Reliable Acid Copper Plating for Metallization of PCB

Maria Nikolova, Senior Research Fellow, Jim Watkowski, Director Metallization Technology, Don DeSalvo, Application Manager for Metallization, and Ron Blake, Application Engineer
MacDermid Inc, Electronics Solutions
227 Freight Street
Waterbury, CT

Abstract
Copper plating is widely used in the electronic industry for fabrication of electronic devices. It is particularly explored for fabrication of printed circuit boards and semiconductors. Copper is electroplated over the surface of a printed circuit board and onto the walls of the through holes. The mass PCB production requires intensification of and at the same time simplifying the metallization process without scarifying and even further more improving the reliability. Various approaches have been studied in order to plate high aspect ratio (AR) through holes with improved micro-distribution and improved mechanical properties of the plated copper such as Tensile Strength and Elongation. Direct current acid copper PTH (plating through holes) at low current densities as well as PPR plating for high AR (>12) were explored. The parameters of a new high throw acid copper plating process are described in this paper. The mechanical properties and the thermal characteristics of the plated copper are presented. The results from the throwing power measurements are provided.
High temperature acid copper process has been also studied. For large number of PCB fabrication facilities in the areas with hotter climate plating at elevated temperature presents difficulties. Reduced brightness, increased grain size, and increased roughness lead to a decrease in the reliability performance. A new process for plating smooth, bright, and planar copper layers at temperatures up to 40^{o}C is described. Tensile strength and elongation measurements as well as the thermal characteristics of copper layers deposited at room temperature and at elevated temperatures are given.

Introduction
Copper plating is widely used in the electronic industry for manufacturing of electronic devices. It is particularly explored for fabrication of printed circuit boards, PCBs and semiconductors. During circuit fabrication, copper is electroplated over selected portions of the surface of the printed circuit board and onto the walls of through holes passing between the surfaces of the circuit board base material. The walls of the through holes are metallized to provide conductivity between the circuit layers of the printed circuit board. The conductive pathway should be of a uniform plating thickness. Thus in many printed circuit board and semiconductor fabrication processes, electroplating has been adopted by industry as the primary deposition means for copper metallization. [1-2].
The tendency for portability along with increased functionality of the electronic devices has driven the miniaturization of PCBs. The mass PCBs production requires intensification of and at the same time simplifying the metallization process without scarifying and even further more improving the reliability. A challenge exists for fabrication of reliable PCBs.
It is mostly desirable to obtain a good throwing power in electrodeposition processes. Particularly in the through hole plating of PCBs a uniform distribution of deposited copper is demanded. In general, copper plating processes that provide better leveling of the deposit across the substrate surface and inside the through holes tend to worsen the throwing power of the electroplating bath. Plating through holes, PTH with various aspect ratios, including high AR presents challenge for the PCB manufactures. High throwing power electrolytes are becoming increasingly important, due to the electronic industry requirements of manufacturing high aspect ratio circuit boards.
In this paper a Hi Throw acid copper plating process with various plating parameters was studied in order to plate through holes with improved micro-distribution and improved mechanical properties of the plated metal such as tensile strength and elongation. The structure of the deposits was examined. The thermal characteristics of plated copper meet the IPC standards and ensure that no failure occurs during the subsequent soldering operations.

A high temperature acid copper process has also been explored. Because the copper plating electrolytes are designed for use at room temperature, they are not generally suited for plating through holes at elevated temperatures. Reduced brightness, increased grain size, and increased roughness lead to a decrease in the reliability performance.
Printed circuit board fabrication has dramatically increased over the past few years in geographic areas with hotter climates. In order to maintain the desired temperature in these areas, chillers or other cooling means are needed. Thus, it is desirable to simplify the process in these areas, to eliminate the need for chillers or other cooling means and still obtain a desired plating deposit. A new direct current process for plating smooth, bright, and planar copper layers at temperatures up to 40°C is described in this paper.

High Throw Acid Copper Plating Process

A typical copper plating solution contains copper sulfate, sulfuric acid, chloride ions, and organic additives that control the deposition process and the quality of the plated coatings [3-6]. The throwing power of an electroplating bath depends on solution conductivity, electrodeposition kinetics (the slope of the polarization curve), cell geometry, and temperature. The purpose of this work was to determine the effect of various organic additive species and their concentration on the throwing power. The effect of the basic solution composition was also studied. A series of copper electroplating solutions were evaluated.

Test Vehicles

Throwing Power Test Vehicle

The test vehicles that were used in the process evaluation were 1.6 mm and 3.2 mm thick boards with various sized through holes. The through holes diameters for 1.6 mm boards were 0.2mm, 0.25mm, 0.35mm, and 0.5mm. The through holes diameters for 3.2 mm boards were 0.2mm, 0.25mm, 0.35mm and 0.5mm, and 0.8 mm. The through holes AR varied from 3.2 to 16. All the geometries incorporated in the test vehicles were simultaneously plated.

Microdistribution

The Microdistribution is defined as the ratio of the deposit copper thickness in the center of the through hole to its thickness at the surface. It is calculated according to the equation:

$$\text{Microdistribution in \%} = \frac{(C+D)*100/2}{(A+B+E+F)/4}$$

Figure 1 shows a cross section of a through hole indicating the points of thickness measurements.

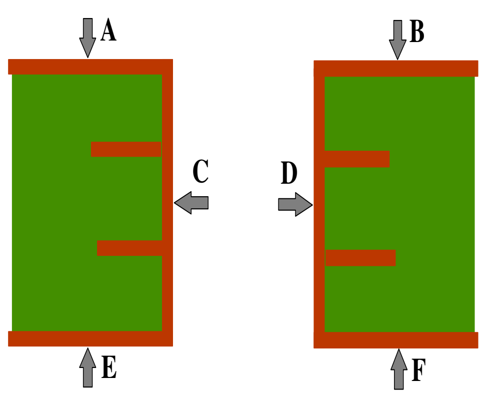


Figure 1 – Cross Section of Plated Panel

Bath constituents

The optimized bath constituents and the plating parameters are given in Table 1. The best results were achieved with a low copper, high acid concentration solution. Plating at low current densities allowed us to reliably plate higher AR through holes.

Table 1 – High Throw Process Parameters

Component	Target	Range
$CuSO_4x5H_2O$	50 g/l	45 – 80 g/l
Sulfuric Acid	250 g/l	220 – 300 g/l
Chloride	75ppm	60ppm – 85ppm
Wetter	10 ml/l	8 - 15 ml/l
Brightener	4 ml/l	2 – 6 ml/l
Temperature	22°C	20 – 24°C
Current Density	1.0 ASD	0.5 – 3.0 ASD

Results from Microdistribution Measurements

The measured microdistribution values for the current density tested are shown on Figures 2 and 3. An excellent micro-distribution was achieved. Depending on the board design an appropriate current density and plating time could be chosen to achieve the required copper thickness on the through hole walls.

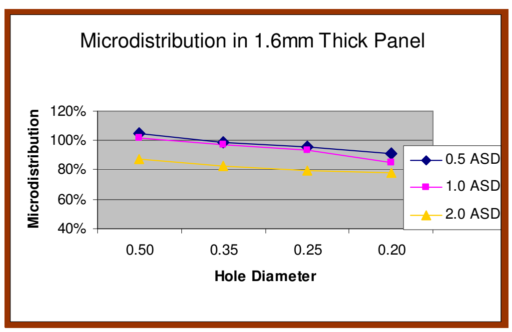


Figure 2 – Microdistribution for 1.6mm Thick Panel

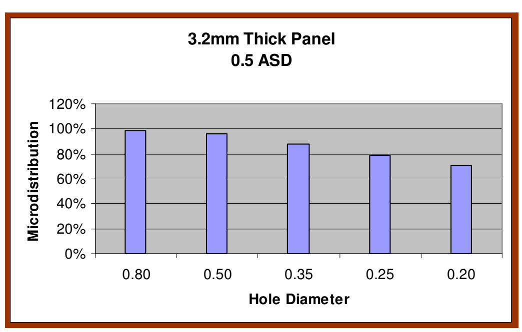
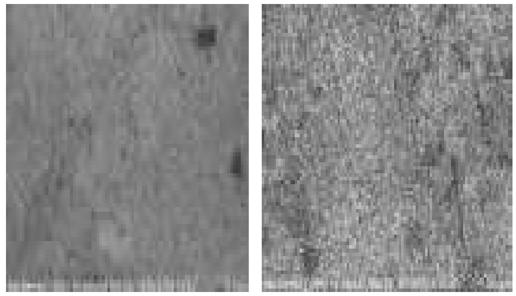


Figure 3 – Microdistribution for 3.2 mm Thick Panel

Process Features

Structure, Surface Appearance

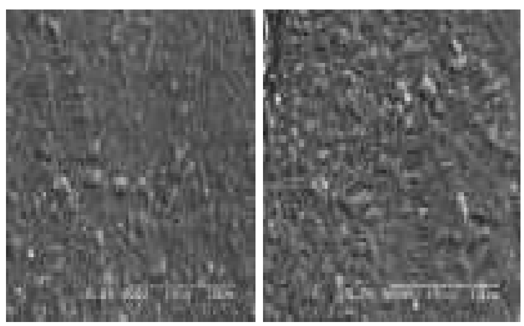
Bright leveled deposits were plated from this electrolyte. SEM pictures were taken from copper surface before and after etching to examine the surface morphology. Figure 4 shows copper deposited on the surface of the panel from a perpendicular view. It reveals small equiaxial grain size structure. No particular texture was determined.



(a) 5000x (b)

Figure 4 - SEM of (a) Board surface (b) Board Surface after Etching

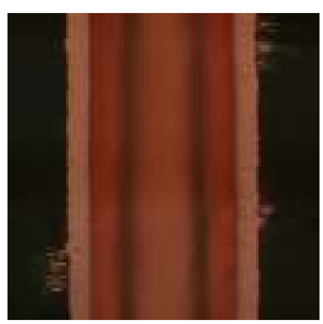
SEM pictures were taken from cross sections of the panel surface (higher current density) and from the inside of the through holes (lower current density). An etch solution was used to expose the crystal structure of the deposit. Pictures of the cross sections are shown in Figure 5. They show a uniform grain orientation. Small grain structure is observed.



(a) 5000x (b)

Figure 5 - SEM Cross Sections of 1.6mm Panel Plated at 0.5 ASD (a) Surface (b) 0.35mm Through Holes

Copper plated inside the through hole on the through hole walls was smooth and leveled. Figures 6 and 7 show pictures of cross sections from boards plated under various plating conditions.



500x

Figure 6 - Cross section of 0.2mmThrough Hole in 3.2mm Panel Plated at 0.5 ASD

1000x

Figure 7 - Cross section of 0.2mmThrough Hole in 1.6 mm Panel Plated at 1.0 ASD

Properties of Plated Copper Coatings

Tensile Strength and Elongation

Tensile Strength and Elongation of plated copper were measured in accordance with IPC TM-650, 2.4.18.1. Vertical and horizontal pulls were measured. The results from the Tensile Strength evaluation are given in Figures 8. Increasing plating over-potential increases the nucleation rate and leads to formation of deposits with higher Tensile Strength. This is shown in Figure 8: increasing the deposition CDs from 0.5 ASD up to 2.0 ASD increases the values of the Tensile Strength measured. The Elongation was up to 19%. Plating at all conditions met or exceeded IPC specifications.

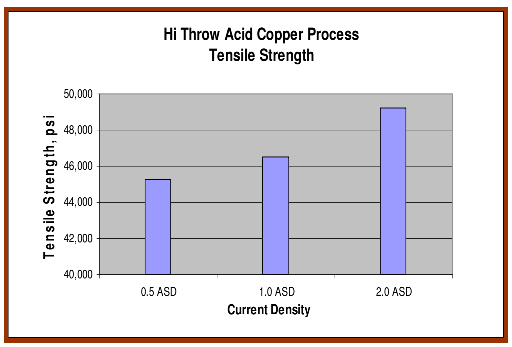


Figure 8 - Tensile Strength versus Current Density

Through-Hole Reliability

Solder shock resistance testing per IPC TM-650 2.6.8 was used to study the thermal characteristics of plated boards. Solder shock conditions were 10 second float at 288ºC for 6 times. Tests were performed for copper foils plated at 0.5, 1.0 and 2.0 ASD. The thermal integrity was excellent for all of the through hole sizes plated. Neither corner cracks nor barrel cracks were observed as shown in Figure 9 across the current densities range studied.

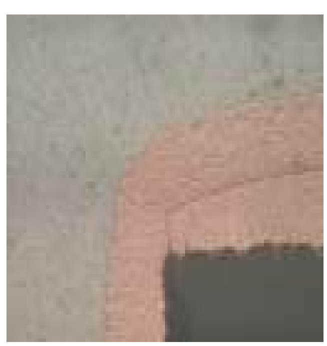


Figure 9 – Hi Throw DC Process, Plating at 1.0 ASD; Cross Section of 0.5 mm through hole after 6x Solder Shock

Summary

A Hi Throw acid copper process was developed for reliably plating of various aspect ratios through holes with an excellent microdistribution. Direct Current mode was used. Plating at low current densities was explored in order to plate higher aspect ratio through holes with the desired microdstribution. Bright, smooth copper was deposited. Good leveling was achieved inside the through holes and on the board surface. Plated copper deposits met or exceeded industry standards for Tensile strength, Elongation and Solder shock resistance.

High Temperature Acid Copper Process

Significant printed circuit board fabrication has migrated to areas of hotter climate. A DC acid copper process for tropical use without cooling was formulated. It was developed in order to meet the requirements for high volume rigid PWB production. The plating bath contains organic additives that are stable at elevated temperatures thus allowing for utilizing the process within the temperature range 22^{o}C - 40^{o}C. The plating parameters are shown in Table 2.

Table 2 – High Temperature Process Parameters

Component	***Target***	***Range***
$CuSO_4x5H_2O$	75 g/l	65 – 85 g/l
Sulfuric Acid	200 g/l	190 – 220 g/l
Chloride	75ppm	60 – 90ppm
HT 100 Make up	8 ml/l	6 – 10 ml/l
HT 100 Wetter	Dosing during the plating	
HT 100 Brightener	0.8 ml/l	0.6 – 1 ml/l
Temperature		22 – 40^{o}C
Current Density	2.0 – 2.5 ASD	1.0 – 4.0 ASD

Process Features

Fine grained deposits were obtained from this electrolyte up to 40^{o}C. Plated copper was smooth and leveled inside the through hole. No thin copper at the knee of the holes was observed. No plating folds and no thin areas inside the hole were measured. Plating thickness was consistent throughout the barrel of the hole.

Microdistribution

Good microdistribution values were measured across a wide current density range, 1.0 ASD - 3.0 ASD, as shown on Figures 10 and 11. Bath performance was consistent for the temperature range studied.

.

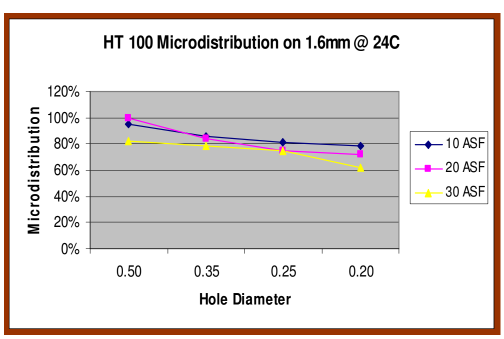


Figure 10 – Microdistribution for 1.6mm Thick Panel Plated 24^{o}C

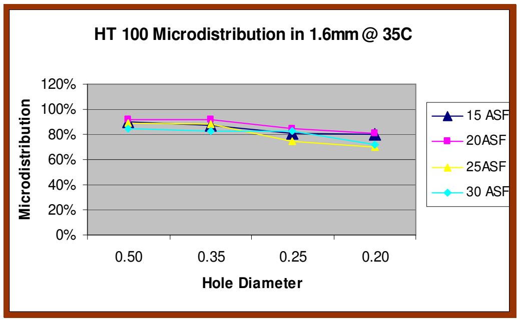


Figure 11 – Microdistribution for 1.6mm Thick Panel Plated 35°C

Properties

Tensile Strength and Elongation

Tensile strength more than 40,000 psi and Elongation in the range 17% - 22% were measured for copper plated from HT 100 bath at various temperatures and various current densities. CD's tested were 1.0, 2.0, and 3.0 ASD. Temperature was 24°C and 35°C. Increasing CD and lowering plating temperatures increases tensile strength. Decreasing CD and increasing plating temperatures increases elongation.

Thermal characteristics

For through hole reliability, sections were taken and solder floated 6 times at 288°C. The holes were examined for any defects. No cracks or starter cracks were present, Figure 12.

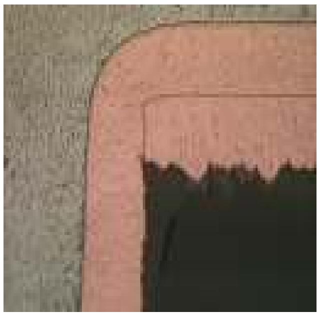


Figure 12 – HT Process, Plating at 35°C, 2.0 ASD; Cross Section of 0.5 mm through hole after 6x Solder Shock

Equipment and Control

Air and no air solution agitation were studied. Euductor nozzles were used. There was no difference in either the appearance or in the properties of the plated copper between air agitation and the eductor nozzles.
The electrolyte was easy to maintain. The organic additives, the wetter and the brightener were CVS analyzable. Hull cell tests could be used to control the process. The additive consumption changed insignificantly with the temperature change.

Summary

A new DC process was formulated for high volume rigid PWB production. The process yield consistent results over a wide temperature range up to 40ºC. Bright, leveled copper deposits were obtained. Plated copper has excellent physical mechanical properties that meet the IPC standards. The process could be used with air or with eductors nozzles in pattern or panel plate mode allowing for greater flexibility. It is CVS analyzable or Hull cell controllable.

References

1. Clyde F. Coombs Jr., *Printed Circuit Handbook*, Fifth edition, New York (2001).

2. Dubin, V.M., "Copper Plating Techniques for ULSI Metallization," Advanced Metallization and Interconnect Systems for ULSI Application in 1997: Materials Research Society Symposium Proceedings, (Jan. 1998) 405-411, Materials Research Society, Warrendale.
3. Yung, Edward K., "Plating of Copper into Through-Holes and Vias," J. Electrochem. Soc., 136 (1989) 206-215
4. J.J. Kelly, C. Tian, A.C. West, J. Electrochem. Soc., 146 (1999) 2540
5. J. Horkans, J.O. Dukovic, in: P.C. Andricacos, J.L. Stickney, P.C. Searson, C. Reidsema-Simson, G.M. Olezek (Eds.), ECS Proceedings on Electrochemical Processing in ULSI Fabrication III, vol. 8, 2000, p.103.
6. J.P. Healy, D. Pletcher, M. Goodenouth , J. Electroanal. Chem., 338 (1992) 179.