Green Technology for the Plated Through Hole Process

Richard Retallick, Ying (Judy) Ding MacDermid Incorporated. 227 Freight Street, Waterbury, CT USA 06702

Abstract

Electroless copper has long been the dominate process for plated through hole (PTH) metallization. The technology is widely used by printed circuit board fabricators and driven by long standing OEM acceptance. However, this established technology has many drawbacks that have a direct impact on our environment. Namely, it contains a known carcinogen, consumes a lot of water and is inherently unstable leading to increased demands on waste treatment operations. Through the years there has been significant work done in this area of the manufacturing process to overcome the challenges associated with electroless copper technologies. The ultimate goal being an environmentally friendly PTH process that maintains well established performance and reliability standards.

In recent years numerous alternatives to electroless copper PTH processes have emerged, many of which have been used extensively in high production applications. Their reported benefits include some or all of the following: reduction or elimination of hazardous chemicals, reduction in water usage, lower energy requirements, and reduced waste treatment and disposal requirements. These innovative technologies offer the same performance as electroless copper with the added benefits of less cost, less space, reduced labor requirements and a better working environment for the operators. However, among these alternative technologies one may ascertain which one can provide the most environmental benefits. For example, does the simple elimination of electroless copper truly classify an alternative as green?

Introduction

In today's marketplace PWB quality is expected and taken for granted. Until recently the major task for the PWB fabricators was to effect cost reduction programs throughout the manufacturing process in order to remain competitive on a worldwide basis. Recently, the impact of this manufacturing process on the environment has quickly become a significant factor for manufacturers to consider as local governments are demanding the use of cleaner, "greener", and more environmentally compatible processes. Electroless copper technology, a standard in our industry, is still the predominant PTH metallization technology in use today. Yet, this existing technology is plagued with challenges that make it difficult to achieve environmental expectations. To conserve water and energy usage, and more importantly, to protect our environment from further pollution and protect production workers from health risks, it is important for us to establish a more environmentally friendly technology for the plated through hole metallization process by replacing the traditional electroless copper process. Fortunately, long standing, production proven technologies do exist that provide a cleaner and safer environment. These include palladium-based systems which in effect have removed the electroless copper from the PTH process and allow for direct acid copper plating over a Pd catalyzed surface, conductive polymer-based systems, and carbon-based systems which include carbon black, graphite, or combinations thereof. One such novel process, carbon-based, is successfully used at many PTH manufacturing operations. It incorporates horizontal automation, a nondynamic chemistry that contains fewer process steps and much lower and simpler analytical controls. Continued efforts on improving conductivity, copper cleaning, and product reliability have yielded an innovative process for the manufacture of printed circuit boards.

What's out there?

Many chemical suppliers provide production-proven technologies classified as direct metallization. Direct metallization provides for copper plating directly to innerlayers, maximizing the interconnect reliability by eliminating the electroless copper layer as depicted in Figure 1. They processes fall into four main categories: carbon, graphite, conductive polymer, and palladium based systems. Figure 2 provides a general overview of these commercially available technologies in terms of reported advantages and challenges when compared to an electroless copper process.



Figure 1 Direct metallization means copper plating directly to innerlayers

Technology	Major advantages	Major challenges
Carbon	elimination of formaldehyde elimination of chelated copper fewer process steps reduced analytical requirements reduced water usage	Post microetch required to prevent ICDs
Graphite	elimination of formaldehyde elimination of chelated copper fewer process steps reduced analytical requirements reduced water usage	Post microetch required to prevent ICDs Fixer step required to improve adhesion
Conductive	elimination of formaldehyde	short monomer bath life
Polymer	elimination of chelated copper	strict analytical control
	fewer process steps	high temperature solution required
	reduced water usage	controlled rinsing requirements
		strict equipment maintenance required
		minimum hold time
		non-peroxide microetch restriction
Palladium	elimination of formaldehyde	cost of palladium
	fewer process steps	water usage comparable to electroless copper processes
		may require post microetch
		high resistivity
		minimum hold time

Figure 2 Direct Metallization Technologies

The Process Cycle

It is clear to see in Figure 3 that a comparison of process cycle alone shows the dramatic impact a novel alternative PTH process can have when compared to traditional electroless copper technology, namely fewer process steps. Although there are multiple available processes that fall into some of these alternatives they are depicted here into generalized process cycles for comparative purposes.

The most profound and effective characteristic a direct metallization process can have on the environment is the amount of water required to run the process. Water usage and its subsequent treatment is quickly becoming the main driver in alternative PTH technology implementation. For example, the rinsing steps for electroless copper are no fewer than seven whereas in a carbon-based metallization process they can be reduced to three or less than half. This signifies a dramatic decrease in the amount of water required to run the process and the amount of water that needs to enter the waste treatment system.

The number of process steps is also an indicator of the number of chemistries that ultimately require waste treatment. Some chemicals may be discharged directly to waste treatment while others will need to be collected and shipped off-site for disposal or reclamation. These alternative processes to conventional electroless copper have, in practice cut waste treatment requirements in half.

Finally, the number of process steps and the types of chemicals used in the process will not only effect waste treatment but will impact energy consumption as well. Pumps, heaters, and dryers all contribute to the environmental impact a PTH process will have.

Process Steps	Electroless Copper	Palladium	Conductive Polymer	Graphite	Carbon
1	Clean/Condition	Clean/Condition	Microetch	Clean/Condition	Clean/Condition
2	Rinse	Rinse	Rinse	Rinse	Rinse
3	Microetch	Microetch	Clean/Condition	Graphite soln	Carbon soln
4	Rinse	Rinse	Rinse	Fixer soln	Blow off / Dry
5	Predip	Predip	Permanganate	Blow off / Dry	Microetch
6	Activator	Activator	Rinse	Microetch	Rinse
7	Rinse	Rinse	Monomer soln	Rinse	Antitarnish
8	Accelerator	Accelerator	Acidic Fixer	Antitarnish	Rinse
9	Rinse	Rinse	Rinse	Rinse	Dry
10	Electroless Copper	Antitarnish	Antitarnish	Dry	
11	Rinse	Rinse	Rinse		
12	Acid Dip	Dry	Dry		
13	Rinse			-	
14	Antitarnish				
15	Rinse				
16	Dry				

Figure 3 Process Cycle Comparisons

Reduction in Rinse Water

Electroless copper processes use a substantial amount of rinse water and generate a large volume of waste water that must be treated. With upwards of 7 rinse station in a conventional electroless PTH process, PWB manufacturers are facing increasing demands in their waste treatment areas. All four categories of alternative direct metallization processes mentioned above have cut down rinse water requirements compared to the electroless copper process. Palladium process and Conductive Polymer process both have 5 rinse stations, while Graphite process and Carbon Process only have 3 rinse stations. In addition, the uses of automated horizontal equipment by most direct metallization technologies further reduce water usage. Among them, the carbon-based PTH process brought the most significant improvements in reducing rinse water usage and waste water treatment enabled by equipment shown on Figure 4. This horizontal

conveyorized carbon-based process requires less than 1.29gal/ssf, while vertical electroless copper processes can use more than 11.7 gal/ssf of water.

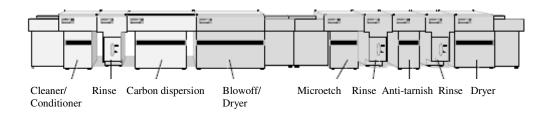


Figure 4 Horizontal Equipment Design

Reduction in Chemistry Usage

The number of process steps in a traditional electroless copper line means more processes requiring waste treatment. In all of the alternative PTH processes the electroless copper bath has been eliminated. When specifically evaluating the consumption of just the electroless copper bath, volumes of 40-50ml of chemistry are typically consumed per surface square foot to provide for an 80µin copper thickness. However, in comparison, a carbon-based process only uses about 2ml per surface square foot. This represents a substantial decrease in the amount of waste entering the treatment process.

Additionally, unlike electroless copper, carbon-based metallization processes do not deplete components selectively, and do not have non-productive side reactions (Figure 5). This indicates the instability of the electroless process ultimately leading to an increased frequency of bath dumps and waste treatment.

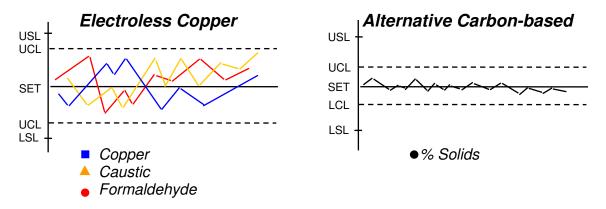


Figure 5 Process stability comparisons

Waste Treatment Reduction

The concentration of the chemicals that may be discharged from industrial facilities is highly regulated by government agencies. Ecological risks of PTH technologies can be evaluated in terms of aquatic toxicity hazards. Copper compounds can result in aquatic toxicity problems if discharged to surface waters. According to a USEPA study, electroless copper process contains eleven chemicals with high toxicity to aquatic organisms, while a carbon-based process only contains two that are easily treatable. Most recently the Chinese government has identified PWB fabricators among their top polluters. A campaign has begun to enforce existing laws and to highly regulate and restrict discharges from PWB fabrication operations. As China is determined to solve its water pollution crisis, complying with a stricter environmental regulation is forcing many PWB fabricators to find ways to reduce and restrict their water discharge.

Alternative PTH metallization technologies simplify wastewater treatment. In the electroless copper bath, chelating agents, such as EDTA, are used to keep metal ions in solution. These chelating agents inhibit precipitation of metals during wastewater treatment and render the treatment more difficult by adding

additional handling steps. Three of the four direct metallization technologies, namely carbon, graphite, and conductive polymer, have eliminated chelating agents, and reduced the need for water treatment chemicals that are used to breakdown chelators. They also provide fewer chemistries that require waste treatment. The environmental friendly chemicals used in the carbon based metallization process make it possible to discharge its components directly into the waste treatment system with no added or extraordinary treatment requirements. This added benefit includes a reduction in costs associated with the waste treatment process.

Reduction in Energy Consumption

As the global demand for energy increases the costs are skyrocketing. Energy costs have become a critical component in the PWB manufacturing process since many of the operations are energy-intensive. Horizontal process automation improves the efficiency of the through hole plating process which inherently leads to a reduction in energy requirements. The carbon-based process uses substantially less energy per ssf of PWB produced. Horizontal automation, low temperature process chemistry and fewer process steps are the crux of this benefit. For example, at a speed of 1.0 meter per minute, a carbon-based process has a throughput of 28.6 panels. Power consumption, including heating and drying, is estimated to be 37.9KW. To process 200 panel square meters per day, the equipment is required to operate for 7 hours. Therefore, total power used would be 265.3KW hours. For the same output, a high build electroless copper needs to operate for 20 hours per day at 54 KW power requirement, which comes out to be 1080KW hours. The power saved by this technology is a whopping 75%!

Minimize Worker Health Risks

be negligible.

Aside from the consumption and treatment of valuable resources there is also the human exposure impact to be considered. Non-conveyorized electroless copper processes expose workers to chemicals by breathing air containing vapor or aerosols from the process lines. Formaldehyde is one such hazardous chemical associated with electroless copper baths. In the non-conveyorized electroless copper process, inhalation of formaldehyde, an irritant and a probable human carcinogen, may present a cancer risk. In contrast, alternative PTH technologies characterized by their choice of chemicals and their applied equipment sets improve the workplace environment. These enclosed conveyorized process lines have extraction systems which vent all fumes away from the workplace as shown in Figure 6. In practice, the inhalation exposure to even the most innocuous chemicals associated with the carbon process is assumed to



Figure 6 Enclosed conveyorized process line

High Performance Reliability and Capability

It is fair to say that many of the commercially available PTH alternatives meet long established performance standards set by electroless copper technology. All of these processes are used by manufacturers and provide benefits and reliability that allow for their continued use. Close to twenty years of experience and a thorough knowledge of operation and technical expertise by both suppliers and PWB manufacturers have helped to promote the carbon-based process to a mature status. Continuous

improvement of this technology continues to drive this process beyond standards that can be achieved with electroless copper. The reliability of a carbon direct plate process has been tested according to various industry standards with typical results shown in Figure 7. Carbon-based product reliability has proven to be not only equivalent but also superior to electroless copper in many ways including IST performance depicted in Figure 8. This process enables a uniform electrolytic coating and an intimate copper to copper bond for the highest reliability interconnects as depicted in Figure 9. Additionally, the carbon-based process has production-proven capability on a wider variety of substrates, including alkaline sensitive laminates, where electroless copper technologies have failed.

Test	Test Method	Qualifier	Cycles	Results
Solder Dip	IPC-TM-650	2.6.8	6	Passed
Thermal Shock	IPC-TM-650	2.6.6	400	Passed
Solder Rework	IPC-TM-650	2.4.36	5	Passed
Interconnect Stress Test	IPC-TM-650	2.6.26	500	Passed

Figure 7 Typical Reliability Test Results

IST CYCLES TO FAILURE

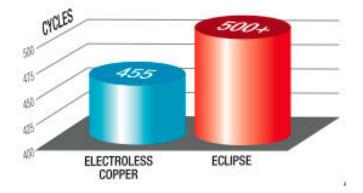


Figure 8 IST cycles to failure

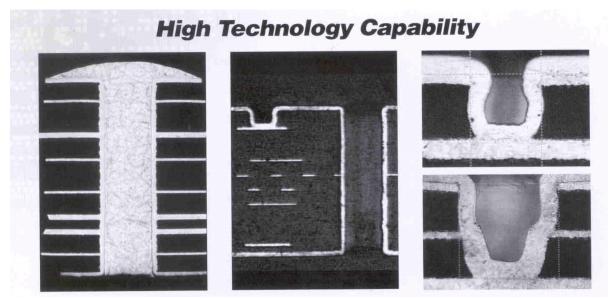


Figure 9 Cross sections of typical process capability

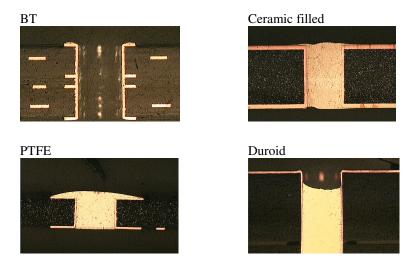


Figure 10 Wide substrate compatibility

Conclusion

Alternative PTH technologies to conventional electroless copper have always appealed to two market needs, reduced cost or improved environment. Today however, these two demands have merged. All of the benefits associated with costs reduction are the same as those associated with environmental impact and vice versa. These environmental benefits can and will have a significant impact on how PWBs are manufactured. More and more countries are becoming increasingly aware of and questioning the impact manufacturing processes can have on their environment. Rinse water reduction, choice and number of chemicals used, simplified waste treatment, reduction in energy requirements, and an improved workplace environment by minimizing worker exposure to harmful chemicals all make the carbon-based technology one of the 'greenest' PTH process alternatives that can provide an immediate answer to environmental concerns.

References

- [1] C.F. Coombs, Printed Circuits Handbook, Sixth Edition, pp. 30.1-30.11.
- [2] Alternative Technologies for Making Holes Conductive, US EPA Doc. EPA 744-R-98-002, Sept. 1998.
- [3] Direct Metallization Report, City of San Jose.
- [4] C. C. Wan, Proc. Natl. Sci. Counc. ROC(A) Vol. 23, No. 3, 1999, pp. 365-368.
- [5] EnvisionTM DMS-E Maximum Reliability in Direct Plating, Retrieved March 31, 2008, from <u>http://www.galvanord.dk/DMSE-presentation.PDF</u>
- [6] M. Carano, Metallization of High Performance Resin Materials with a Graphite-based Direct Plating System, Retrieved March 31, 2008, from <u>http://pcdandf.com/cms/content/view/3415/95/</u>
- [7] Official policies and regulations from the Chinese Government, Retrieved March 31, 2008, from <u>http://www.cpca.org.cn/admin1/webedit/uploadfile/200789161621688.DOC,</u> http://www.cpca.org.cn/admin1/webedit/uploadfile/2007716141057520.DOC