

# **ADVANCED CU ELECTROPLATING PROCESS FOR ANY LAYER VIA FILL APPLICATIONS WITH THIN SURFACE COPPER**

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## **ABSTRACT**

High density interconnect (HDI) technology is one of the fastest growing in Printed Circuit Board industry. Consumer electronics such as smart phones and laptop computers getting lighter, smaller, and faster pushed the HDI technology even further. Currently design architects utilize this HDI technology to move from standard multilayer PCB boards, to HDI multilayer boards. Which, allows more components in the same amount of PCB area with far less layers than standard multilayer PCB. Advantages of this densification are, shrinkage in size, fast signal transmit, reduced signal loss, and most importantly reduced cost per square inch of PCB. In modern day, this HDI technology is extremely important for the customer driven market when it comes to consumer electronics. With all the above-mentioned advantages, researchers are highly motivated to formulate solutions for HDI market, especially acid copper via fill solutions.

Here we discuss an innovative DC acid copper via fill formulation, for VCP (Vertical Continues Plating) applications. The formulation discussed here has distinctly rapid filling performance, which allow this formulation to plate very thin Copper on the surface while, filling the via. For an instance a 125x75  $\mu\text{m}$  via was seamlessly filled with only 10  $\mu\text{m}$  Cu at the surface. When it comes to next steps in the panel processing such as laser drill the next stacked via layer, having a flat profile of the via top is a huge advantage. X-ray diffraction study was done to obtain information about the grain structure (texture) of the deposit. Based on determination of the Lotgering factor the study shows that the (111) plane has a slight preference (Lotgering factor appr. 0.2) over other typical planes e.g. (200), (220), and (311). According to the X-Ray Diffraction (XRD) data and Focus Ion Beam (FIB) technique

combined with Scanning Electron Microscopy (SEM) pictures showed the grain structure remained the same even after the bath was aged up to 150 Ah/L. This formulation contains no harmful formaldehyde. In 2016, reclassification of formaldehyde for its carcinogenicity by the European Union, restricted its use in electroplating formulations. These regulations in the future, could expand in to other regions as well. Therefore, having no formaldehyde is an added advantage for safe operation and waste disposal.

**KEY WORDS:** Copper electroplating, Via Fill, PCB metallization.

## **INTRODUCTION**

The Printed Circuit Board (PCB) industry has evolved immensely over the last few decades. PCB architecture has pushed boundaries and realized unimaginable accomplishments within a short period. The conventional board design had large amount of PCB real-estate left over due to the lack of technology at the time to densify the design. However, with introduction of the high-density interconnects (HDI) technology, for example sequential build up (SBU) technologies incorporating microvias, modern PCBs can accommodate more surface mount components. [1] These new designs with blind and buried vias, directly impact multilayer processing. Reliable via filling materials and methods are necessary and in high demand to fulfill the needs of PWB boards with deeper blind and buried vias. Now with the help of advanced materials, equipment, and processes, PCB designers ~~could~~ can increase the wiring density and use most of the board to install components.

## **ACID COPPER VIA FILL**

Electrodeposited Copper has become the fundamental choice for via fill applications due to the exceptional conductivity and cost. Electroplating is done in a typical electrolyte consisting of acid, Copper and Chloride ions. Sulfate based electrolyte systems are preferred in PCB industry owing to their low cost, convenient operation, safety and ease of waste treatment. [2] Compositions for Copper via filling baths typically run with high concentrations of Copper (up to 250 g/L Copper sulfate) and lower concentrations of acid (approximately 100 g/L sulfuric acid). An additive free electrolyte will only give a deposit with poor physical properties and conformal plating. In order to get the desired consistent via fill while plating minimum amount of Cu on the surface, carefully designed additives

are vital. These additives are key for filling vias of various diameters and depths. Typical systems will contain carriers, brighteners, and levelers. In theory, it is possible to fill vias only with carrier and Brightener [8]. However, in practical standpoint the dimple will be large and fill be conformal, also the brightener concentration will be very low making it difficult for the CVS analysis [9]. In order to raise the concentration of the brightener and obtain a good fill, levelling agents must be used.

Carrier and leveler in these formulations act as suppressors but in different ways and can be classified as different types of suppressors [10]. Type I suppressors like carriers can be deactivated by the brightener (antagonistic, selective adsorption to Chloride only) whereas type II suppressors like levelers do not undergo deactivation (synergistic, non-selective adsorption due to electro-static interaction).

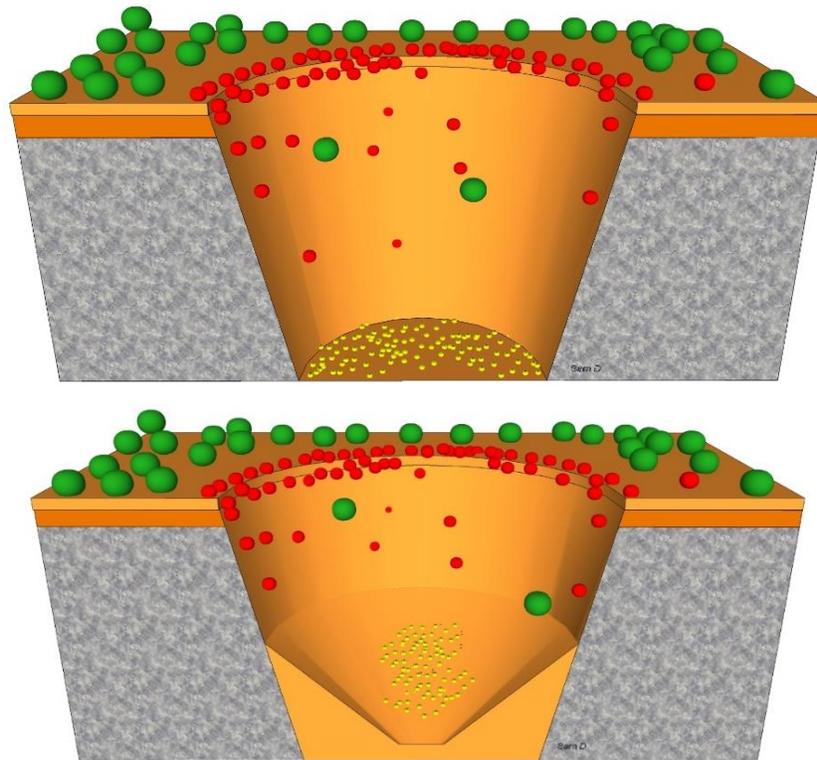
Carriers or suppressors, are typically high molecular weight polyoxyalkyl type compounds. Typically, carriers are adsorbed at the surface of the cathode. They form a thin layer by interacting with chloride ions. Thus carrier suppresses the plating rate by increasing the effective thickness of the diffusion layer [3]. Consequently, the energy level over the cathode surface topography is being equalized (same number of electrons locally for plating at any cathode surface spot) so that the resultant deposit becomes more uniform and a more evenly distributed Copper deposit thickness can be obtained. On the other hand, brighteners increase the plating rate by reducing the suppression. They are typically small molecular weight Sulfur containing compounds, also called grain refiners.

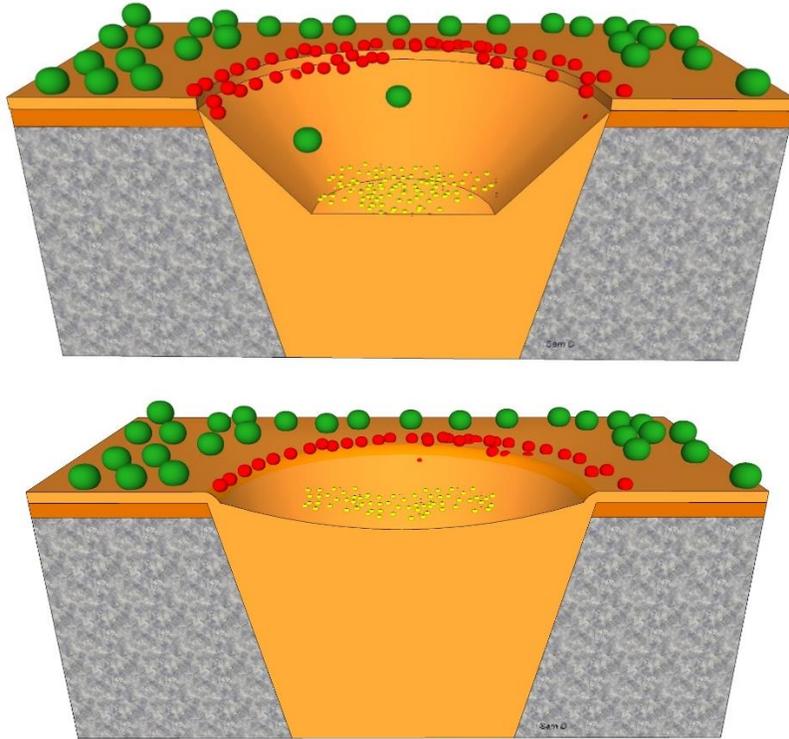
Levelers typically consists of nitrogen bearing linear/branched polymers, heterocyclic or non-heterocyclic aromatic compounds being typically quaternized (positively charged). These compounds will adsorb selectively on high current density sites such as edges and corners, local protrusions and prevent copper over plating in high current density areas. [4]

## **VIA FILL MECHANISM**

The difference in growth rate of Cu inside and outside any via is governed by the additives. Shown below is a schematic representation of a via growth. Chemical adsorption is exaggerated here to show the different role played by each additive. However, both selective and non-selective adsorption occur during plating. Additive compositions must be controlled in a set range in order to get the desired “bottom-up filling”. Analytical tools such as Cyclic Voltammetry Stripping (CVS) analysis, is the most common in the industry, may be utilized. Although other techniques such as HPLC (High Performance Liquid Chromatography) are available to determine the concentrations of the additives.

In the following scheme, wetter or suppressor is represented with green, leveler with red and brightener with yellow. Wetter molecules predominantly adsorb on the surface suppressing the surface, while the leveler adsorb selectively on to the high current density areas, due to the positively charged, quaternized N group. This prevents over plating at the edges and avoids premature closure of the via leaving voids in the center of the via. Brightener being a small Sulfur containing molecule diffuses faster into the via and accelerates the plating. [5] During the plating process since the geometry of the via changes the brightener become concentrated inside the via causing a rapid plating in the via. This is called the *curvature-enhanced-accelerator coverage* (CEAC) mechanism. [6] Finally, when the via gets leveled with the surface and the plating rates inside the via and on the surface become equal, the bottom up filling stops.





**Figure 1.** Schematic representation of bottom-up filling

### CONDITIONS AND BATH COMPONENTS

Table 1 shows the operational conditions and optimum additive levels. Typically, via fill baths have high copper and low acid to achieve the desired bottom up fill.

**Table 1.** Bath components and plating conditions

Parameter	Range	Optimum
Current Density	1.0 – 3.5 ASD (10-32 ASF)	2.2 ASD (20 ASF)
Temperature	20 - 27°C (68 - 80°F)	23°C (73°F)
Wetter	9 - 25 mL/L	10 mL/L
Brightener	0.5 - 1.5 mL/L	1 mL/L
Leveler	0.5– 2.5 mL/L	1.5 mL/L

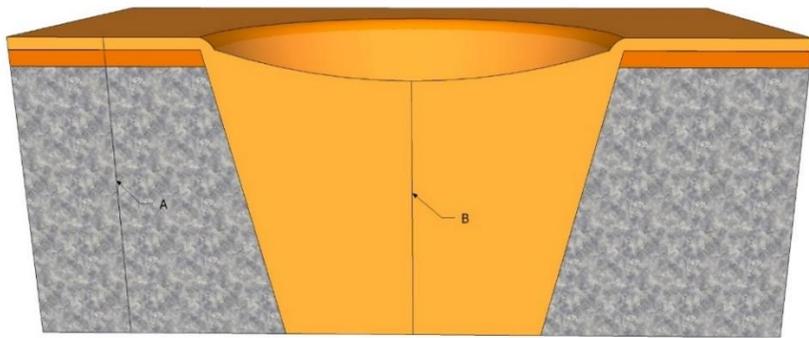
Parameter	Range	Optimum
Copper Sulfate (CuSO <sub>4</sub> .5 H <sub>2</sub> O)	230 - 250 g/L	240 g/L
Free Sulfuric Acid 66°Be Electronic Grade	55 - 65 g/L	60g/L
Chloride Ion (Cl <sup>-</sup> )	40 – 60 ppm	50 ppm

**TEST VEHICLES**

Test panels with different via sizes were used during the evaluation. The thickness of the test vehicles used in the process evaluation were 1.6 mm with via diameter range from 75 – 175 μm, and the via depths 75 and 100 μm. All geometries for each test board thickness were plated at the same time in the same tank and later the fill ratio was calculated by using cross section analysis. Where fill ration is defined as;

$$Fill\ Ratio = \frac{B}{A} \times 100\% \dots \dots \dots Eq1$$

Figure 2 shows a typical cross section of a filled via with a dimple, dimple is the fill difference A-B.



**Figure 2.** Via fill ratio

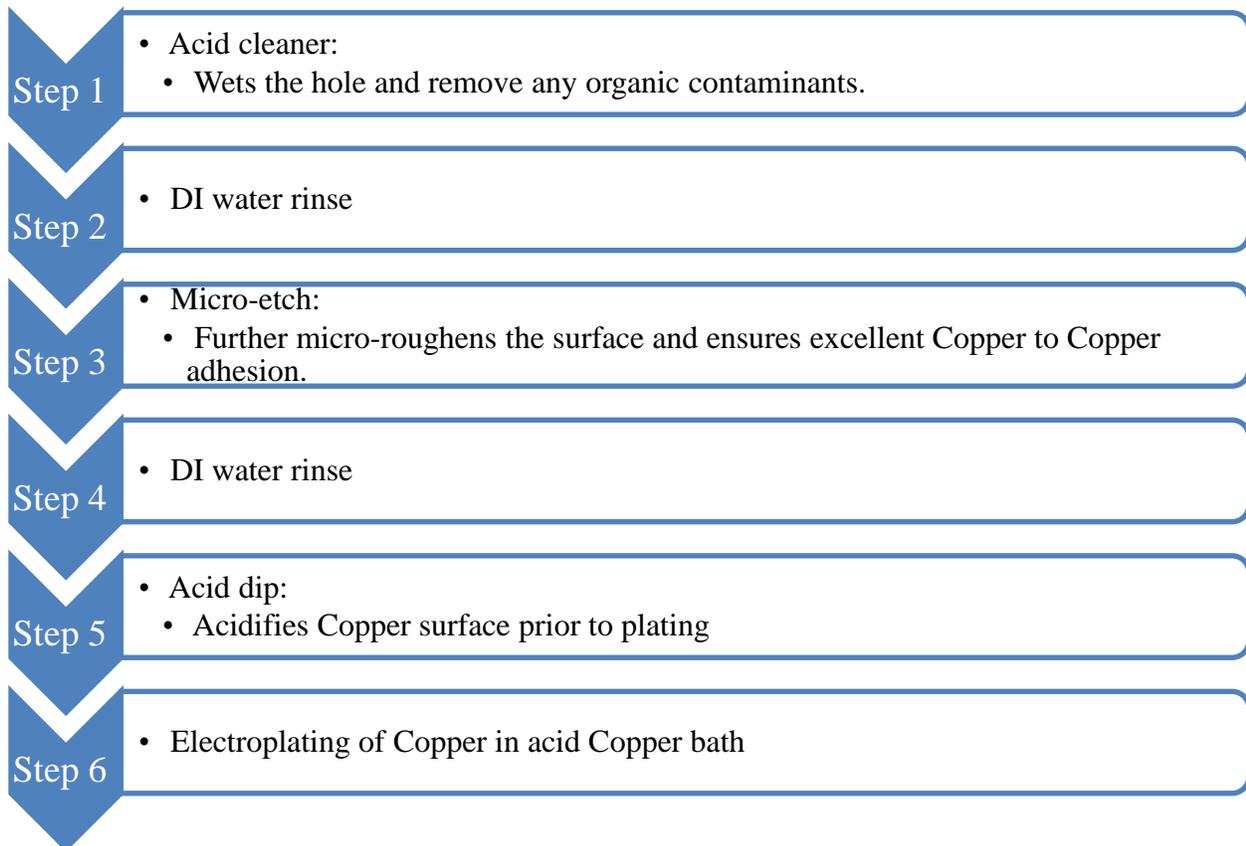
**CROSS SECTION ANALYSIS**

Cross section analysis was started with the sample preparation process by punching or routing sections from a desired area on the board or test panel. Pre-grinding of the coupon was done to get a flat surface closer to the through holes. Plastic index pins were used to align the coupon vertically to the grinding surface. A fast-cure acrylic resin was used to mount the coupons. A ratio of 1-to-1, hardener-to-resin, was used to provide optimum penetration and a quick cure rate (10-15 minutes). After the section

hardened they were subjected to grinding, polishing, and microscopic inspection. Figure 2 shows a cross section of a via indicating the points of measurements.

## PROCESS FLOW

The process flow included the following operations:

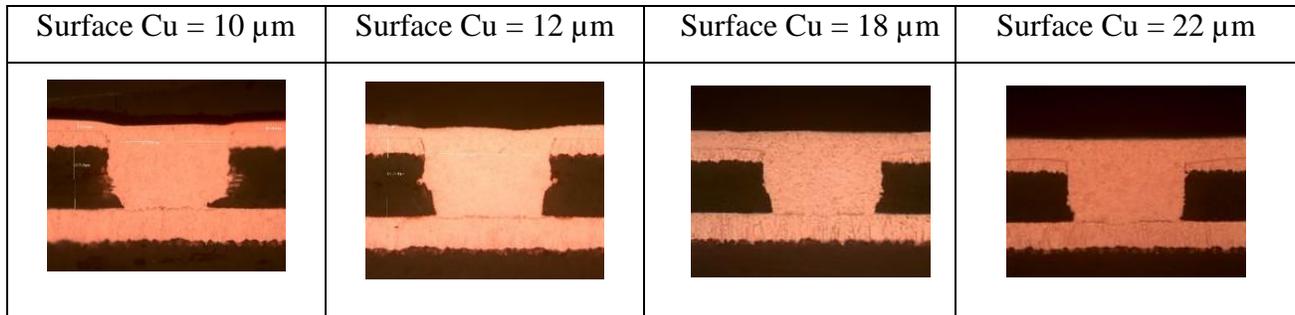


## RESULTS AND DISCUSSION

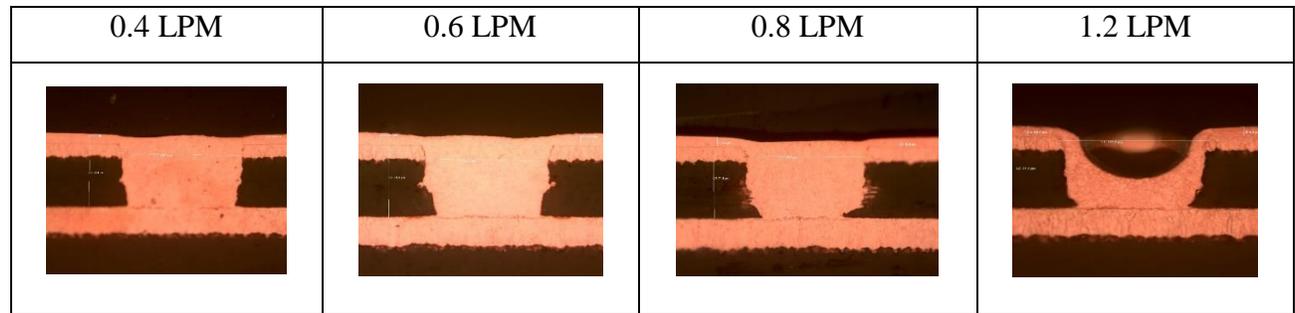
### VIA FILL AND BATH PLATING PERFORMANCE

Initial plating results showed that excellent filling can be obtained with different surface Cu amounts. A 125x75  $\mu\text{m}$  via can be filled even with only 10  $\mu\text{m}$  Cu on the surface as shown in figure 3. Flow rate variation showed that, the formulation has a wide range of operation from 0.4 LPM to 0.8 LPM results are shown in figure 4. A larger dimple was observed at very high flow rate. A typical plating was done under the conditions summarized in table 1 and followed the process flow given above,

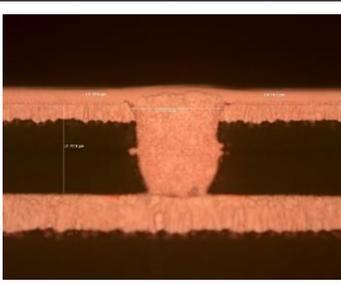
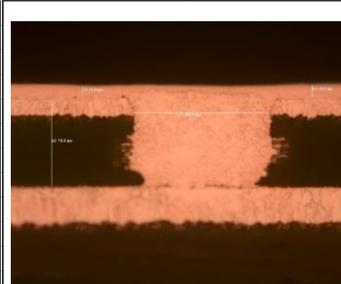
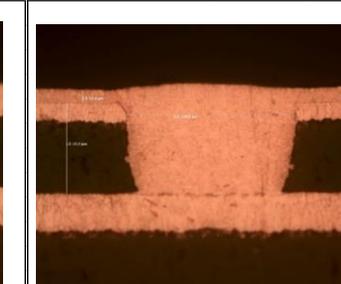
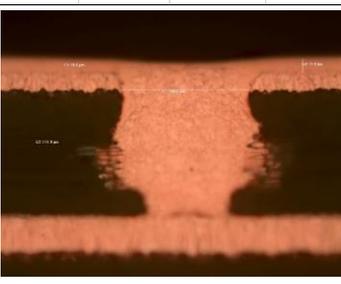
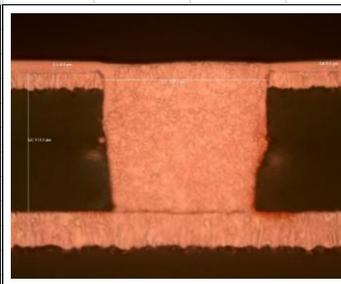
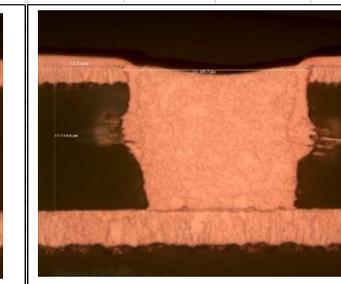
resulted a via fill shown in figure 5. Via diameter 150  $\mu\text{m}$  and depth 100  $\mu\text{m}$  was seamlessly filled without any issue. Surface was flat and the deposit was bright with surface Cu thickness at only 8-11  $\mu\text{m}$ .



**Figure 3.** Via fill performance of 125 x 75  $\mu\text{m}$  with different surface Cu.

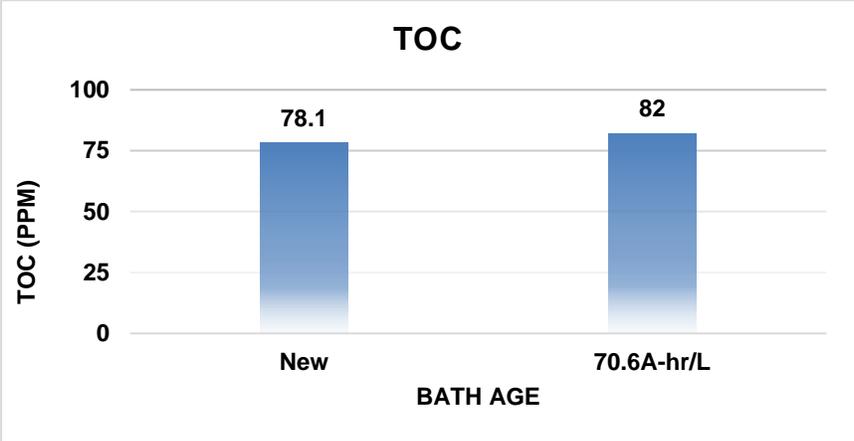


**Figure 4.** Via fill performance of 125 x 75  $\mu\text{m}$  with different solution flow rates 0.4, 0.6, 0.8, 1.2 liters per minute (LPM)

3X3	Dimple	Surface	4X3	Dimple	Surface	5X3	Dimple	Surface
				10.4				10.4
								
4X4	Dimple	Surface	5X4	Dimple	Surface	6X4	Dimple	Surface
		10.8			8.5			7.7
								

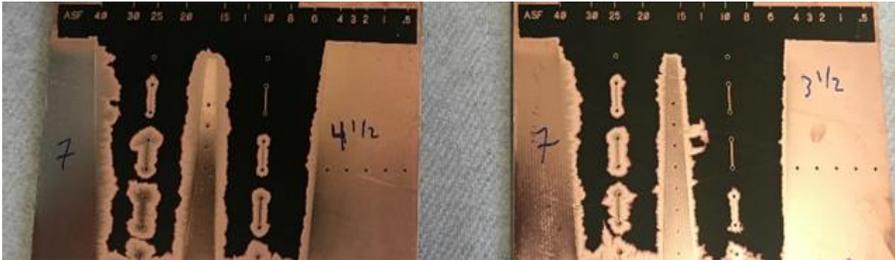
**Figure 5.** Typical via fill capability for different via diameter and depth at surface Cu ~ 8 – 11  $\mu\text{m}$ .

Total Organic content (TOC) of the bath was obtained for fresh and aged bath. According to the data summarized in the figure 6, the TOC did not change significantly over time and also the fresh bath has very low TOC. Low TOC in the fresh makeup means, the bath will have prolonged lifetime and stability. Since the organic buildup is very low with age, bath requires less frequent Carbon treatment. This makes the process environmentally benign and hassle free waste treatment.



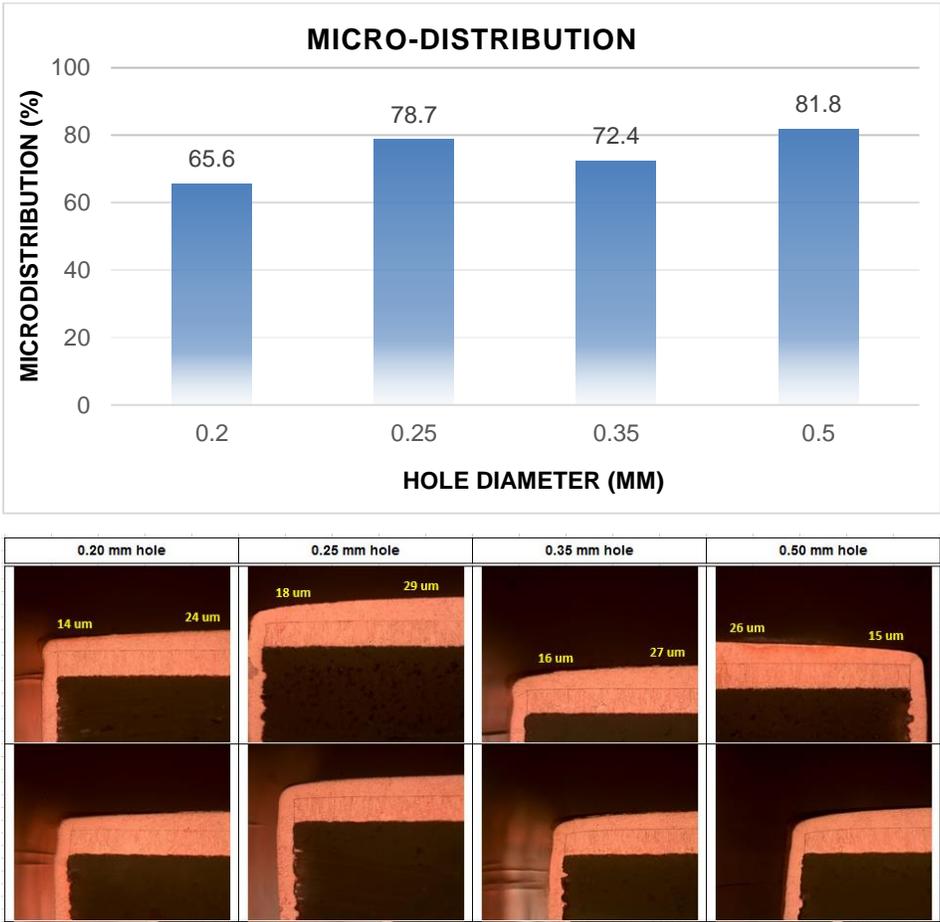
**Figure 6.** Total Organic Content of the new bath and aged bath

Compatibility of this via fill formulation in direct metallization was evaluated by plating propagation panels. These are panels with 8 through holes alternatively connected and processed with a carbon based direct metallization layer. Maximum propagation result is 8, two regions for high current density and low current density were plated simultaneously in a Hull Cell. According to the results summarized in figure 7, the formulation reported here has an excellent propagation at high current density area and low propagation at low current density area.



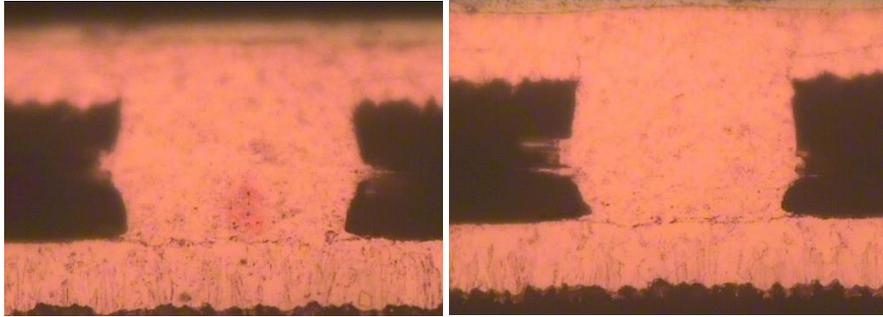
**Figure 7.** Propagation results for direct metallization applications

A 1.6 mm thick through hole panel was plated to evaluate the Micro distribution. The Micro Distribution is defined as the ratio of the average copper deposit thickness in the center of the through hole to the average Copper deposit thickness at the surface. According to the data shown in Figure 8, greater than 65% micro distribution was obtained even in an electrolyte designed for via fill, that is a high copper and low acid electrolyte. The cross-section evaluation of the through holes showed no thin corners, however a sloping was observed from the bulk surface to the through hole edge.



**Figure 8.** Throw power for 1.6 mm board thickness

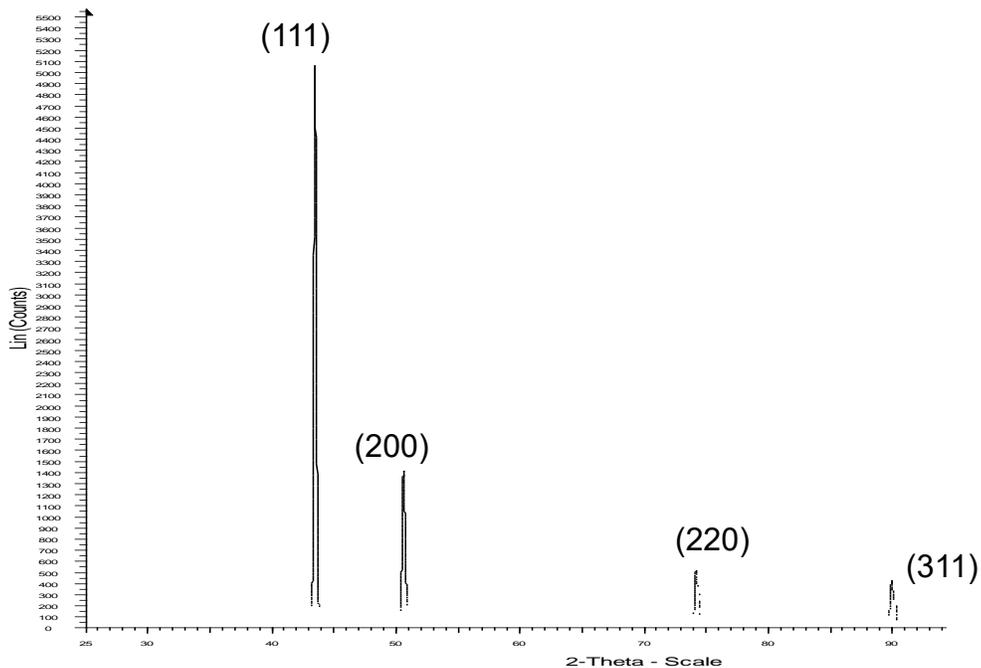
Further, solder float test was performed to evaluate thermal characteristics of the deposit in accordance with IPC TM-650 2.6.8. Solder shock (SS) conditions were 10 seconds float at 288°C for 3 times on the same side of the test coupon. Results are shown in Figure 9. After 3X SS testing, no cracks, or via bottom separation was observed.



**Figure 9.** Solder float results

### **STRUCTURAL ANALYSIS, HARDNESS AND IMPURITIES**

X Ray Diffraction (XRD) study was performed for the plated deposits to identify the crystal phase and different planes. Typical diffraction pattern was obtained as the standard reported in the literature, figure 11 with reflections from planes (111), (200), (220), and (311) were observed. [5] Narrow sharp peaks in the XRD pattern were observed which indicates highly ordered Cu crystals in the deposit. Table 2 and 3 shows, no significant change in the major peaks, lattice constant or density of the plated Cu after aging. This is an indication that the crystal phase of the deposit is similar even after bath aging up to 150 Ah/L.



**Figure 11.** X Ray Diffraction pattern for Cu deposit plated using current formula

$$\text{Average Crystallite Size} = \frac{0.94 \lambda}{\beta \cos\theta} \dots \dots \dots \text{Eq2}$$

$\beta$  = Line broadening at the FWHM in radians.

$\theta$  = Bragg angle.

$\lambda$  = X-ray wavelength

Tabulated in table 3 is the crystal size calculated from the Full Width at half maximum (FWHM) from the XRD peaks using the Scherrer equation (Eq.1). Data shows no substantial changes in the crystal size, which agrees with the FIB images (Table 4) showing the grain structure of the plated Cu at different bath age. Beside the relative intensities of the crystal orientations, the crystallographic density and the lattice constant is also of interest whether there is a preferred orientation. Lotgering factor needs to be considered in order to verify this. The Lotgering factor, f, is for each Miller index (*hkl*) showing whether it is in the range of the thermodynamic stable Miller index distribution for Copper (literature values) or which crystal orientation is more preferred up to a certain degree. [7] The calculation of the Lotgering factor for each Miller index is performed according to the following equation (here for the example (00l):

$$f_{00l} = \frac{P_{00l} - P_o}{1 - P_o} \dots \dots \dots \text{Eq3}$$

where  $P_{00l}$  is the sum of the relative intensities for all (00l) diffractions divided by the sum of the intensities of all (*hkl*) diffractions ( $\Sigma I_{00l} / \Sigma I_{hkl}$ ), and  $P_o$  is similarly defined for a randomly oriented sample ( $\Sigma I^0_{00l} / \Sigma I^0_{hkl}$ ). The max obtainable value for the Lotgering factor is 1. This means that there is a very high preference for this Miller index. Table 4 shows the positive values for (111) plane, indicating that the deposits have a slight preference for (111) plane over others, which is the densest plane of all.

**Table 2.** X-Ray diffraction data of the deposit at different bath age.

<b>Data</b>	<b>Literature</b>	<b>0 Ah/L</b>	<b>50 Ah/L</b>	<b>100 Ah/L</b>	<b>150 Ah/L</b>
<b>(111)</b>	100	100	100	100	100
<b>(200)</b>	46	28.4	45.7	38.4	35.2
<b>(220)</b>	20	10.4	12	14.6	10.5
<b>(311)</b>	17	8.4	9.9	8.3	7.6
<b>Lattice Constant [Å]</b>	3.615	3.613	3.611	3.613	3.613
<b>Density [g/cm<sup>3</sup>]</b>	8.92	8.953	8.963	8.952	8.948

**Table 3.** Crystal Size of the deposit at different bath age

<b>Crystal plane</b>	<b>Crystal Size [Å]</b>			
	<b>0 Ah/L</b>	<b>50 Ah/L</b>	<b>100 Ah/L</b>	<b>150 Ah/L</b>
<b>(111)</b>	373.1	368.4	371.5	376.3
<b>(200)</b>	308.0	302.7	305.9	309.1
<b>(220)</b>	283.6	282.8	287.6	291.8
<b>(311)</b>	314.6	291.7	304.3	315.5

**Table 4.** Lotgering factor at different bath age for different XRD peaks

<b>Crystal plane</b>	<b>Lotgering Factor</b>			
	<b>0 Ah/L</b>	<b>50 Ah/L</b>	<b>100 Ah/L</b>	<b>150 Ah/L</b>
<b>(111)</b>	0.29	0.11	0.16	0.23
<b>(200)</b>	- 0.08	0.03	-0.02	-0.03
<b>(220)</b>	-0.04	-0.12	-0.02	-0.05
<b>(311)</b>	-0.04	-0.04	-0.05	-0.05

**Table 5.** Grain Structure of the deposit over bath age.

Bath Age (Ah/L)	3 kx	5 kx
0		
50		
100		
150		

The hardness of the Copper foils is independent from the bath age at  $79 \pm 8 \text{ HV}_{0.05}$ . Furthermore, up to 150 Ah/L the incorporation of Carbon, Sulfur, Nitrogen and Chloride into the copper lattices was investigated. The results are shown in table 6. Impurity analysis was done as follows, C and S using combustion IR method (e.g. with a LECO tool), N by using carrier gas hot extraction (CGHE) and for Cl X-ray fluorescence spectroscopy (XRF spectroscopy).

**Table 6.** Impurity analysis over bath age.

Sample	C [% w/w]	S [% w/w]	N [% w/w]	Cl [% w/w]
AVF-700_0	0.008	< 0.002	< 0.002	< 0.05
	0.005	< 0.002	< 0.002	< 0.05
AVF-700_50	0.005	< 0.002	< 0.002	< 0.05
	0.004	< 0.002	< 0.002	< 0.05
AVF-700_100	0.007	< 0.002	< 0.002	< 0.05
	0.007	< 0.002	< 0.002	< 0.05
AVF-700_150	0.006	< 0.002	< 0.002	< 0.05
	0.006	< 0.002	< 0.002	< 0.05

Beside Carbon, no other none-Copper elements were detected. Carbon is being incorporated only in very small quantities. No significant increase in C content was observed as the bath aged.

**PHYSICAL AND THERMAL PROPERTIES**

Two most important physical properties to the PCB manufacturing are tensile strength and elongation %, these properties show the tolerance of the deposit for thermal stress. The Cu deposit plated with additives suppressor, grain refiner, and leveler will show characteristic physical properties.

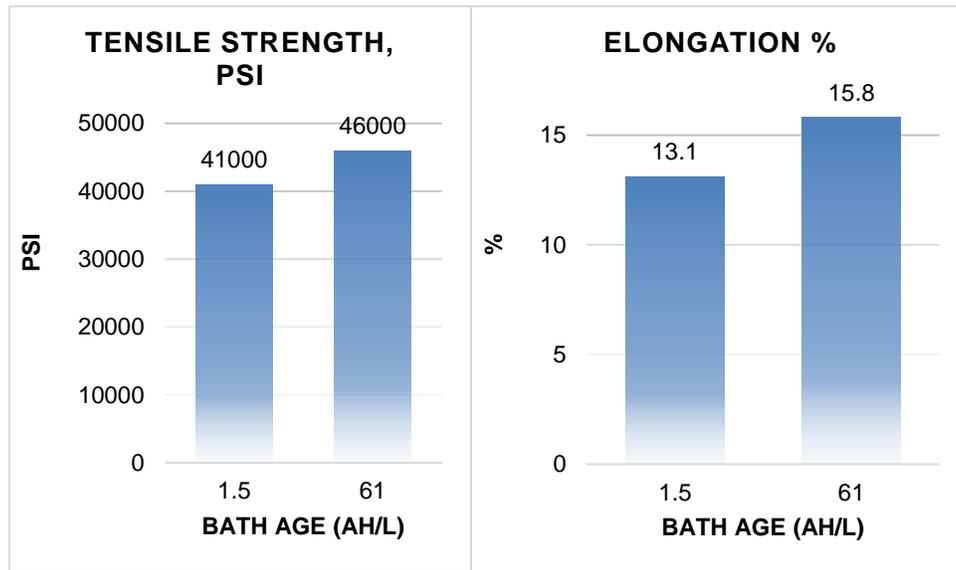
$$\text{Mean average cross sectional area (in}^2\text{)} = \frac{\text{Weight of the sample (lbs)}}{\text{Length of tensile sample (in)} \times \text{density of copper (g/in}^3\text{)}} \dots\dots\dots \text{Eq 4}$$

$$\text{Tensile Strength} = \frac{\text{Maximum load (lbs)}}{\text{Mean cross sectional area (in}^2\text{)}} \dots\dots\dots \text{Eq 5}$$

$$\text{Elongation} = \frac{(\text{Length at break} - \text{Original gage length})}{\text{Original gage length}} \times 100\% \dots\dots\dots \text{Eq 6}$$

Tensile strength and elongation were measured according to the IPC TM-650, 2.4.18.1 standards. A stainless-steel panel was plated with the current formulation. Sample strips were extracted from the plated panel and baked in an oven at 125°C for four to six hours.–An Instron instrument was used to

test the strips. The measurements were used to calculate tensile strength and elongation % using equations 4, 5, and 6. Figure 12 shows the results at two different bath ages, fresh bath and bath age around 62 Ah/L. According to the results properties improved with the bath age.



**Figure 12.** X Ray Diffraction pattern for Cu deposit plated using current formula

## CONCLUSION

As summary, a new via fill chemistry is introduced in this work. Formulation showed excellent via fill capability, with minimum surface Cu. Over bath age very low TOC was observed and insignificant foreign elements uptake in the Copper deposit was observed. Evaluation of structure showed stable crystal structure during aging, with a slightly preference on (111) plane. The hardness of the plated deposit was  $79 \pm 8$  HV<sub>0.05</sub> regardless the bath age. The physical properties, tensile strength and elongation improved as the bath aged. All the additive components can be analyzed with Cyclic Voltammetry Stripping analysis.

## REFERENCES

- [1] Clyde F. Coombs Jr., Printed Circuit Handbook, Sixth edition, McGraw-Hill, New York, 2008.
- [2] Mordechai Schlesinger, Milan Paunovic., Modern Electroplating, Fifth edition, John Wiley & Sons, Inc., Hoboken, New Jersey, 2010.
- [3] K. B. Herbert; S. Adhikari; J. E. Houser, *Journal of the Electrochemical Society*, 152 (5) C324-C329, 2005.
- [4] S. Dharmarathna et. al. High Throw DC Acid Copper Formulation for Vertical Continuous Electroplating Processes. *IPC APEX Expo 2017*, San Diego, California, February 14-16, 2017.
- [5] Y. Zhang, G. Ding, P. Cheng, H. Wang, Numerical Simulation and Experimental Verification of Additive Distribution in Through-Silicon Via during Copper Filling Process, *Journal of The Electrochemical Society*, 162 (1) D62-D67 (2015)
- [6] F. Wang, Z. Zhao, N. Nie, F. Wang & W. Zhu, Dynamic through-silicon-via filling process using copper electrochemical deposition at different current densities. *Scientific Reports* 7, Article number: 46639 (2017)
- [7] R. Furushima, S.Tanaka, Z. Kato, K. Uyematsu, Orientation distribution–Lotgering factor relationship in a polycrystalline material—as an example of bismuth titanate prepared by a magnetic field. *Journal of the Ceramic Society of Japan* 118 [10] 921-926 2010
- [8] W.P.Dow, M.Y.Yen, W.B.Lin, S.W. Ho, Influence of Molecular Weight of Polyethylene Glycol on Microvia Filling by Copper Electroplating. *Journal of The Electrochemical Society*, 152 (11) C769-C775 (2005)
- [9] W.P. Dow, C.W. Liu, Evaluating the Filling Performance of a Copper Plating Formula Using a Simple Galvanostat Method. *Journal of The Electrochemical Society*, 153 (3) C190-C194 (2006)
- [10]P.Broekman, A.Fluegel, C.Emnet, M.Arnold, C.Roeger-Goepfert, A.Wagner, N.T.M.Hai, D.Mayer, Classification of suppressor additives based on synergistic and antagonistic ensemble effects. *Electrochimica Acta*, Volume 56, Issue 13, 1 May 2011, Pages 4724-4734