cleaning steps prior to metallization. These include a pre-etch, plasma and chemical desmear.

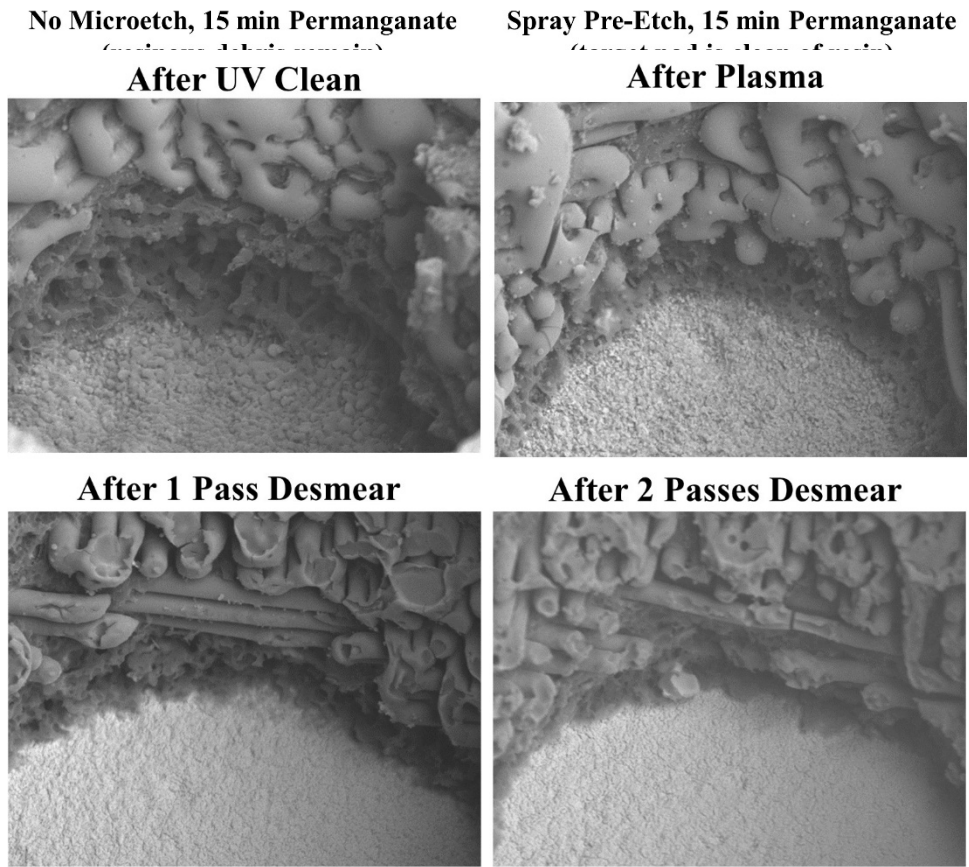


Figure 2 – UV-CO₂ laser drilled microvias shown after shown after UV clean, plasma, and desmear.

Chemical Cleaning

Horizontal pre-etches are widely used in HDI mass production. The pre-etch removes 0.5 to 1.0 micron (20-40 μ'') of copper per pass with two passes with a flip in between being common. Pre-etch lines utilize spray bar modules similar to copper reduction designed for a high degree of etch uniformity across the panel surface. Hydrogen peroxide etchants are most common, but persulfate etchants are suitable as well. The pre-etch removes recast copper, excessive roughness and may undercut and remove some remaining resinous debris, as can be seen in Figure 3.

Chemical desmear acts as the main microvia cleaning step. Plasma and desmear can be used in combination depending on the laminate material and plasma capacity at the fabricator's facility. Fortunately, chemical desmear is the same process used for through-holes and can be run horizontally or vertically. Most horizontal lines will run desmear twice, flipping panels between runs. Vertical lines can also run HDI panels twice by programming the hoist movements. The chemical desmear process includes a solvent swell, sodium permanganate and a neutralizer. Sodium permanganate is utilized due to its high solubility that prevents flash drying within the microvia during drip time and transfer. Either a non-etching neutralizer or a sulfuric peroxide etching neutralizer may be used. Etching neutralizers are balanced to etch a minimum amount of copper. A glass frost (1-3 g/L) or glass etch (>55 g/L) can also be included in the neutralizer bath or in a separate step.

A 2 level DOE test comparing type of UV-CO₂ Laser, 2X and 4X desmear cycles, and with / without flash plating was conducted. The response was failure rate in simulated IR reflow, specifically the lower the mean failure rate of 50X reflow cycles, the better as shown in Figure 4. The Pareto chart in Figure 4 shows the interaction of the desmear and UV clean as significant in improving reliability. The defocused UV clean and extra cycles of desmear had the lowest mean rate of failure. It was also determined that the use of flash plating or simply going directly into copper via filling without flash plating was not significant in this study.

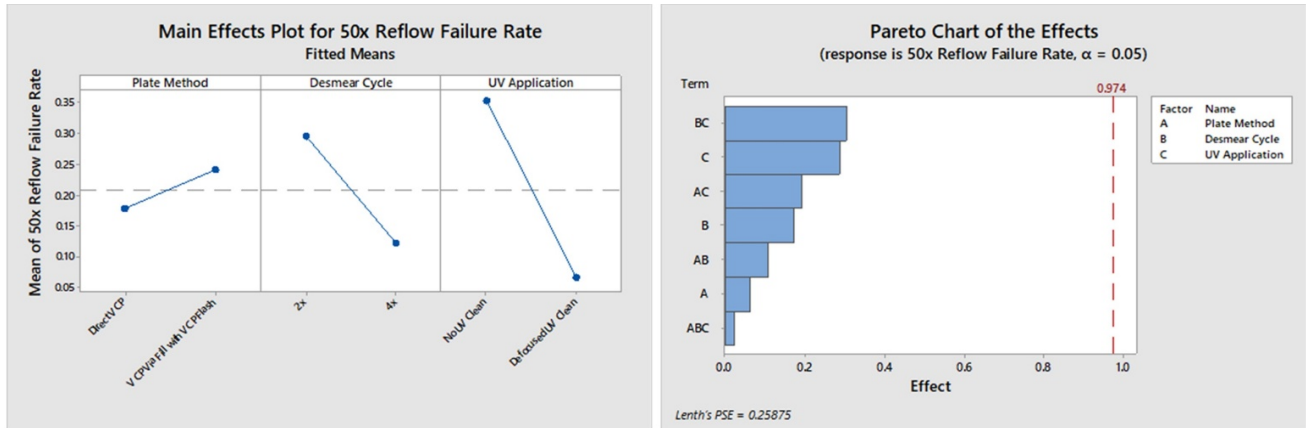


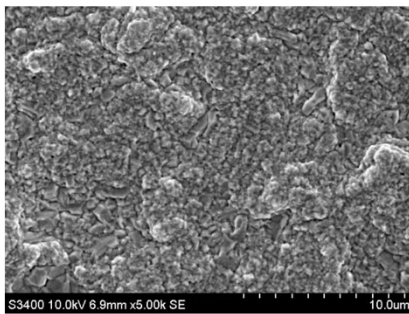
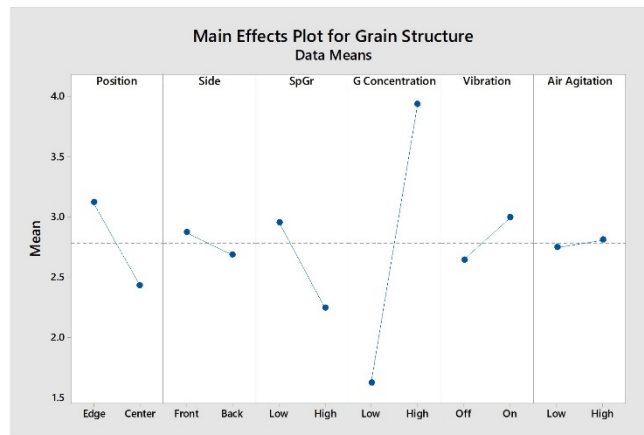
Figure 4 – 2 Level DOE results for UV clean, desmear cycle, and flash plating impact on 50x reflow failure rate.

Best Practices for Electroless Copper Deposition

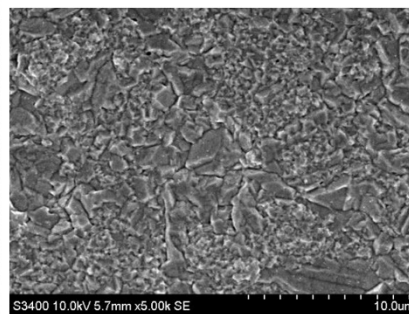
It has been determined that the electroless copper grain structure type is critical to microvia reliability. Over a two-year time span of global auditing of desmear-electroless copper lines with the goal of increasing process robustness and improving microvia interface, a set of best practices for maintaining good electroless copper grain structure have been determined. The desmear process is followed by the electroless copper metallization. Most desmear/electroless copper lines will run together with the panels going wet to wet. This is the preferred sequence. If this is not the case, it has been determined that the Cleaner/Conditioner on the electroless copper line should utilize either ultrasonics (horizontal lines) or vibration and thump (vertical lines) to de-gas microvias and wet all surfaces quickly and uniformly. With thousands of microvias on a typical HDI panel surface, a single gas bubble can ruin a panel. Furthermore, it is recommended that vertical lines are equipped with vibration capability for all process tanks in addition to the cleaner/conditioner.

A dense, angular electroless copper grain structure is preferred with a strong, 1, 1, 1 oriented, face centered cubic crystal structure. 1,1,1 is the densest atomic packing of copper atoms with the lowest total energy state. Grain structure can be evaluated with a simple top-down comparison using SEM imaging at 1,000X and 5,000X of the surface copper and target pad copper. Both grain structures should look similar. It was found that controlling the grain structure required good solution exchange into the microvia and maintenance of the concentration of the primary grain refiner agent in the bath. Electroless copper grain refiners work by temporarily adsorbing on the cupric ions at the surface during plating, increasing the activation energy and causing a two-step reduction process from cupric⁺² to cuprous⁺¹ to copper. Grain refiner components are typically easy to analyze and most commercial electroless copper formulations maintain an adequate concentration with normal bath replenishment.

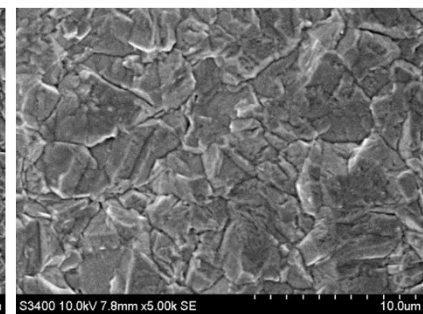
It was also found that chemical exchange into the microvia is important to obtain the desired grain structure at the target pad. Because of the shape of the blind microvia structure, achieving proper solution exchange is more difficult than in open through holes. The main reactants in the electroless copper reaction are diffusion controlled so the exchange to the bottom of the via is critical. Copper ions, sodium hydroxide, and the methylene glycol ion (formaldehyde reducing agent) are smaller ions in g/L quantities. The stabilizers and grain refiners are larger ions and are in ppm and ppb levels. These components are diffusion controlled. Solution exchange is critical to maintain all components during the initiation and autocatalytic phases of electroless plating. A 2 level DOE was run to investigate the influence of panel location in the rack, specific gravity, grain refiner concentration, vibration and air agitation. The response was the grain structure of the target pads at 1,000X and 5,000X SEM images using a rating on a scale of 1 – 5 (higher is better). Figure 5 displays a summary of the results of this



Rating: 1



Rating: 3



Rating: 5

Figure 5 – Top, main effects plot for solution movement DOE. Bottom, copper grain structure at base of target pad rating system examples.

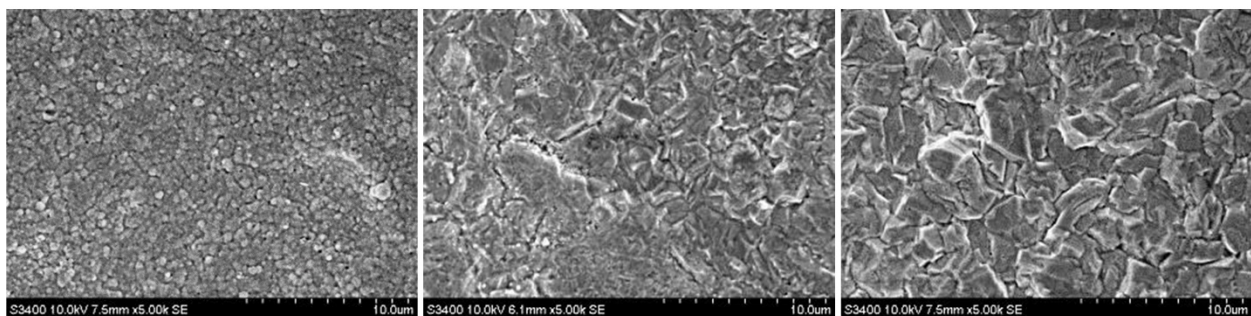
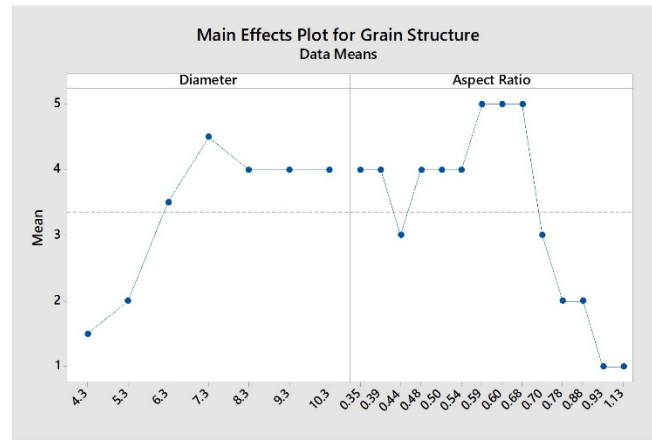
study. The grain refiner concentration, specific gravity, vibration, and location on the panel rack were found to be significant factors in the quality of the electroless copper plated at the target pad.

Panel racking is an important factor for solution exchange in microvias in HDI processing. Racks should hold panels 90° vertically to not favor either side, differing from the way through-hole only panels would be processed in an angled configuration in earlier PCB manufacturing. Vibration is run on an on/off cycle to increase solution exchange in the microvias and dislodge hydrogen gas bubbles generated during electroless copper plating. From a chemical reactant standpoint, two moles of hydrogen will evolve for every mole of copper plated, so the gas removal is an important factor to control and understand. An accelerometer can be used to check the vibration energy level. 4 mm/s is recommended. The rack must secure the panels tightly to ensure transfer the energy to the panels completely and in a repeatable manner.

General bath solution movement also plays a role on grain structure development. It was found that panels racked on the outside of the basket saw more solution movement than those racked on the inside giving the outside panels a more desirable grain structure at the microvia target pads. In horizontal lines, it is easier for hydrogen gas to escape on the top of the panel versus the bottom of the panel, which also complicates solution exchange and hydrogen gas bubble removal during plating. This can be remedied by the usage of multiple fluid bars to help remove the trapped gas.

It was found that aspect ratio of the microvia structure also has an influence on electroless copper grain structure at the target pad. A study was conducted with 7 different via diameters drilled on one panel. The dielectric on one side was 3.5 mils and

5.5 mils on the other side giving aspect ratios of 0.35, 0.44, 0.60, 0.78, 0.88, 0.93 and 1.13. Grain structure was evaluated on a scale of 1 – 5 (higher is better). It was found that the microvias with aspect ratios of 0.75 and lower allowed for good solution transfer and better electroless copper grain structure at the target pad area. As the aspect ratio increases to 1 and greater, the transfer of solution declined and the grain structure deteriorated. This can be seen in Figure 6, which shows the results of the study. In all, it is hypothesized that the variation in grain structure is related to the solution transfer since higher aspect ratio vias have an increased diffusion layer, which reduces the PPM level of the grain refiners that are utilized in the formation of the deposit.



Rating: 1 AR 1.1

Rating: 3 AR 0.88

Rating: 5 AR 0.60

Figure 6 – Top: Experimental results that display the effect on microvia aspect ratio and diameter on grain structure quality. Bottom: Example of plated electroless copper at the via target pad and the rating of grain structure.

If the pitch and target pad diameter of the design allow for it, a slightly larger diameter microvia can be beneficial to the robustness of the via interface. This is limited by via filling chemistry however, as current copper micro via filling processes cannot effectively fill vias wider than 150 microns (6 mils) in diameter with a flat surface or less than 5-micron dimple.

Rinsing is an often-overlooked step in the metallization process. Several troubleshooting efforts undertaken during the auditing study have found poor rinsing to be causal to microvia separation or microcrack starts. The separations might not be catastrophic or occurring on the first reflow cycle but can result in a shortened number of reflow cycles or show up as partial or starter cracks near the wedge area during examination. Rinse water contamination has often found to be the main contributor to microvia failure, even more so than rinse time. Contamination of rinse water is one of the most difficult causes to pin down as review of the process when troubleshooting will show no issue associated with the rinsing time, and any water contamination that may have caused the defect will often no longer be present by the time the defect is found. Other areas of concern for rinsing include the wetting agents that are included in the cleaners, and the impact that these may have on the effectiveness of the activation process. In auditing the lines, it was found that treating every tank as a separate process to control on its own allowed insight on previously unexamined factors that impact the robustness of the microvia target pad interface.

Through a study of a specific board build that experienced pad separation before reaching the required 1,000 cycles in IST testing it was found that the specific gravity of the electroless copper bath was a significant factor. Lowering the specific gravity by 0.2 units from the maximum specific gravity on as identified by the commercial technical data sheet for the process helped mitigate the separation problem and allowed the IST test to run to the censor point. Through this study it was determined that for running HDI panels, suppliers of commercial electroless coppers should recommend that the specific gravity of the bath should be slightly below the maximum level compared to that of through-hole only builds. It is hypothesized that the higher level of byproducts, formate and carbonate species, are competing with the main reactants at the diffusion layer as shown in the earlier study as a significant interaction. The results of this study can be seen in Figure 7 below.

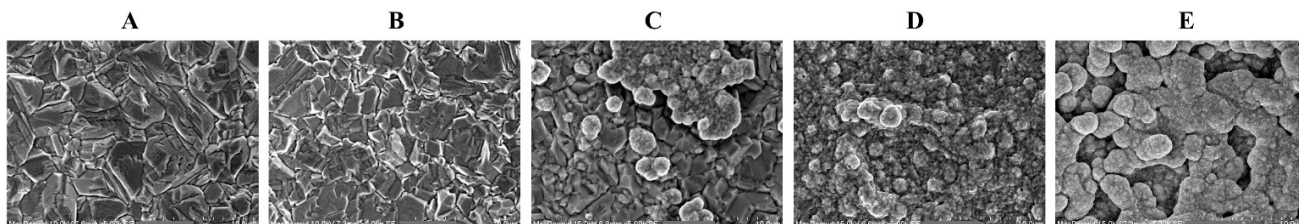
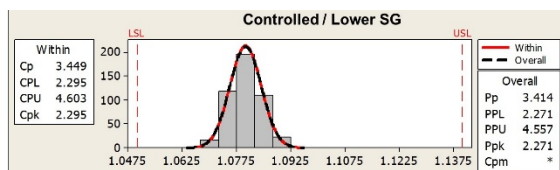


Figure 8– Electroless copper grain structure plated at various sites around the world.



Original / Higher SG:
Failures at 654 and 812 IST Cycles

Controlled/Lower SG:
All Passed 1,000 IST Cycles

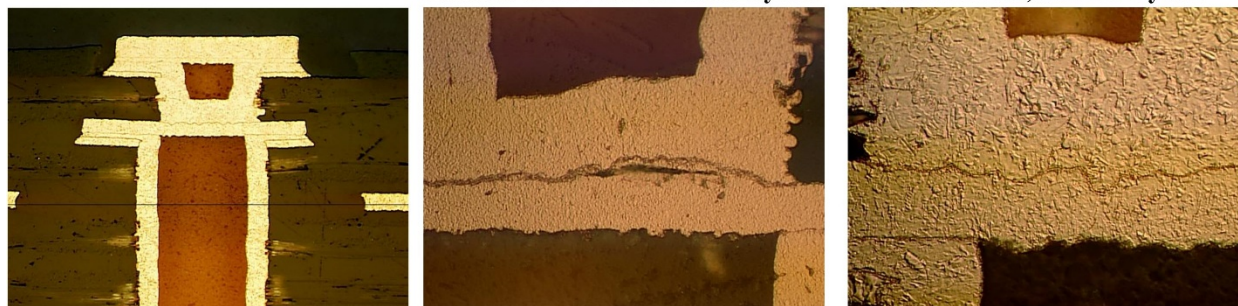


Figure 7 – Study: Adjustment of the control levels for the specific gravity of the electroless copper bath for HDI.

A study was done, selecting panels run at various sites around the world to see the effect the grain structure had on simulated reflow testing per IPC 2.6.27. Figure 8 shows the electroless copper grain structure at the via target pad for the various sites A-E. The same electroless copper formulation was run at different sites for A, B, C and D. Site E was a different electroless copper formulation. Sites A and B show the ideal angular grain structure. Sites C and D show a dense structure but not ideal. Site E appeared porous and cauliflower like. Sites A and B passed 24 OM cycles as the censor point while the other panels had some level of failures before 24 cycles.

Epitaxial Grain Growth

Epitaxial copper growth is important for both electroless and electrolytic copper plating. Epitaxy refers to the ordered crystal growth over the substrate copper, wherein the case of electroless copper plating in the microvia, the deposition will mimic the

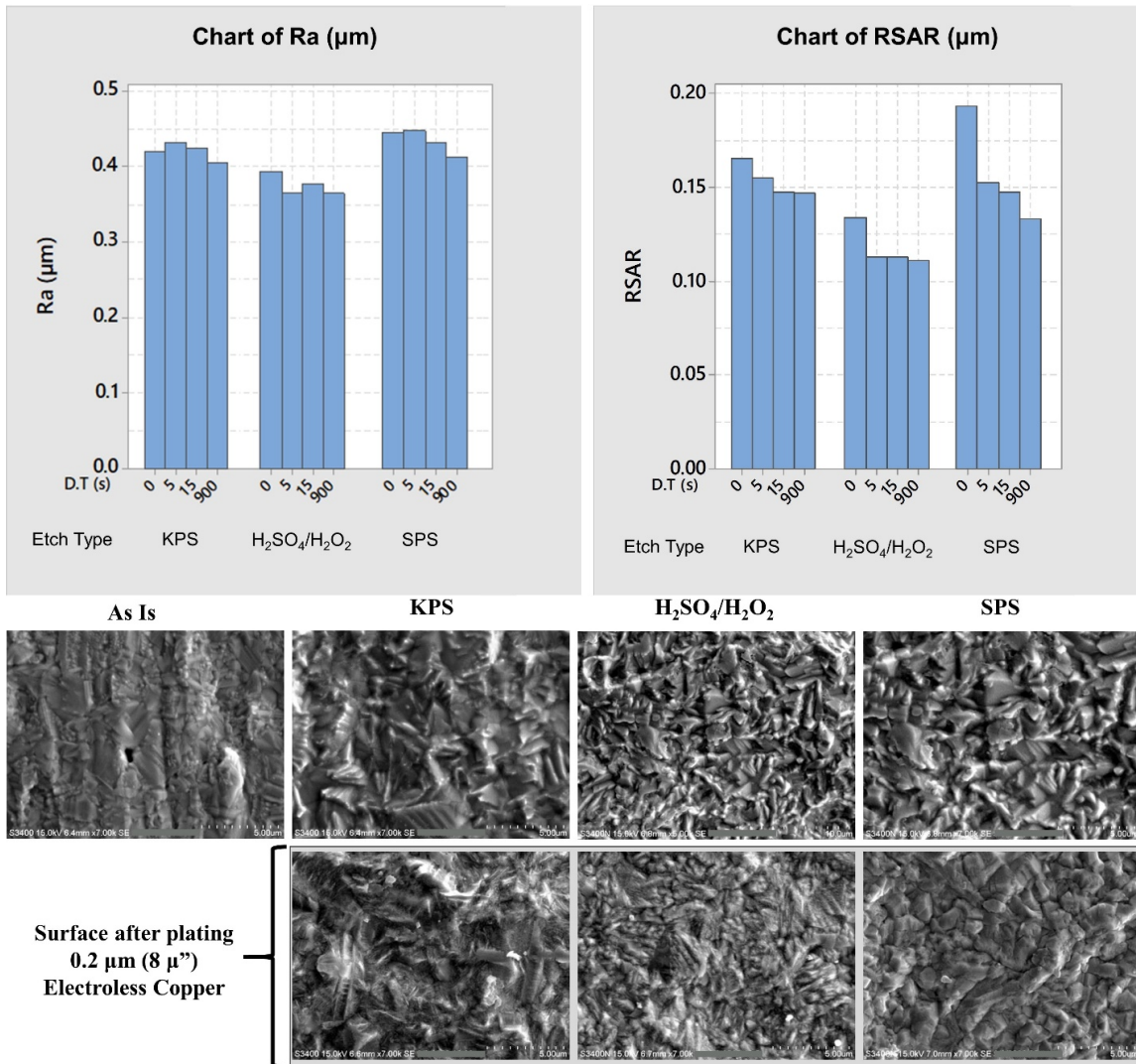


Figure 9 – Etch chemistry impact on roughness and topography of the underlying substrate copper, bars are dwell time.

parent target pad copper.⁵ The quality of the substrate copper is the reason for this paper's earlier discussion of the laser via formation and pre-etch steps as removal of unwanted recast copper and excessively rough copper is an important factor to proper grain growth.

To achieve an epitaxial copper structure, the initial copper deposit needs to mirror the substrate crystal structure. If the target pad has recast copper, the structure is amorphous and the resulting target pad interface will be weak. If the target pad is too rough, the electroless copper solution will be in contact with too many crystal facets to grow uniformly possibly resulting in a porous coating with nodules. It was found that the ideal surface roughness for the target pad after microetching is between 0.4 and $0.5 \mu\text{m}$ Ra or 0.15 and $0.20 \mu\text{m}$ RSAR. A persulfate or sulfuric peroxide etch on the copper will provide topography in this range, with the persulfate being more matte and the peroxide less so. A study was conducted that examined how the roughness of the base copper changed after mono potassium persulfate (KPS), sodium persulfate (SPS), and sulfuric-peroxide etches ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$), and the appearance of the subsequent electroless copper plating grain structure over the various etches. It was found that the electroless copper deposited over the micro roughened base copper will replicate the topography. The details of this study can be seen in Figure 9 above.

Thickness of the electroless copper deposit is another factor to be considered. Both thin dep, $\sim 0.3\text{-}0.5\ \mu\text{m}$ ($12\text{--}20\ \mu''$), followed by an electrolytic copper flash or medium dep, $0.8\text{-}1.25\ \mu\text{m}$ ($32\text{-}50\ \mu''$), have track records of being reliable. The copper deposits will form an identical structure over the substrate copper. Heavier deposits of $2\text{-}2.5\ \mu\text{m}$ ($80\text{-}100\mu''$) are not recommended for HDI. It should be noted some electroless copper baths will plate less copper on copper than on epoxy dielectrics. This is considered a favorable characteristic allowing for good coverage of the dielectric in the via wall while keeping the copper deposit on the copper land thinner.

Electrolytic Copper Via Fill Guidelines

Electrolytic copper via fill follows the electroless copper seed layer in crystal shape.⁶ The goal is to continue the grain orientation in the 1,1,1 crystal plane. If the target pad and seed electroless copper have followed the epitaxial crystal structure, the electrolytic copper will follow the same crystal orientation. For conventional HDI panels, pattern or button plating are common. Microvias are plated first, followed by a second pattern plating cycle for through holes. Today there are commercial chemistries available for simultaneous via fill and through hole plating with the through hole aspect ratios limited to approximately 6:1.

Panel plating is utilized for Anylayer HDI designs which have no through-hole plating. The panels are processed from the electroless copper directly to copper via fill without the imaging step in-between. This less complex metallization cycle is mainly used in mobile applications and is the largest segment of HDI globally.

Electroless copper lines with low dep thickness will typically be followed by an in-line flash. This is important to protect the thin dep copper during imaging and pre-cleaning for plating. In-line flash plating is ideal to prevent the formation of oxides on the copper surface. If the lines are not connected wet to wet, then the panels should be held for a limited time in dilute sulfuric acid or coated with an anti-tarnish.

Some lines for copper via fill chemistry start with an acid cleaner and light microetch while others have an in-line flash plate. Re-activating the copper surface after dry film development and rinse is important to have uniform plating without dimples. A dilute persulfate microetch of $0.1\text{-}0.2\ \mu\text{m}$ ($5\text{-}8\ \mu''$) is recommended. The sulfuric pre-dip before plating should be changed to prevent the buildup of copper. Copper concentrations over 200 mg/L have been found to degrade reflow survivability.

Copper via fill current densities should follow the supplier's recommendations. A multiple step current density ramp is often used with lower current density to promote bottom up fill and then increase the current density for productivity. On plating lines with direct impingement, the flow rates can also be adjusted. A high flow is used in the beginning to promote bottom up plating but then the flow rate is lowered so the plating height is uniform without dimple.

Copper Recrystallization Across the Interface

If best practices have been maintained over the metallization process sequence, the plated copper will undergo grain growth under time and temperature.⁷ During this self-annealing, the crystal structure coarsens to reduce grain boundaries. A study of this phenomenon utilizing cross sectioning and FIB (Focused Ion Beam) and IM (Ion Milling) SEM imaging showed a continuous structure across the three interfaces when proper metallization process guidelines were maintained. Figure 10 below shows an IST coupon with 3+N+3 stacked vias over a filled buried via, which is one of the types of designs that has shown concern for microvia reliability. The coupon was run 9 times in IR reflow at 260°C followed by 1,000 cycles of IST. After the thermal-mechanical stresses of the test, the electroless copper deposit could not be detected in the FIB image.

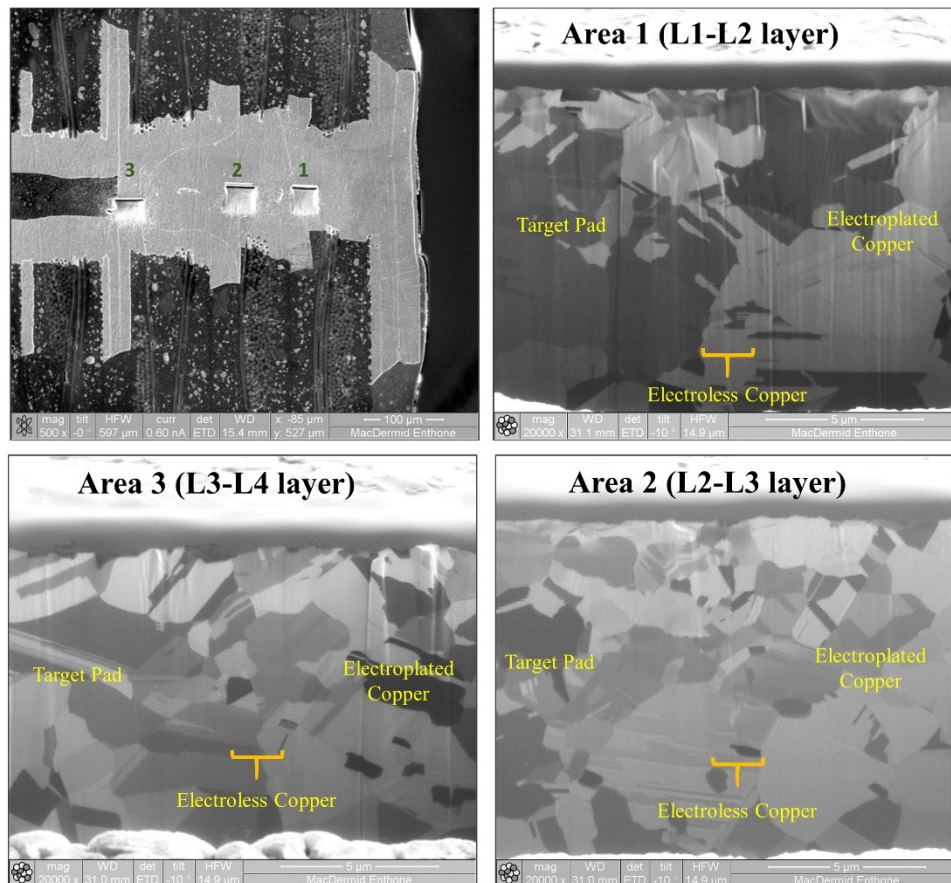


Figure 10 – 3+N+3 Stacked microvias showing continuous grain structure and strong layer to layer bonding.

Recrystallization had formed a continuous grain structure indicating strong layer to layer bonding. Lack of recrystallization across the various copper interfaces can be attributed to several factors. Recrystallization can be interrupted by a macro-rough surface on the target pad, from recast copper, from a layer of oxidization on any interface during metallization, dry film or developing residues, or by a non-epitaxial copper structure that did not follow the orientation of the substrate. Recrystallization may not have occurred uniformly across the interface leaving a weakened interface. A porous or cauliflower electroless copper deposit may leave hydrogen entrapment or nanovoids in the layer.

Summary and Conclusions

The microvia has been the primary enabler of high-density interconnect since its inception but concerns over weak via target pad interfaces have so far limited the usage of this design feature in devices that require very high reliability. As HDI designs are becoming more widely utilized in mission-critical and safety-oriented applications, the focus on solving the issues behind the weak microvia interface has never been more important. Continued studies such as the ones presented in brief in this review are necessary to facilitate the next step in high reliability design. Important areas to focus on are the condition of the copper at the target pad before plating begins including the presence of recast copper, surface roughness, selection of laser equipment, and chemical etching treatments. These factors have a large impact on the topography and grain structure of the subsequent electroless copper deposit and are critical to achieving the uniform recrystallization required to have a sound target pad interface. Additional factors discussed such as rinsing, electroless copper grain refiner concentration, solution movement, panel racking and control of hydrogen gas during plating of copper are important and should be maintained according to best practices to achieve reliable results.

References

- [1] IPC-WP-023, The Hidden Reliability Threat – Weak Microvia Interface, Jerry Magera, MSI, May 2018
- [2] The Keys to 100% Effective Reliability Testing and Failure Analysis of HDI/Microvias, Kevin Knadle, *IPC High-Reliability and Microvia Summit*, May 2019, S16-03
- [3] Microvias: Links of Faith Are Not Created Equally, Jerry Magera

- [4] Studies on CO₂ Laser Drilling: Formation Mechanism of Residual Thin Materials at the Bottom of Laser Via, Ryoji Inaba, and others, Hitachi Via Mechanics, *IEEE*, Vol 24, No 1 January 2001
- [5] Microstructure Evolution during Electroless Copper Deposition, J. Kim, *IBM Res Develop*, Vol 28, Nov 1984
- [6] Substrate effect on electrodeposited copper morphology and crystal shapes, Swastika Banthia, *Surface Engineering*, 2018, Vol 34
- [7] Crystallographic study on self-annealing of electroplated copper at room temperature, Eri Shinada, *Mat'l Sci in Semiconductor Processing*, 16 (2013)
- [8] Time Evolution of Stress and Microstructure in Electroless Copper Films, Tanu Sharma, *Electrochimica Acta*, 196 (2016)