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'Bridging the Gap' – Technical Capabilities of a Direct Plate PTH Process

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Abstract

In contrast to electroless copper, direct metallization processes are inherently less expensive to operate, more environmental friendly, requires less floor space and are more efficient. Among the three common direct metallization methods, namely carbon based, conductive polymer based and palladium based, carbon based is the most attractive option, with the lowest cost and 'greenest' ingredients. However, despite past predictions to the contrary, electroless copper processes are still the most widely accepted through-hole metallization technologies in today's market.

In their infancies, implementation of direct plate processes at PWB manufacturers produced panels of questionable reliability. This led many major OEMs to write specifications refusing to accept any alternatives to conventional electroless copper for through-hole metallization in PWB fabrication. However, despite the lack of official acceptance by certain OEMs, carbon-based direct metallization is widely used by PWB fabricators where lower costs and environmental concerns are the industries major drivers.

This paper, focusing on higher technology applications, provides PWB fabricators and OEMs with current up to date comprehensive data on improvements made to the technical capabilities and reliability of this unique carbon-based direct metallization system. Additionally, the data supports the acceptance of this direct metallization technology as a viable alternative to conventional electroless copper processes.

Introduction

The process of metallizing through-holes in PWB manufacturing has long been dominated by electroless copper. Many established PWB manufacturers have over the years invested significantly in equipment and the technical expertise necessary to run and maintain such processes. Early attempts at introducing alternatives to electroless copper, such as direct plate systems, yielded questionable results in terms of consistent product reliability. The end result was lack of acceptance by numerous OEMs who would write specifications clearly refusing to accept PWBs that were manufactured with direct plate processes.

Today, however, direct plate processes are no longer in their infancies. Close to twenty years of experience and a thorough knowledge of operation and technical expertise by both suppliers and PWB manufacturers have promoted these processes to a mature status. In fact, carbon-based product reliability has proven to be superior to electroless copper. This is based on the consistency in the manufacturing operation through horizontal automation and the non-dynamic chemistry that contains fewer process steps and much fewer and simpler analytical controls. (Figure 1)

Continuous improvements to this carbon-based direct plate process due to ever increasing product design challenges further promote its use and reliability for PWB manufacturing.

Electroless Copper	Carbon-based 2 step	Carbon-based 1 step
Conditioner	Cleaner/Conditioner	Cleaner/Conditioner
Microetch	Carbon Dispersion	Carbon Dispersion
Predip	Conditioner	Microetch
Activator	Carbon Dispersion	Antitarnish
Accelerator	Microetch	
Electroless Copper	Antitarnish	
Antitarnish		

Figure 1 - Chemical Process Steps in Metallization Processes (Excluding Rinses)

Chemical Enhancements to Carbon Black Process

Desmear Neutralizer Chemistry

For the PTH process of multilayer printed circuit boards, it is desirable to subject the board to a desmear process to remove resin that coats the innerlayer copper surface in the drilled hole. A typical desmear process involves resin swelling, treatment with an alkaline solution of permanganate ions followed by neutralization process to remove residual permanganate from a board.

The resin swelling treatment involves contacting a printed circuit board with a suitable swelling agent at an elevated temperature. The swelling agent may include an aqueous alkaline solution containing an alkali metal hydroxide and a glycol ether or other solvent. Alternatively, the swelling agent may be a nonaqueous solvent.

After resin swelling, a printed circuit board is treated with an alkaline permanganate solution, which is usually made from a mixture comprising water, an alkaline hydroxide and an alkaline permanganate. Other ingredients such as surface reducing agent can also be used depending on the specific applications. An alkaline permanganate can be a permanganate salt of ammonium, alkali metal, and alkaline earth metal ions. A multilayer board is contacted with an alkaline permanganate solution for an effective time and at an elevated temperature depending on the dielectric materials used to build the board.

After removing resin smear with permanganate solution, a printed circuit board is contacted with an aqueous neutralizer solution. A neutralization solution is comprised of water and at least one neutral or acidic reducing agent. A reducing agent can be selected from any chemicals that can reduce the excess permanganate and manganese ions. Possible reducing agents include dihydrazine sulfate and hydroxylamine salts. Peroxide/ sulfuric acid based neutralizer also reduces permanganate and manganese dioxide residues and slightly etches copper surface removing “nail head” in through holes and creating ideal topography for improved adhesion.

Conditioner Chemistry

In the conditioner process, the dielectric surface is coated with positively charged conditioner molecules, which will facilitate the adhesion of negatively charged carbon particles to the board. The conditioner solution includes a cationic conditioning agent and a surface tension reducing agent in an alkaline buffering matrix.

Alkaline conditioner usually includes chelating amine compound to provide and stabilize the alkalinity of the solution. As an effort to provide a more environmental-friendly direct metallization process, a non-chelating alkaline buffer system for the conditioner was developed. The effect of concentrations of the other components such as cationic conditioning agents and surfactant was investigated. It is found that lower concentration of those components still provide equivalent performance in the process, which will make the process more cost effective and environmental friendly.

Dispersion Chemistry

Conditioned printed circuit boards are coated with conductive carbon using aqueous carbon dispersion. This aqueous carbon dispersion contains three critical ingredients; a conductive carbon species such as carbon black and/or graphite, one or more surfactants to disperse the carbon and a liquid dispersing medium such as water. The desirable properties of the carbon dispersion are long-term stability and good conductivity of the applied carbon coating. The other challenge of a carbon based direct metallization process is the compatibility with acid copper electroplating systems. In some cases, carbon-processed boards showed different plating performance in different acid copper electroplating systems due to the organic “brightener” system and the highly absorbent nature of carbon black coatings. These issues were addressed and improvements were made through extensive research described below.

Carbon - Carbon black is inherently conductive although the performance varies depending on their particle size, surface area, structure and other chemical and physical properties. Preferred carbon blacks for direct metallization are the ones easily dispersed in aqueous media, stable in dispersion and conductive in an applied coating on the board. Several treatment methods for carbon black were developed and studied in our research efforts including chemical modification of the carbon surface and by blending different carbon particles to achieve synergistic effects on conductivity and stability in the dispersion. For example, when oxidized carbon black is mixed with non-oxidized, highly conductive carbon black, it is easy to be dispersed due to the hydrophilic nature of oxidized carbon and improves the conductivity of applied coating due to the highly conductive, non-oxidized carbon black. As a result of these modifications, a new dispersion showed long-term stability, significantly improved conductivity as an applied coating and excellent compatibility with various acid copper systems.

Dispersant - Since carbon particles are hydrophobic and hard to be dispersed in water, dispersant is added to the dispersion to provide a hydrophilic barrier around the carbon particles. Anionic dispersants are preferred since they promote adhesion of carbon particles to the cationic conditioner on the dielectric surface. Anionic dispersants also generate repulsion between negatively charged carbon particles preventing agglomeration. Various dispersing agents with different chemical properties were tested including phosphate esters, sulfonates and alkoxylated alcohols. The amount of dispersant added to the dispersion is also important and optimized by experiments. When the concentration of dispersant is too low, carbon particles agglomerate and settle down. Excess amount of dispersant forms dielectric barrier between carbon particles, which decreases conductivity in the final coating. This optimization process resulted in improved stability of the dispersion and enhanced conductivity of the dried carbon coating.

Microetch Chemistry

The microetch process removes excess carbon on the copper surfaces by penetrating the carbon coating and etching the copper surface. This lifts the carbon coating from copper surface while giving those surfaces a micro-roughened structure for either copper electroplating or dry film adhesion. Microetch solutions contain oxidizers such as persulphate or peroxide, an acid and other additives. The etch rate varies by the concentration of oxidizer, operating temperature or the concentration of other ions and additives. A desirable microetch system is the one that cleans the copper surface with minimal loss of copper. The cleanliness of inner layer copper in small holes and blind microvias are especially important in high technology PWB manufacturing. Various chemical and mechanical adjustments were made to improve the performance of the microetch. Novel additives were found which clean the copper surfaces effectively at etch rates as low as 10-20 microinches per minute.

Another improvement in the carbon removal process is the use of a brief rinse prior to microetch. Rinsing the circuit board for a short time (10-20 seconds) with water or slightly acidic water will loosen dried carbon particles, which accelerates the cleaning process in the microetch. The rinsing condition is optimized to prevent loss of conductive layer from dielectric surface.

Mechanical Enhancements to Carbon Black Process

As with any metallization system the equipment utilized and the mechanical application of the chemistry will have a dramatic impact on performance. Originally many direct metallization systems were offered as vertical processes. However, the major growth in market penetration for direct metallization systems occurred after many converted to horizontal processing. Horizontal applications are often preferred due to process automation and integration with preceding or subsequent steps. However, in the case of direct metallization the conversion to horizontal processing also resulted in significant enhancements to product performance and technical capability.

The horizontal application of direct metallization offers several benefits:

- Simplifies small hole processing (no requirement for vibration)
- All panels see the exact same conditions (no rack and/or location effects)
- Process integration (capable of integration from deburr, desmear, dry film lamination or panel plate)

These benefits have been a major factor in the growth of direct metallization systems for the past 10 years. However, the technology of printed circuits has changed dramatically over that time. Aspect ratios from 8:1 to 10:1 are common, 10 mil via holes are routine, and the use of microvias and larger blind vias is rapidly growing. These technological challenges have necessitated a re-evaluation of the current state of the art for horizontal direct metallization systems.

For us the challenge was to determine the mechanical enhancements necessary to process this technology using our carbon based direct metallization systems. In particular we noted several areas for improvements:

- High aspect ratio holes in quantity with robust results (eliminate sporadic voids on high density product)
- Carbon residues on difficult configurations (effectively clean small hole posts, microvia capture pads)

We evaluated a number of mechanical enhancements in conjunction with the development of new carbon based dispersions and associated chemistry. Field-testing resulted in several improvements as follows:

- The application of high flow/high volume top/bottom impingement systems (Viahead™)
- Addition of a Predip prior to microetch

The utilization of Viahead™ impingement has several benefits of which the most critical is the enormous improvement in both degree and uniformity of impingement. This ensures the complete application of the chemistry to all types of vias, both blind and through, and small and large. Testing further indicated that these impingement improvements allowed for significant reductions in process contact times.

Carbon based direct metallization systems are post etch systems, meaning that the material that facilitates metallization (in this case carbon) is deposited on all of the product, both dielectric and copper, requiring a subsequent copper etch prior to dry film lamination or panel plating. Current technology utilizes a mixture of conventional spray nozzles for impingement and undercutting of the outerlayer surfaces, and flood impingement for innerlayer posts. Testing indicated that the addition of a short Predip prior to the micro-etch spray section enhanced carbon removal. This facilitated an additional improvement in allowing for decreases in the amount of etch necessary to ensure complete carbon removal.

Reliability Test Results

As a result of both chemical and mechanical enhancements, this newly developed direct metallization PTH process outperformed our previous process and offers equivalent or superior performance to most commercial electroless copper systems. To assess reliability of various PTH processes, we conducted thermal stress tests, IST (interconnect stress tests), and propagation tests.

Thermal Stress Test

The thermal stress test is carried out in the form of solder shock. The 22-layer test vehicle is shown in Figure 2. After the test coupons (40mil holes) were cut out of the finished boards, they were typically baked to dry at 130°C for 2hr. A minimum of 6 times solder shocks were done by repeatedly floating the coupons on the 288°C solder bath for 10 seconds followed by cooling to room temperature.

Coupons from 3 different PTH processes, which are an electroless copper process from a top manufacturer, our traditional carbon-based direct PTH process, and our improved carbon-based direct PTH process, were subject to the solder shock test. The results are shown in Figure 3. Our improved carbon-based direct PTH process had no interconnect defects after six times solder shocks, while our traditional process had 5.8% defects, indicating a better overall carbon removal and cleaning at the posts brought by our microetch chemistry and mechanical enhancements.

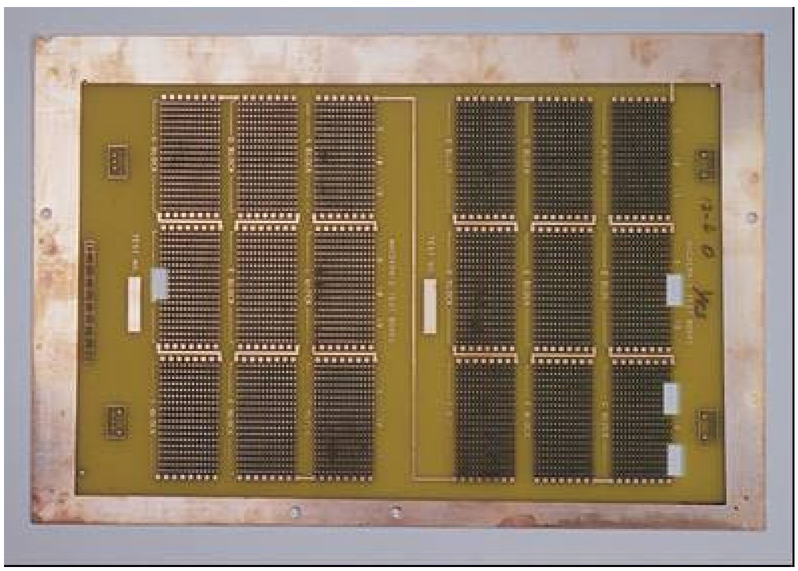

Figure 2 - Test Vehicle Design for Solder Shock Test

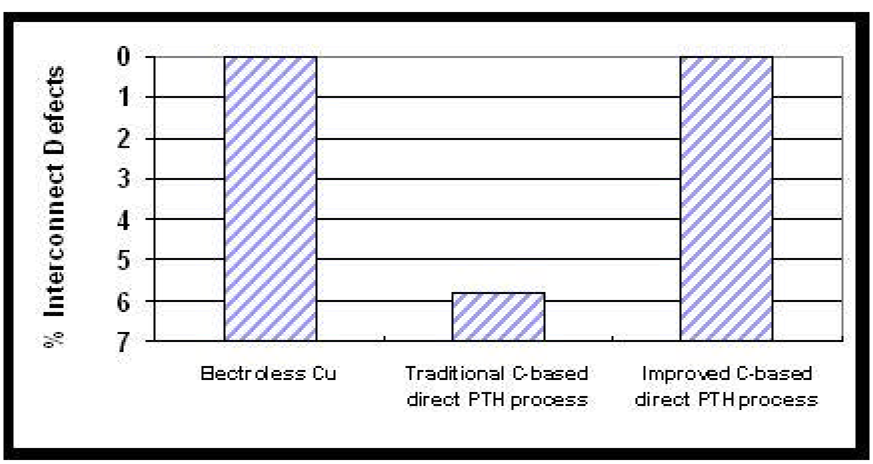

Figure 3 - Solder Shock Results for 3 Different PTH Processes

Interconnect Stress Test (IST)

The IST method is an electrical test method for accessing PTH integrity and detection of post separation. This method uses the copper traces to heat up the test coupon to a desired temperature and cool down to ambient temperature with forced air. The test vehicle used is shown in Figure 4. This 22-layer test board contains 2 designs, GT 4080 and GT 50100. Both designs are generic IST coupons for Through Hole Technology up to .125 inches in thickness. GT 4080 is designed on .040” and .080” grid sizes, while GT 50100 is designed on .050” and .100” grid sizes.

Prior to the IST test, all coupons received three exposures to an assembly simulation profile, i.e. ramped to 230°C three times. For the IST test, the upper temperature was at 150°C. The average IST cycles to fail for two electroless copper and the two C-based direct PTH processes are shown in Figure 5. The Electroless Cu Process I is a popular product used by many PWB fabricators. Electroless Cu Process II is currently under development. All failed for barrel crack except Electroless Cu Process I, which failed for post separation. Under the same testing conditions, our improved C-based direct PTH process demonstrated a reliability that is not only higher than the traditional C-based direct PTH process, but also higher than the commercially available electroless copper process.

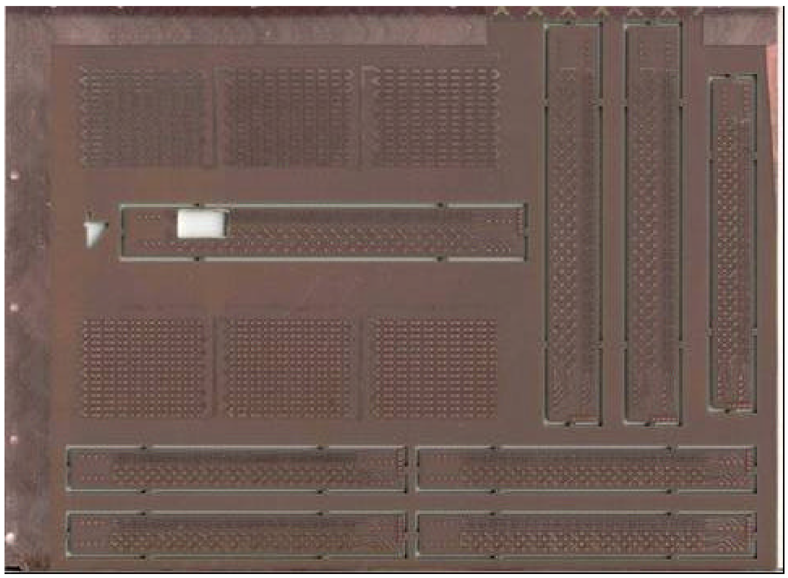

Figure 4 - 22-Layer IST Test Boards with GT4080 and GT50100

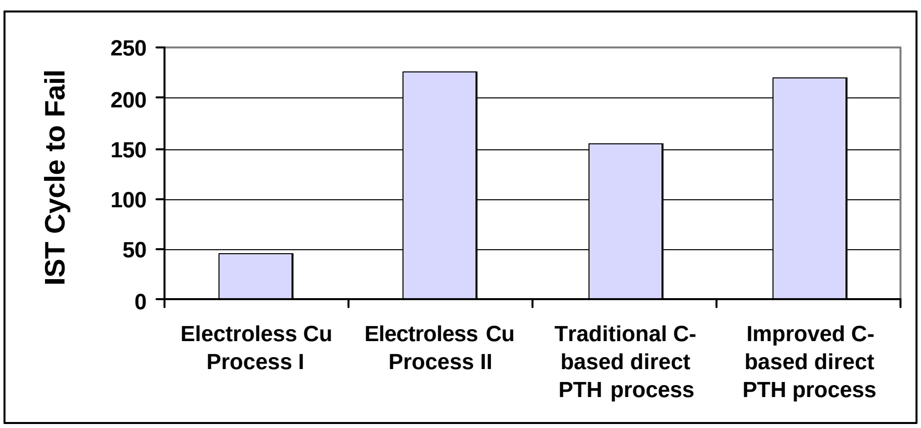

Figure 5 - IST Results Of Different PTH Processes

Propagation Test
This test method was developed to evaluate the conductivity of direct plate. The test panel is shown in Figure 6.

After the hull cell chain panel was plated with carbon black, it was then electroplated in a hull cell at 1A for 10minutes. The two vertical daisy chains were at different current densities, left side at higher current density and right side at lower current density. The series of holes in the middle of the two daisy chains were with different aspect ratios. Figure 7 shows how the panel looked like after plating in a hull cell. The number of holes propagated were then counted and recorded for comparing conductivity.

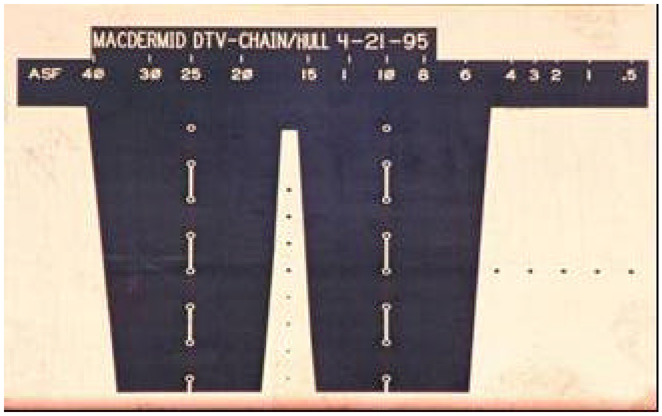

Figure 6 - Hull Cell Chain Panel for Propagation Test (Before Electroplating)

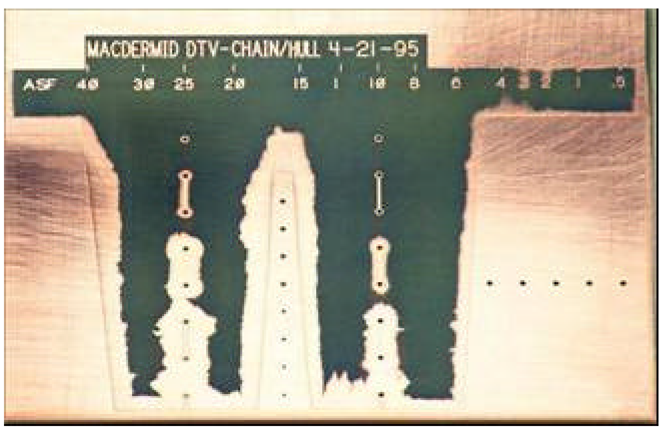

Figure 7 - Hull Cell Chain panel after Electroplating

From the propagation tests, we found that with the enhancements made in our carbon dispersion chemistry, the conductivity has more than doubled compared to the traditional carbon black process. Also, the new dispersion is less sensitive to conditioning and less sensitive to the type of acid copper chemistry.

Conclusion
Carbon-based direct plate processes have overcome the belief that they are inferior in product reliability to electroless copper processes. The data presented in this paper combined with data from numerous production installations shows that carbon-based direct plate processes provide performance and reliability results superior to conventional electroless copper systems. Fabricators and OEMs alike should take note of the unique attributes of carbon-based direct plate processes including horizontal automation, inherently lower manufacturing costs, and a significantly more favorable impact on the environment. All of which support the use of this technology in an extremely competitive market. Chemical enhancements, mechanical enhancements, and product maturity are “bridging the gap” and support the continued growth, desirable use and higher technology capability of these processes in today’s PWB manufacturing environment.