INNOVATVE ACID COPPER PROCESS FOR SIMULTANEOUSLY FILLING VIAS AND PLATING THROUGH HOLES

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ABSTRACT
This paper relates to copper plating processes in the manufacturing of printed circuit boards, IC substrates, and semiconducting devices for electronic applications. The innovative plating process is particularly useful for filling recessed structures with copper, such as vias and plating of through holes.
The increased demand for electronic devices in recent years has led to an extensive research in the field to meet the requirements of the industry. Aqueous acid plating baths for electrolytic deposition of copper have been very important in the manufacturing of PCB and IC substrates where fine structures like blind micro vias (BMV), trenches, through holes (TH), and pillar bumps need to be filled or build up with copper. The complex circuit board designs require simultaneously filling of via structures and plating TH. This is highly challenging since the commonly used electrolytes for filling vias are not suitable for plating of the through holes and vice versa. The requirements include filling BMV, while depositing no more than 18 - 20 µm of copper onto the planar substrate areas, dimple no more than 10 µm, and micro-distribution for the plated TH => 75 - 80%.
The described DC acid copper plating process is designed for simultaneously filling blind micro-vias and plating through holes across a variety of geometries in a variety of equipment applications with insoluble anodes, including vertical continuous plating equipment, VCP. The bath produces a bright, fine grained, ductile deposit. The thermal and physical mechanical properties of the copper deposits are excellent. Tensile strength => 42,000 psi and elongation > 20 % had been measured for deposits plated in a fresh and in an aged bath. The organic additive ranges have been optimized. All bath components are CVS analyzable and the electrolyte has an extremely long life.

Key words:
copper electroplating, via fill, through hole plating, metallization

INTRODUCTION
Copper is the most preferable metal used in electronic industry due to its electrical and thermal conductivity properties and the possibility of electroplating. The acid copper plating process is widely used in the mass production. It is utilized in the fabrication of printed circuit (PCB) boards and semiconductors [1, 3]. The increased demand for electronic devices in recent years has led to an extensive research in the field to meet the requirements of the industry. Aqueous sulfuric acid baths for electrolytic deposition of copper have been very important in the manufacturing of PCB and IC substrates where fine structures like blind micro vias (BMV), trenches, through holes (TH), and pillar bumps need to be filled or build up with copper [4-6]. As circuit miniaturization continues, developing of a process that simultaneously fill vias and plate TH with various sizes and aspect ratios, while minimizing the surface copper thickness is critical.
The highly challenging requirements of the complex printed circuit board designs are to be met. Filling BMV and PTH at the same time, presents great difficulties for the PCB manufactures. The conventional copper filling technologies are not capable of filling BMV and PTH in the same electrolyte due to the reliability problems.
Organic additives are usually present in a copper electroplating bath during the production of PCBs, chip carriers, and semiconductors [2-3]. They act as accelerators (brighteners) and suppressors (wetter and levelers) enabling a uniform deposition of copper on different regions of the PCB including through holes and BMVs. In general, copper plating processes that provide good via fill and leveling of the deposit tend to worsen the throwing power of the electroplating bath.
The purpose of this work was to develop a new process in respond to the continuously increasing electronics industry need of a copper plating technique capable of simultaneously via filling and through hole plating.
The factor that affect process performance are shown. The effect of the organic compounds on the via filling characteristics and TH micro-distribution have been studied. Various plating parameters were applied to achieve a good via fill across a wide range of via sizes and an improved micro-distribution of the through holes. The optimum conditions of the DC process such as current density (CD), solution agitation, educator usage, flow rates, etc. for filling up the vias and simultaneously plating though holes were determined. Direct electroplating on black holes were included in the tests.
The mechanical properties such as tensile strength and elongation, thermal characteristics and structure of the deposits were also examined.
It is shown that a highly reliable copper metallization can be achieved utilizing the innovative DC copper plating technique.

ACID COPPER PLATING PROCESS

The sulfuric acid copper electroplating baths contain copper sulfate, sulfuric acid, chloride ions, and organic additives such as brighteners (grain refiners), suppressors, and leveling agents [7-12]. The Wetter (suppressors, high molecular weight polyether compounds and polyoxyalkylene glycols) in the presence of chloride ion has a polarizing influence. Brighteners (sulfopropyl sulfides, etc.) have a depolarization effect, accelerating the deposition process. The brightener compounds are smaller molecules than the wetter molecules and act as grain refiners. Leveler adsorbs preferentially near the most negatively charged sites of the cathode, thus slowing down the plating rate at high current density areas. The organic additives affect the secondary and tertiary current distribution. They control the deposition process and the quality of the metal deposits.
In this study a low organic additive system was combined with a high copper to free acid ratio electrolyte.

TEST VEHICLES

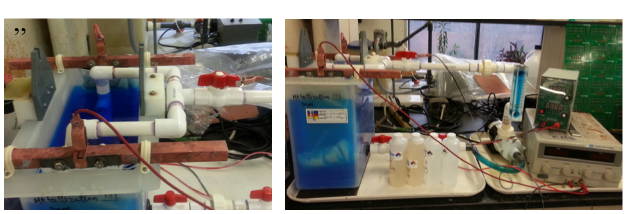
The test vehicles used in the process evaluation were 0.8 mm and 0.4 mm thick boards with various sized BMVs and through hole diameters. On one side: vias 75 microns deep; via diameters 75, 100, 125, and 150 microns and on the other side: vias 100 microns deep, via diameters 100, 125, 150, and 175 microns; glass re-enforced dielectric. The through hole diameters were 0.15, 0.20, 025, and 0.30 mm. All via and through hole geometries incorporated in the test vehicles were plated simultaneously.

Process Flow and Plating Equipment

The process flow includes the following operations:

- Acid cleaner: Wets the hole and removes contaminations;
- Rinse;
- Micro-etch: Etches remaining debris and ensures good copper to copper adhesion.
- Rinse;
- Acid dip: Acidifies copper surface prior to plating.
- Plating in acid copper bath MacuSpec VF-TH 200

Plating equipment:
Tests were run in 12liter plating bath and in 200liter pilot lab. tank. Agitation: side eductors, anodes: insoluble, DC rectifier. Current Densities used: 10, 15, 20, 25, and 30 ASF.



Anode to cathode distance: 5.0 inches (12.7 cm)
Eductor to cathode distance: 2.5 inches (6.35 cm)
3 educator nozzles vertically each side

Figure 1. 12 liters plating cell.

MEASUREMET STANDARDS

Via Fill

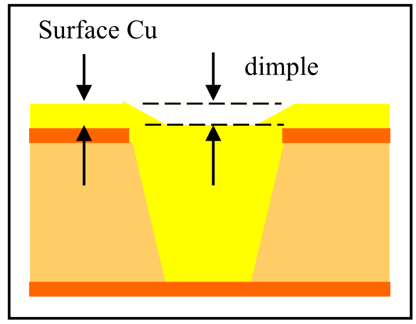


Figure 2. BMV

Figure 2. shows a cross section of a BMV.

Through Hole Plating

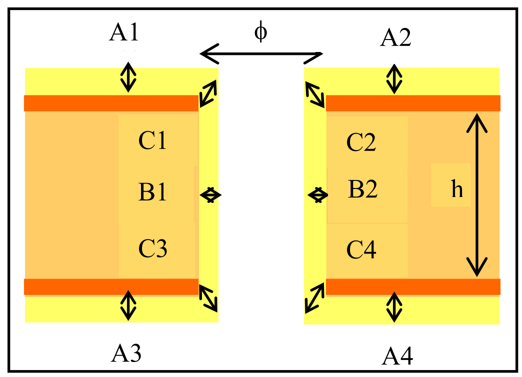


Figure 3. Through Hole

The points of thickness measurements in a cross section of a through hole are indicated in Figure 3.

$$TP_{min} = \frac{Avg.\ (B1\sim B2)}{Avg.\ (A1\sim A4)} \qquad TP_{knee} = \frac{Avg.\ (C1\sim C4)}{Avg.\ (A1\sim A4)}$$

Throwing Power minimum, TP_{min} (micro-distribution) is defined as the ratio of the deposit copper thickness in the center of the through hole to its thickness at the surface. TP_{knee} is the ratio of the deposit copper thickness at the hole corners to its thickness at the surface.

Industry Requirements:

- Surface copper thickness: 18 - 20 microns
- Via fill:
  - dimple =< 10 microns for the small diameter vias: 3x3, 4x3, 5x3, and 4x4 mils;
  - dimple =< 25 microns for the larger diameter vias
  - no voids (cavities)
- TH: no "slope" on the surface around TH

  TP_{min} = >75% TP_{knee} = >75%
- Surface appearance: bright, smooth, uniform.

BATH COOMPOSITION

The bath constituents and the plating parameters are given in Tables 1.

The process can be used at varying basic electrolyte (VMS) compositions to optimize performance.

Table 1. Bath Constituents

COMPONENT	MacuSpec VF-HT 200 Target	MacuSpec VF-HT 200 Range
$CuSO_4x5H_2O$	250 g/l	220 – 250 g/l
Sulfuric Acid	50 g/l	40 – 70 g/l
Chloride	50ppm	45ppm – 55ppm
Wetter	20 ml/l	18 - 22 ml/l
Brightener	2.0 ml/l	1.5 – 2.5 ml/l
Leveler	12.5 ml/l	10.5 – 14.5 ml/l
Temperature	71 – 75 F (22 - 24°C)	68 – 77 F (20 – 25°C)
Current Density	10 ASF – 30 ASF (1.1 ASD – 3.2 ASD)	

Diffusion of Cu^{2+} is the rate limiting step in copper deposition process. Sulfuric acid and Cu^{2+} concentration in the basic electrolyte (VMS) are critical for achieving certain type of deposition. A high copper bath allows for applying higher CDs without "burning", due to the increase of the limiting current density. Such a bath is favorable for filling the vias. On the other hand, a high TP $_{min}$ is typically achieved in low copper, high acid electrolytes. Organic additives play an important role in the plating process, changing the current distribution over the cathode surface, mass transfer, filling small features, etc. The innovative copper process described in this paper uses proper organic species chosen by carefully selection that made possible simultaneously filling vias and achieving a very good throwing power in a high copper, low acid VMS.

RESULTS

Via Fill

Important characteristics of copper plating process are the via dimple depth and the surface copper thickness. Small or none dimple and as minimum as possible surface copper thickness are desired, especially in case of stuck via designs or if planarization is not applicable. The larger via size, (the diameter and the depth), more difficult is to fill it up while keeping a low surface copper thickness. Cavities inside the filled vias are not desirable because they negatively affect the reliability.

Plating results show that an excellent via fill for various diameters vias can be achieve using the innovative process. Figure 4 demonstrates a typical via fill result for a plating in 12 L bath. It was performed at 20 ASF for 60 minutes, flow rate: 2.4 LPM, eductors: 3 nozzles/side (total 6 nozzles), 0.4L/min per nozzle; various via sizes.

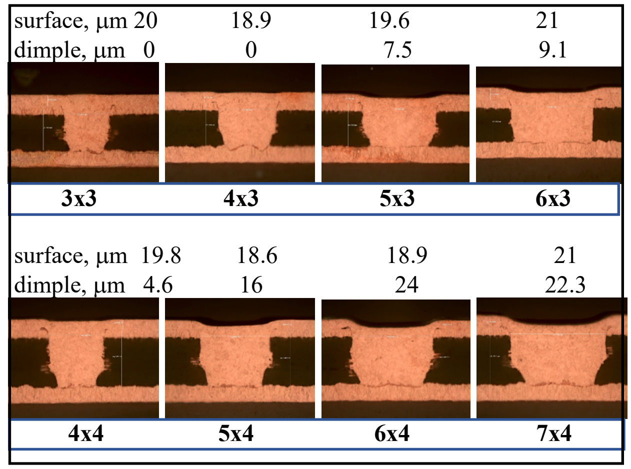


Figure 4. Cross sections of various diameter vias sizes, 3 and 4 mils deep (75 and 100 microns deep).

Figure 5 shows the filling of shallower vias, depth 50 – 60 microns, diameter 100 and 120 microns. The surface copper is 18 microns and the dimple is < 10 microns.

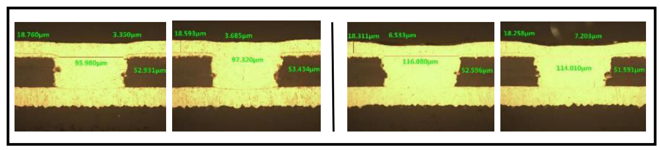


Figure 5. Cross sections of 50 microns deep vias, diameters: 100 and 120 microns.

The surface copper thickness and the dimple depth met the requirements. No voids were observed for any size vias by utilizing the described process.

TH Plating

The through holes were plated simultaneously with the vias. Figure 6 presents the measured values for TP $_{min}$ and TP $_{knee}$ for a 0.25 mm diameter hole in 0.8 mm panel.

Hole	A1	A2	B1	B2	A3	A4	Surface	TH	TP min
250µ	19,8	18.3	19.7	18	21	21	20.03	18.85	94.1

TP knee = 84.8%

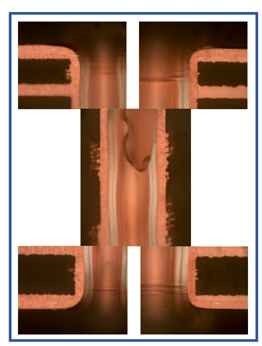


Figure 6. TP $_{min}$, TP $_{knee}$ and cross section pictures of a 0.25 mm TH.

The higher the through hole aspect ratio (AR), the less copper is plated on hole walls, inside the barrel, the lower the TP min is. The organic additives strongly affect the polarization characteristics of an electroplating solution, determining its throwing power and the through hole corner plating. The results for a plating in a pilot lab. 200liter tank are given in Figures 7 and 8. The solution flow rate was 0.2 L/min per nozzle (0.1 bar). TP min and TP knee were measured for different size through holes. Cross section pictures of 0.15 mm, 0.20 mm, 0.25 mm, and 0.30 mm through holes, 0.8 mm thick board are shown. No thin corners were observed and the surface copper thickness was uniform on the cathode surface around the through hole opening (no “slop”).

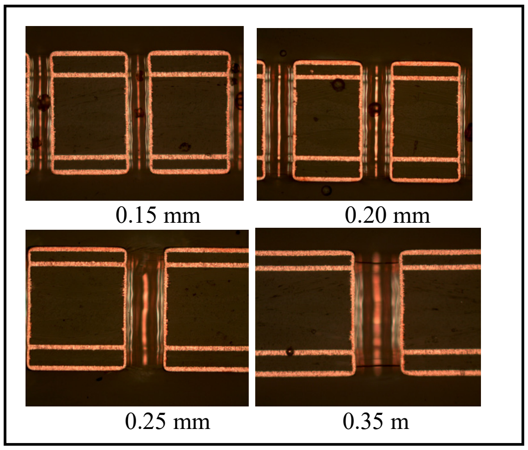


Figure 7. Cross sections of plated through holes; hole dimeters 0.15, 0,20, 25, and 0.30 mm.

TP min and TP knee measured are presented in Figure 7.

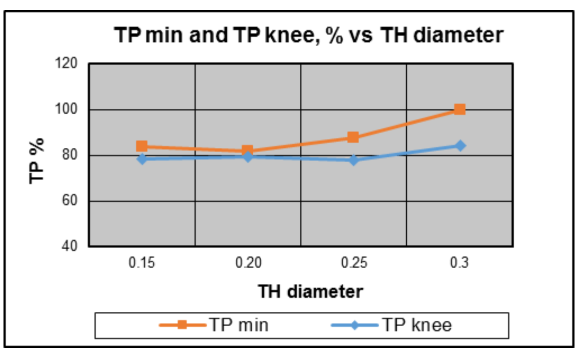


Figure 8. TP min and TP knee for various TH sizes.

Table 2. Via Fill measurements

Via	surface	dimple	Via	surface	dimple
3x3	19.8	3.7	**4x4**	19.6	11.7
4x3	20.3	4.6	**5x4**	21.8	17.1
5x3	18.6	7.9	**6x4**	18.7	23.8
6x3	20.0	15.8			

For all through hole sizes, the measured values met or exceeded the requirements. TP min was => 75% and TP knee was => 75%. Via fill measurements for the same plating in 200liter bath were within the required limits, Table 2.

Direct Plate

Plating on Direct Metallization was also included in the tests. Blackhole technology is a carbon-based system used as an alternative to conventional Electroless copper. It is formaldehyde free and it is applicable to a wide variety of materials. The plating on Eclipse and Shadow showed the similar results as the plating on Electroless copper. Via fill and TH plating met the industry standards.

Via fill growth performance

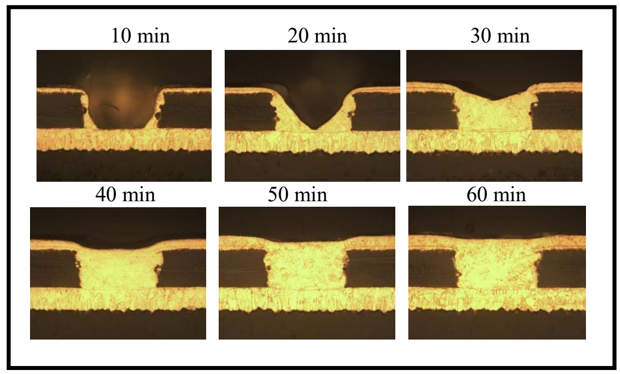


Figure 9. Stages of via fill process. BMV 100 x 60 microns; target Cu thickness 15 microns.

Plating at different stages of the process was studied, Figure 9. The organic additives are selectively adsorbed on the different area of the cathodes. The brightener is adsorbed at low current density areas, while the leveling agents, that act as suppressors are adsorbed on the high current density areas. At the early growth stage the side walls at the via bottom (near the capture pad), started to grow faster than the surface copper, due to this preferred adsorption of the brightener (accelerator) within the via. The leveler that was used in this process had a polarization effect, thus reducing the deposition rate at the board surface. After 30 minutes of plating, via bottom was raised up: curvature accelerated growth mechanism. The vias were filled up for 60 minutes and surface copper thickness was 15 microns.

Effect of Electrolyte Components on Via Filling Performance

Organic Additive Concentrations

Work was done on the effect of the Wetter, Brightener, and Leveler concentrations in terms of the via filling. The dimple size for 100 and for 120microns diameter vias as a function of the additive concentration is shown in Figures 10, 11, and 12.

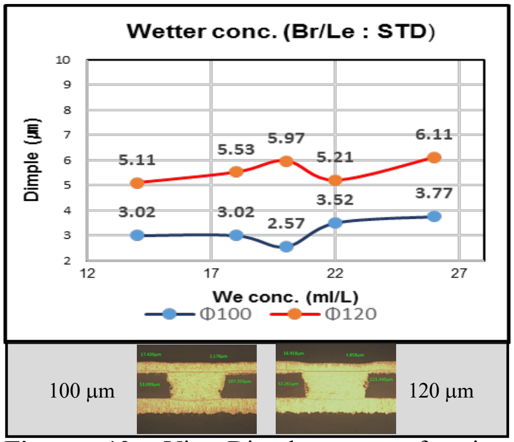


Figure 10. Via Dimple as a function of Wetter concentration in the bath.

As it could be seen from theses data, process is running reliably within very large ranges of the additive concentrations. The bath is stable in time and have very long life. No accumulation of the secondary breaking product, that could adversely affect via fill in time, were identified.

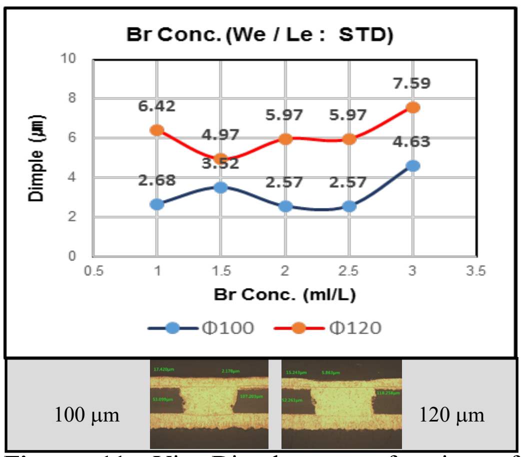


Figure 11. Via Dimple as a function of Brightener concentration in the bath.

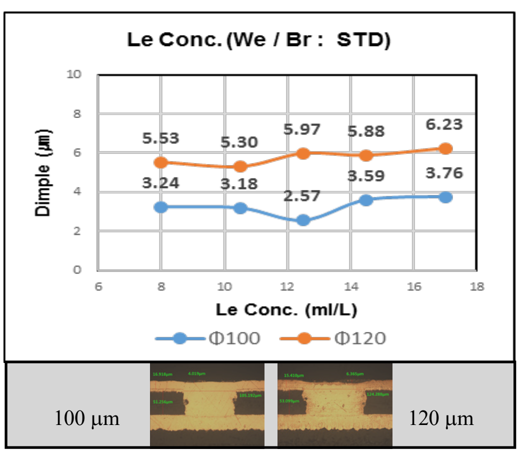


Figure 12. Via Dimple as a function of Leveler concentration in the bath.

Plating Parameters

Current density and solution flow affect the plating process performance.

Solution Flow:

The results obtained showed, that the low flow is optimal for both via fill and TH plating in this electrolyte.

Via fill: Cross section pictures of vias plated under three different solution flows are presented in Figure 13. Increasing the flow, the dimple depth increases, the effect being very pronounced for the large diameter vias. Increasing the solution flow, the supply of the leveling species to the cathode is enhanced. This leads to leveler compounds adsorption inside the vias, thus reducing the deposition rate there.

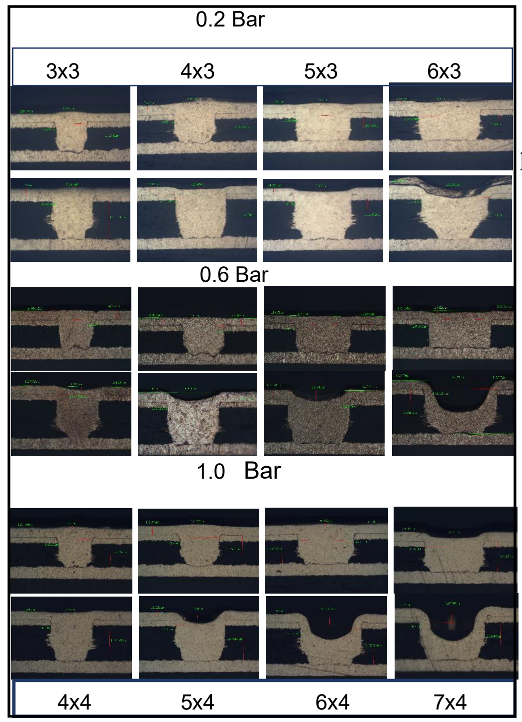


Figure 13. Cross sections of vias plated at solution flows: 0.2, 0.6, and 1.0 Bar.

Through holes plating: At a low solution flow rate, 0.2 Bar, a better TH plating was achieved, as shown on Figure 14. Since the used VMS (basic solution) is a high copper electrolyte, increasing the flow, does not change significantly the supply (by convection) of Cu ions at the cathode surface. It could however disturb the surface layer, causing change in the diffusion of the discharging ions.

Current Density:

The other way of mass transfer is ion migration, under the electrical field. The current density effect on the process performance was studied next. The results obtained indicate that decreasing the CD improves via fill (decreases the dimple size), and improves TP $_{min}$, and TP $_{knee}$. Decreasing the CD, more uniform copper thickness over the substrate, including inside the THs, was achieved due to the more uniform current distribution.

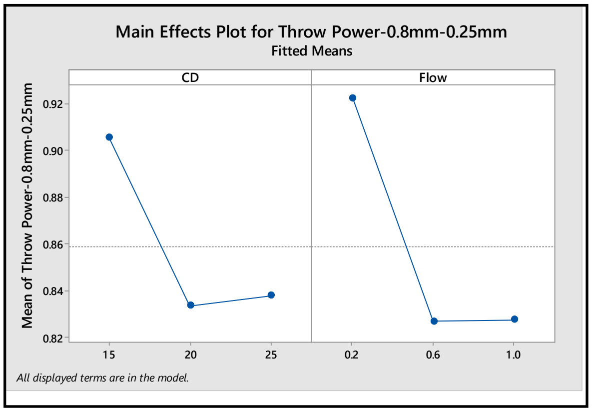


Figure 14. TP min for a 0.25 mm diameter hole in 0.8 mm board as a function of CD and solution flow.

The test results for the TH plating are summarized in Figure 15.

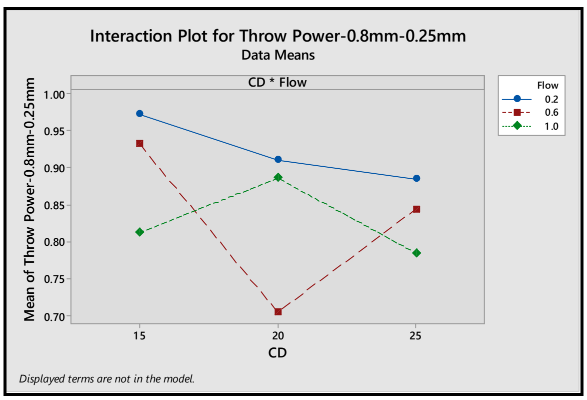


Figure 15. Throwing power, TP min of 0.25mm hole, 0.8 mm board, interaction plot.

The flow rate and the plating CD could be easily adjusted depending on via size and filling requirements.
Relatively high current densities for via fill, 20 – 25 ASF, could be applied with the new formula, that intensifies the process. Faster filling speed contributes to more efficient equipment utilization and reduced cycle time

Through Via Fill for HDI of PCBs and IC Substrates
Tests were run to determine the capability of the process for filling X-through via holes. Figure 16 is an example or X-through vias, 75 microns diameter, 100 microns thick. The plating was performed at 30 ASF for 40 minutes, solution flow 250 LPM. Surface Cu thickness 18-19 microns, dimple < 10 microns, no voids.

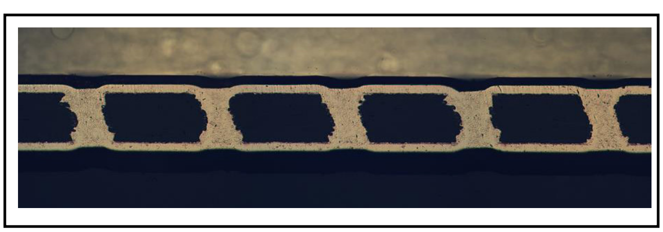
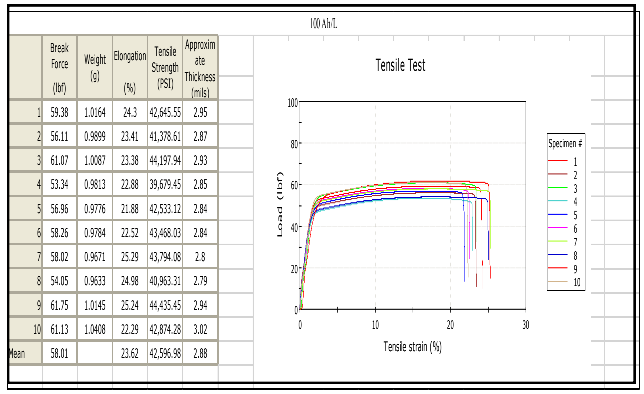


Figure 16. X-through via fill.

PROPERTIES
The physical mechanical properties of the deposited copper are critical for the reliability of the electronic devices in which it is used. Tensile Strength and Elongation of plated copper were measured in accordance with IPC TM-650, 2.4.18.1. Plated copper foils were baked for 4 hours at 125ºC then tested on an Instron pull tester.
Properties measured for the plated copper are given in Figure 17.



100 Ah/L

	Break Force (lbf)	Weight (g)	Elongation (%)	Tensile Strength (PSI)	Approximate Thickness (mils)
1	59.38	1.0164	24.3	42,645.55	2.95
2	56.11	0.9899	23.41	41,378.61	2.87
3	61.07	1.0087	23.38	44,197.94	2.93
4	53.34	0.9813	22.88	39,679.45	2.85
5	56.96	0.9776	21.88	42,533.12	2.84
6	58.26	0.9784	22.52	43,468.03	2.84
7	58.02	0.9671	25.29	43,794.08	2.8
8	54.05	0.9633	24.98	40,963.31	2.79
9	61.75	1.0145	25.24	44,435.45	2.94
10	61.13	1.0408	22.29	42,874.28	3.02
Mean	58.01		23.62	42,596.98	2.88

Figure 17. Tensile Stress and Elongation measurements, bath age 100 Ah/L

Figure 18 shows Tensile Strength and Elongation measurements for a fresh bath and aged baths. No change in the deposited metal properties were found as the solution aged.

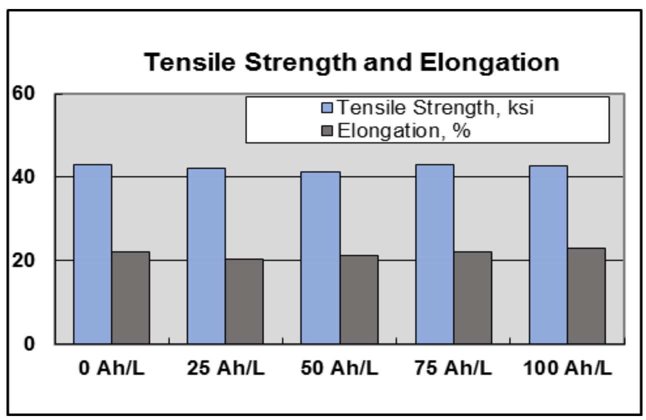


Figure 18. Tensile Strength and Elongation at different stages of the bath life.

The plated copper meet and exceed the standard requirements of Tensile strength and Elongation (T&E).

Thermal Characteristics
Through-Hole Reliability
Solder shock resistance tests as per IPC TM-650 2.6.8 were conducted to study the thermal characteristics of plated boards. 3x and 6x solder shock tests were run. The solder shock conditions were 10 second float at 288ºC for 3 or 6 times.

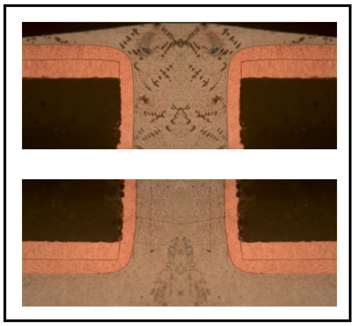


Figure 19. Cross section of 0.25 mm TH after 6x Solder Shock; plating at 20 ASF.

Plated copper deposits met industry standards for Solder shock resistance. Neither corner cracks nor barrel cracks were observed as shown in Figure 19. The thermal integrity was excellent for all through hole sizes plated.

Surface Appearance and Structure

Under the plating condition shown in Table 1, MacuSpec VF-HT 200 process produces bright, smooth, and uniform metal deposits on the panel surface, as this could be seen in Figure 20.

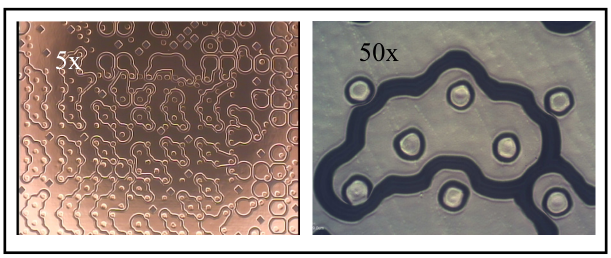


Figure 20. Surface of a panel plated in VF-TH 200.

Plated copper is leveled inside the through holes and the plating thickness is consistent throughout the barrel, demonstrated in Figure 21.

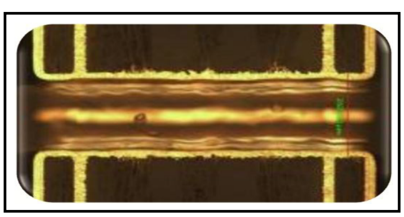


Figure 21. Cross section of a TH, diameter 0.25 mm, 0.8 mm thick panel.

SEM Study

Fine grained deposits were deposited from the electrolyte discussed in this paper. No columnar or fibrous copper was observed. Fine-grained copper is usually stronger and harder than the copper with a different type structure.

SEM pictures were taken from cross sections of the panel surface (higher current density regions) and from cross sections of the inside of the through holes and inside the vias (lower current density regions). An etch solution was used to expose the crystal structure of the deposit. Pictures of the cross sections are given in Figures 22 and 23. They show uniform grain structure.

SEM study of plated copper on the surface (top view) was performed before and after etching to examine the surface morphology. Figure 24 shows SEM pictures of the deposited metal surface. <111> preferred orientation is possible to some extent, that could be useful for some applications. This should be further verified by studying the texture using XRD (X-ray diffraction).

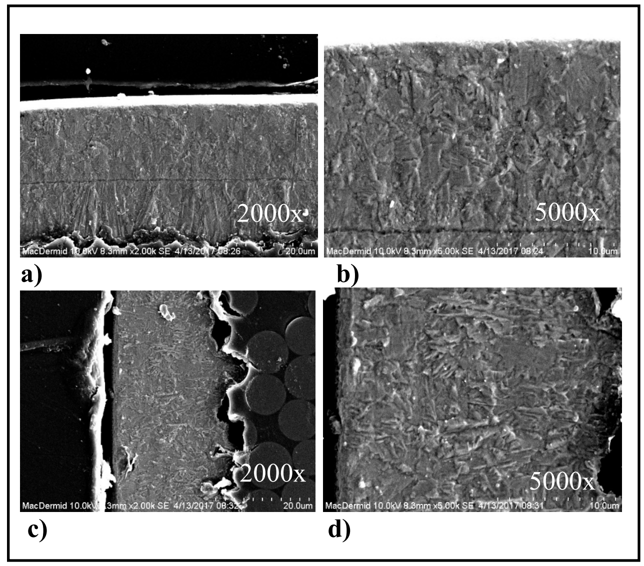


Figure 22. SEM. a) and b) Cross Section pictures of the Surface around 0.20 mm TH; b) and c) Cross Section pictures of copper plated inside the TH, on the hole walls. Panel Plated at 20 ASF.

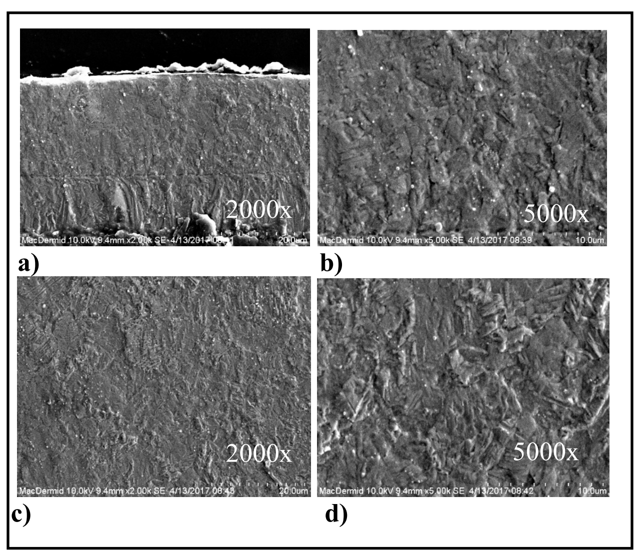


Figure 23. SEM. a) and b) Cross Section pictures of the Surface around 4x3 via; b) and c) Cross Section pictures of copper plated inside 4x3 via. Panel Plated at 20 ASF.

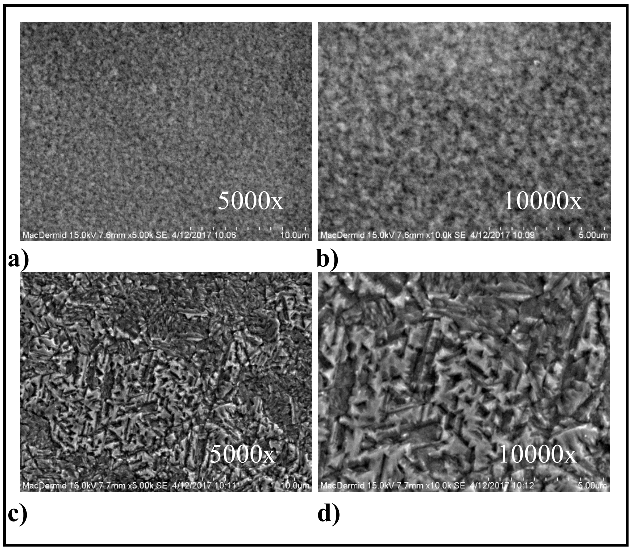


Figure 24. SEM. a) and b) Panel surface, top view; c) and d) Panel Surface, top view after Etching. Plating at 20 ASF.

BATH CONTROL

CVS analysis is easily used for bath control and solution chemistry adjustment. All organic additives are independently controlled and can be mixed together for auto-dosing. Hull cell tests also can be used to monitor the bath performance.

CONCLUSIONS

An innovative DC copper electroplating process, MacuSpec VF-HT 200, was developed to meet the electronic industry need for a technology capable of simultaneously filling vias and plating through holes. The new formula provides a reliable copper metallization in respond to the highly challenging industry requirements. The via filling is excellent across a wide range of via sizes while the thickness of plated copper on the board surface and dimple depth are minimal. The throwing power of the bath exceeds the throwing power of conventional via fill acid copper electrolytes. The micro-distribution of the plated through holes meets the requirements for such a process.
MacuSpec VF-HT 200 can be used for direct plating (on black holes) or on electroless copper. The bath has a wide operating window and an extremely long life. Plating at relatively high effective CDs makes this process much desirable in the fast-paced environments.

Deposited copper is bright, smooth, and leveled on the surface and inside the through holes. The ductility and tensile strength are excellent. The thermal characteristics of plated copper meet the IPC standards and ensure that no failure occurs during the subsequent soldering operations.
The process is easily controlled by CVS analysis and Hull cell tests.

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