

Advanced Cu Electroplating Process for Any Layer Via Fill Applications with Thin Surface Copper

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ABSTRACT

Copper-filled micro-vias are a key technology in high density interconnect (HDI) designs that have enabled increasing miniaturization and densification of printed circuit boards for the next generation of electronic products. Compared with standard plated through holes (PTHs) copper filled vias provide greater design flexibility, improved signal performance, and can potentially help reduce layer count, thus reducing cost. Considering these advantages, there are strong incentives to optimize the via filling process.

This paper presents an innovative DC acid copper via fill formulation, for VCP (Vertical Continuous Plating) applications which rapidly fills vias while minimizing surface plating. For instance, a 125x75 μm via was filled with only 10 μm Cu deposited on the outer layer surfaces. X-ray diffraction studies were 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, which was classified in 2016 by the European Union as a carcinogen, thereby restricting its use in electroplating formulations. These regulations in the future, could expand into 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 in response to the need for increased densification and miniaturization of designs. The use of blind and buried vias, made possible in part by advances in plating chemistries, have enabled the use of sequential build up (SBU) technologies to accommodate more and finer-pitch 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.

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 the 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 a practical standpoint the dimple will be large and fill will be conformal, also the brightener concentration will be very low making it difficult for the Cyclic Voltammetric Stripping (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 (Figure 1). 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 adsorbed 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.

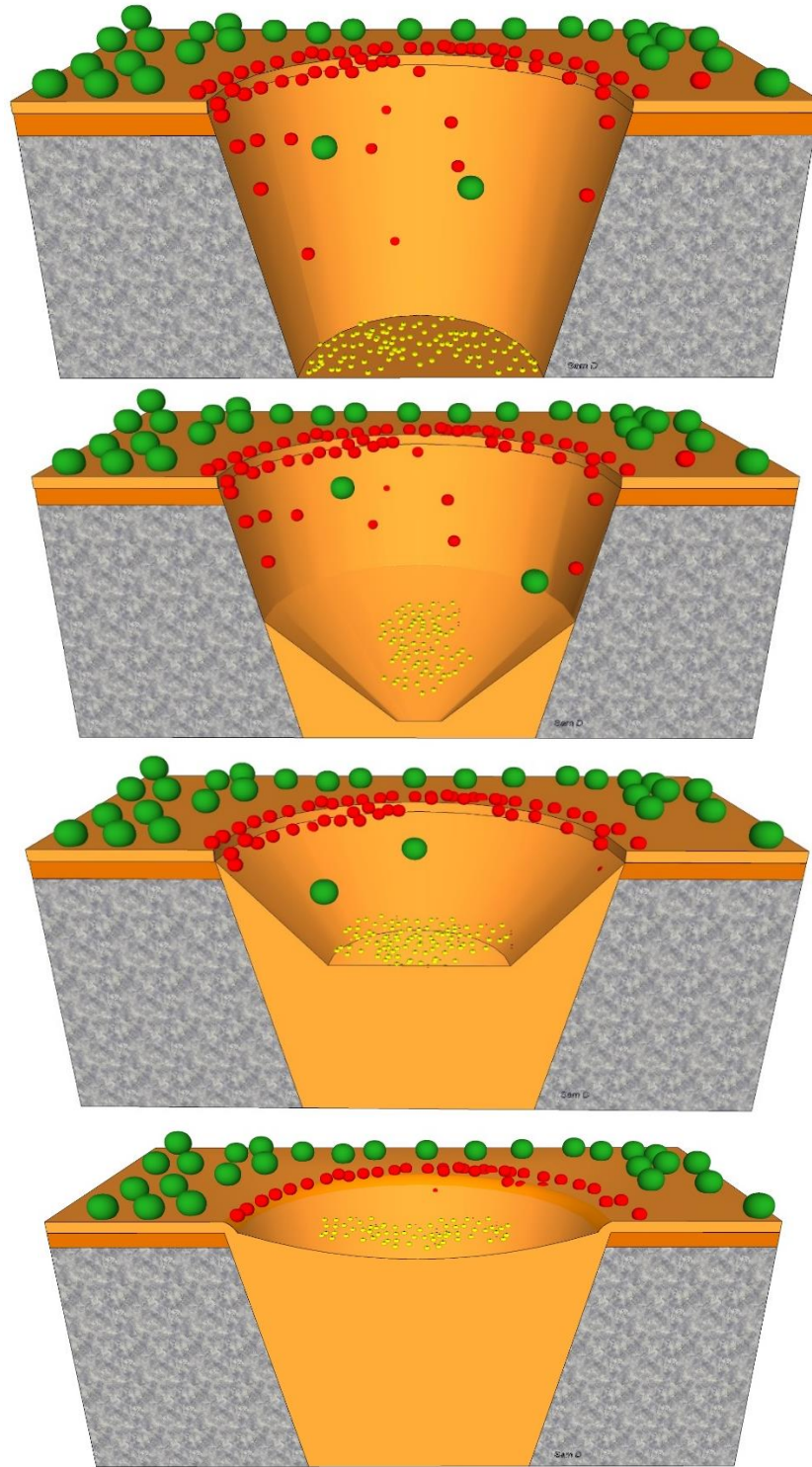


Figure 1. Schematic representation of bottom-up filling
CONDITIONS AND BATH COMPONENTS

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
Copper Sulfate (CuSO ₄ .5 H ₂ O)	230 - 250 g/L	240 g/L
Free Sulfuric Acid 66°Be Electronic Grade	55 - 65 g/L	60g/L
Chloride Ion (Cl ⁻)	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 ratio 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.

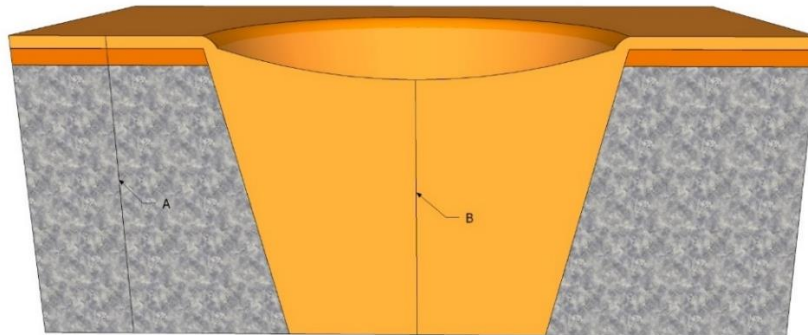


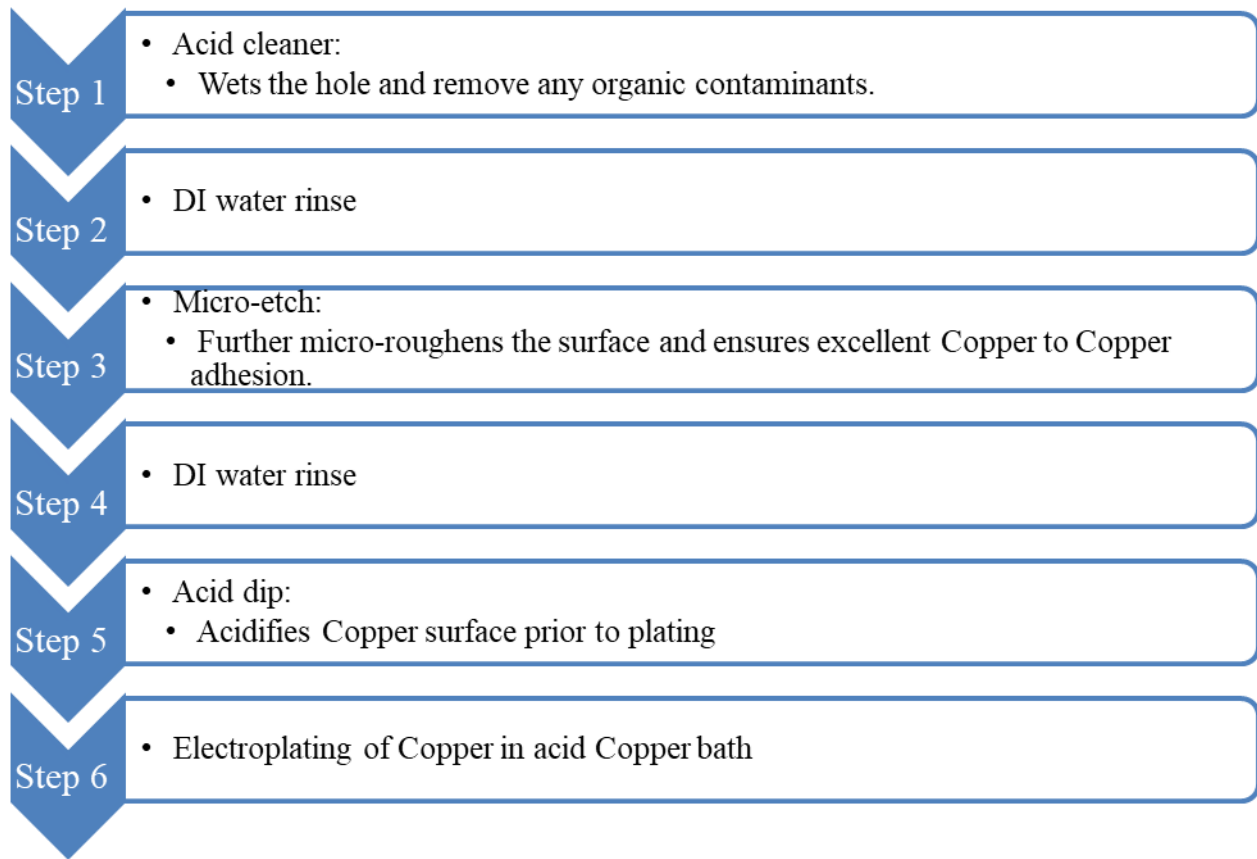
Figure 2. Via fill ratio

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 μm via can be filled even with only 10 μm 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 with results 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 in a via fill shown in figure 5. Via diameter 150 μm and depth 100 μm was seamlessly filled without any issue. Surface was flat and the deposit was bright with surface Cu thickness at only 8-11 μm .

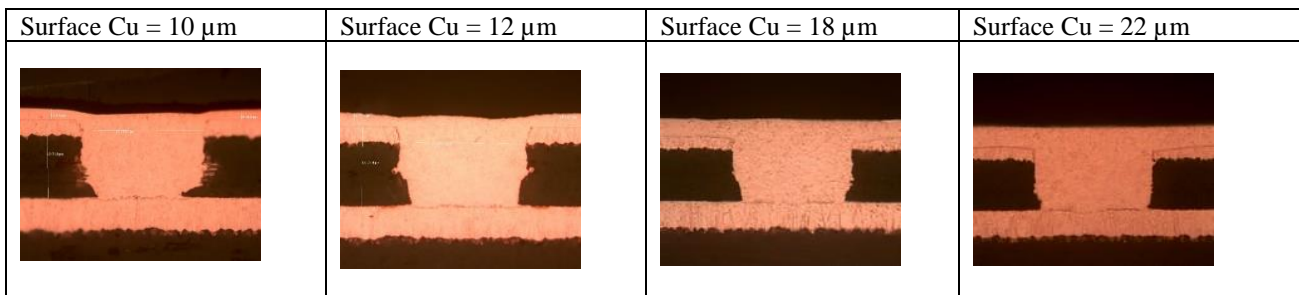


Figure 3. Via fill performance of 125 x 75 μm with different surface Cu.

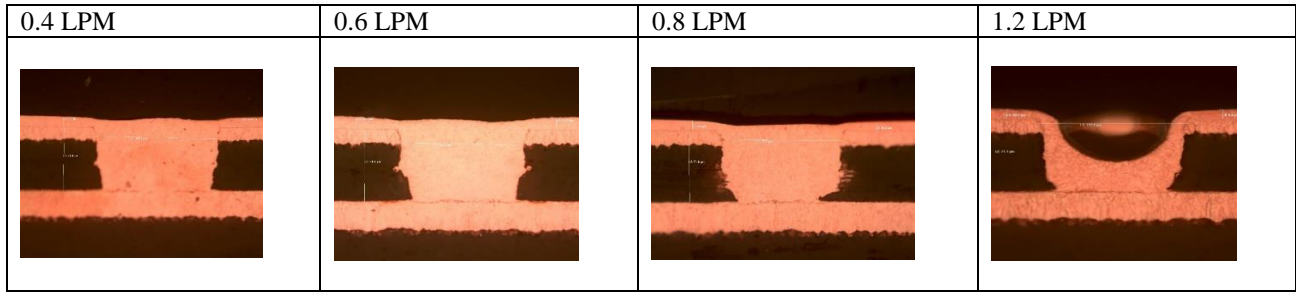


Figure 4. Via fill performance of 125 x 75 μm with different solution flow rates 0.4, 0.6, 0.8, 1.2 liters per minute (LPM)

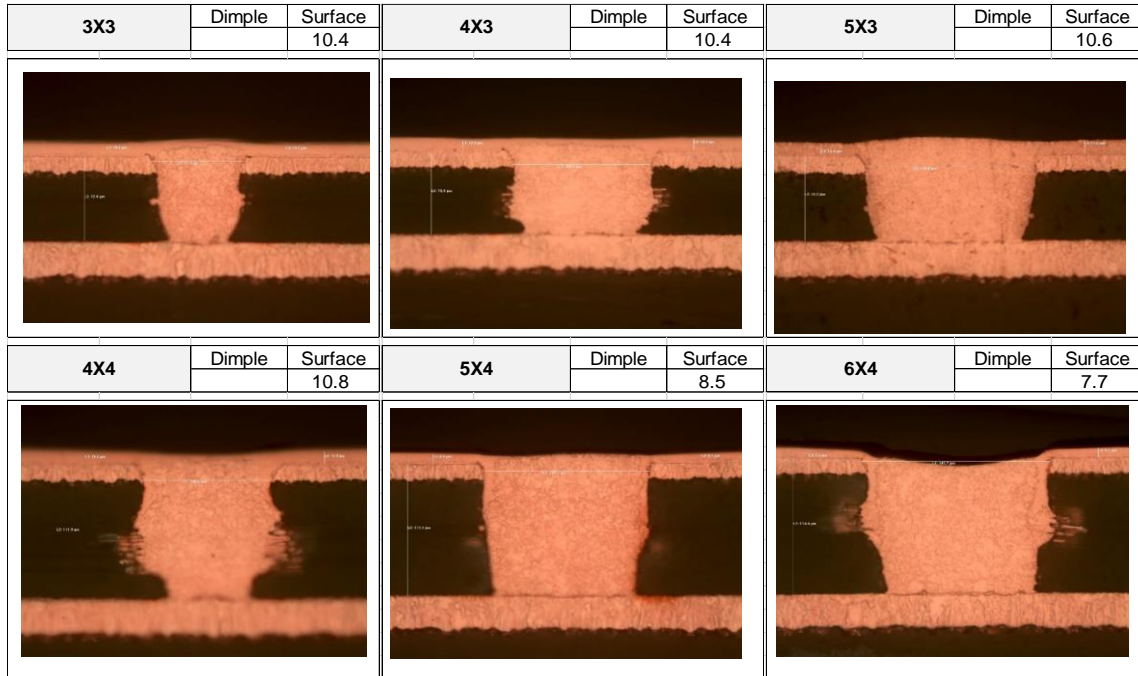


Figure 5. Typical via fill capability for different via diameter and depth at surface Cu ~ 8 – 11 μm .

Total Organic content (TOC) of the bath was obtained for the fresh and aged bath. According to the data summarized in 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 more environmentally benign and hassle-free in terms of waste treatment.

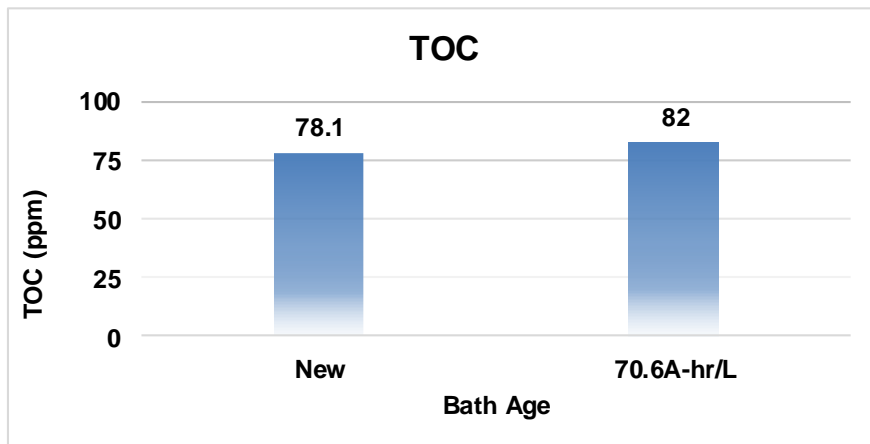


Figure 6. Total Organic Content of the new bath and aged bath

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.

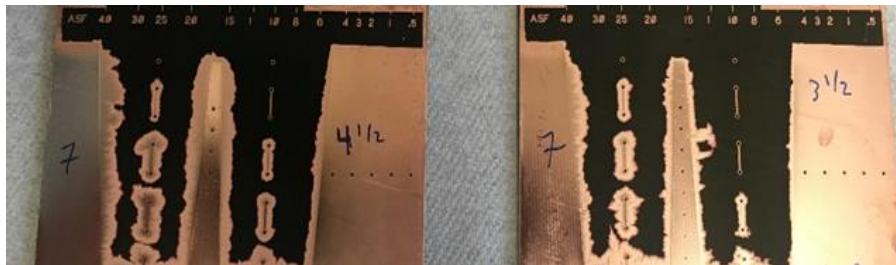


Figure 7. Propagation results for direct metallization applications

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.

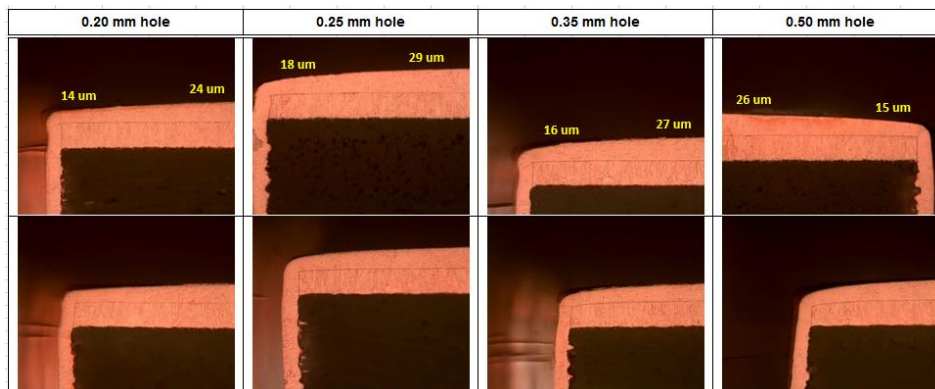
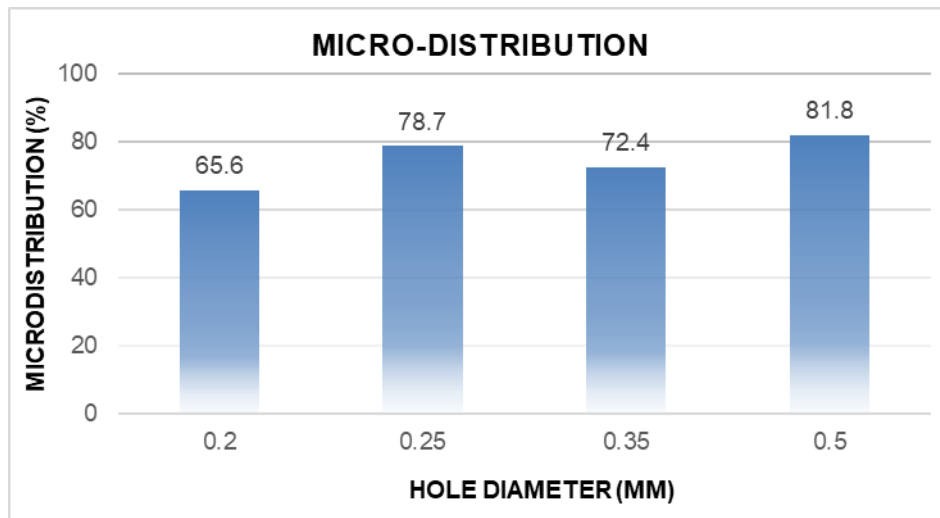


Figure 8. Throw power for 1.6 mm board thickness

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.

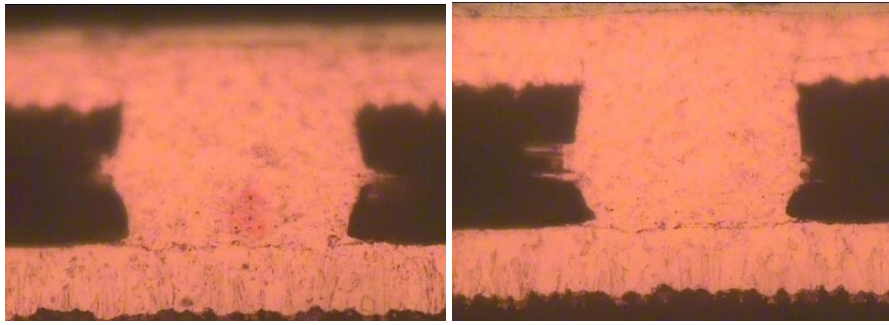


Figure 9. Solder float results

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.

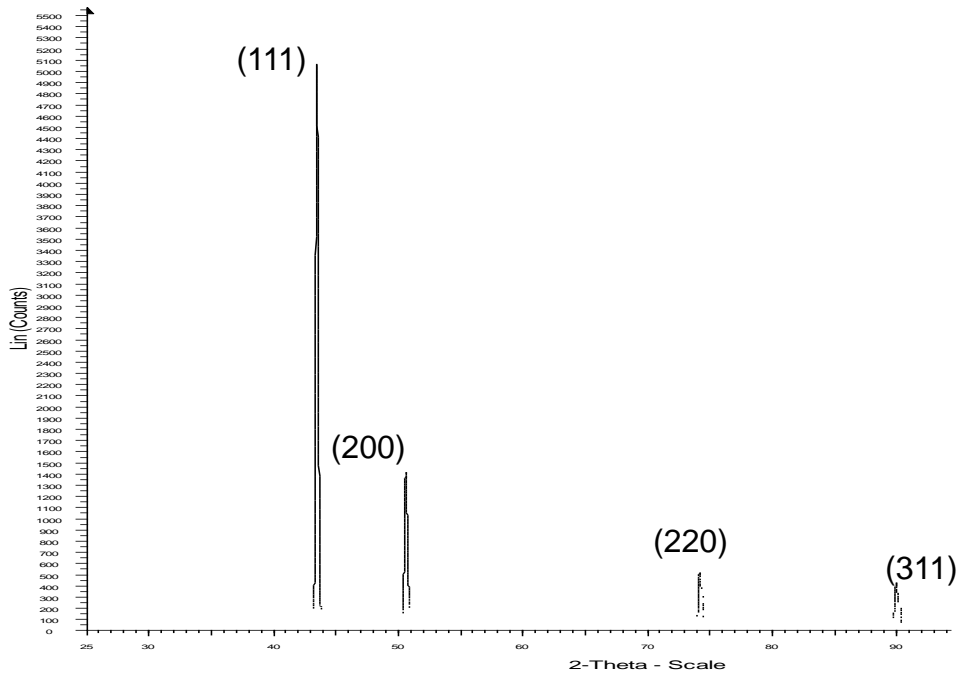


Figure 11. X Ray Diffraction pattern for Cu deposit plated using current formula

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

- β = Line broadening at the FWHM in radians.
- θ = Bragg angle.
- λ = 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.2). The data show no substantial changes in the crystal size, which agrees with the FIB images 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 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 (001)):

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

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 ($\Sigma I_{00l}^0 / \Sigma I_{hkl}^0$). The maximum 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.

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

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

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

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

Crystal plane	Lotgering Factor			
	0 Ah/L	50 Ah/L	100 Ah/L	150 Ah/L
(111)	0.29	0.11	0.16	0.23
(200)	- 0.08	0.03	-0.02	-0.03
(220)	-0.04	-0.12	-0.02	-0.05
(311)	-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 using production analysis equipment, 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]
Product A_0	0.008	< 0.002	< 0.002	< 0.05
	0.005	< 0.002	< 0.002	< 0.05
Product A_50	0.005	< 0.002	< 0.002	< 0.05
	0.004	< 0.002	< 0.002	< 0.05
Product A_100	0.007	< 0.002	< 0.002	< 0.05
	0.007	< 0.002	< 0.002	< 0.05
Product A_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 for 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 test method standard. 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—A production mechanical property test 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.

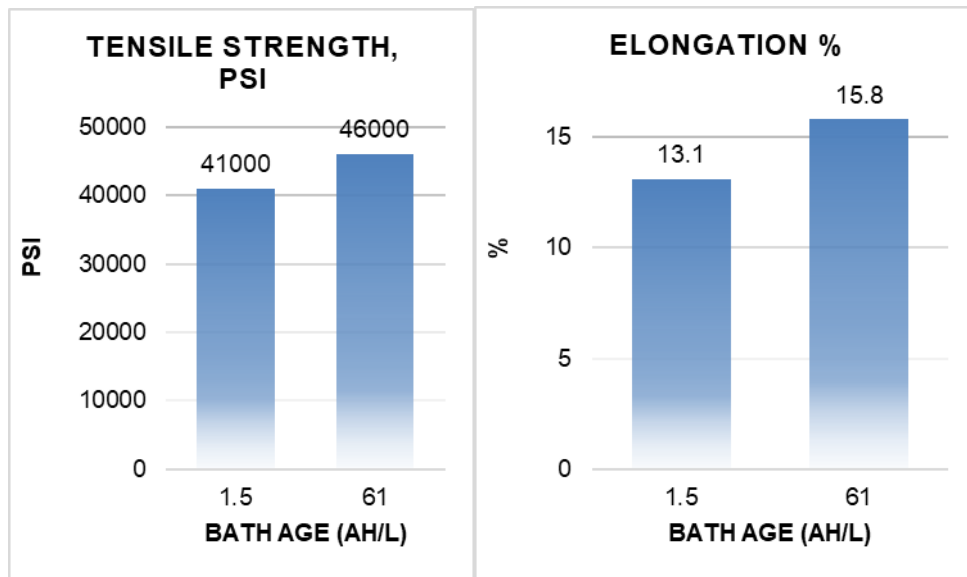


Figure 12. Tensile Strength and Elongation of the plated deposit.

CONCLUSIONS

In summary, a new via fill chemistry is introduced in this paper. The formulation showed excellent via fill capability, with minimum surface Cu. Over bath age very low TOC was observed and insignificant foreign element uptake in the copper deposit was observed. Evaluation of structure showed stable crystal structure during aging, with a slightly preference on the (111) plane. The hardness of the plated deposit was 79 ± 8 HV_{0.05} regardless of 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.

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Advanced Cu Electroplating Process for Any Layer Via fill Applications with Thin Surface Copper

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MacDermid Enthone Electronic Solutions

Product A is an advanced, direct current acid copper system offering excellent via filling with reduced plated surface copper for Any Layer Build applications

Key features:

Fill microvias up to 7 mils x 4 mils

Dimple < 5 μm

Surface Copper < 12-15 μm

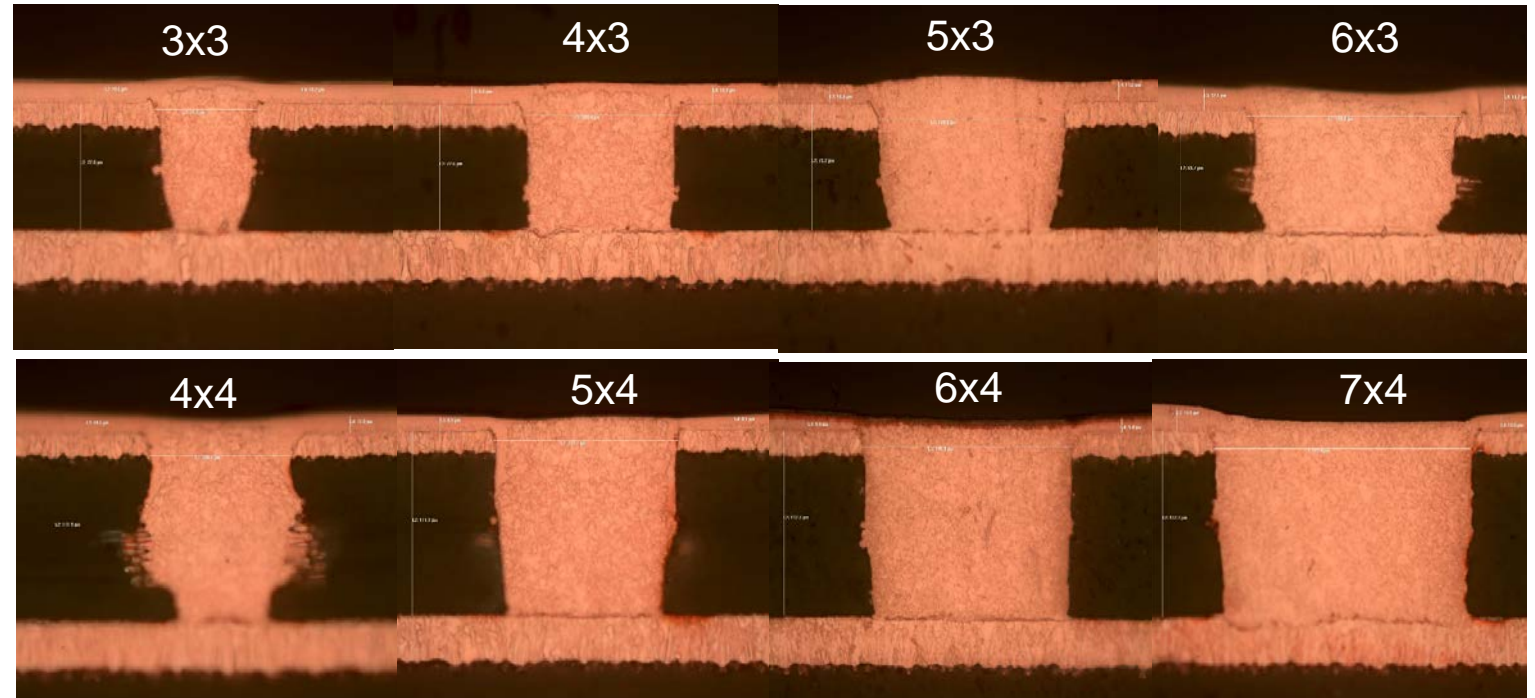
Bright Appearance

No predip required

No flash plate required

Compatible with direct metallization
or electroless copper

All components analyzable by CVS



Process Cycle and Operating Parameters

Bath Make-up:

Make-up	Chemistry	Concentration
VMS	CuSO ₄	240 g/L
	H ₂ SO ₄	60 g/L
	Cl ⁻	50 ppm
Additives	Wetter	10 ml/L
	Brightener	1.5 ml/L
	Leveler	1.5 ml/L

Equipment And Plating Cycle:

Plating Tank - Eductor agitation

Plating Cycle – Dependent upon via size

Anodes - Insoluble

Panel Type – Tested with DTV-MV panels

- High Cu / Low Acid for better via fill performance

Process Cycle and Operating Parameters



- Preclean process
 - Proper cleaning, wetting and activation of the copper within the via
- Plating process
 - Ensure solution transfer within the via
 - Supply critical additives for bottom up filling
 - Minimize any tendencies for cavities
- Current / Solution flow
 - Minimize the potential for cavities in small or poorly drilled microvias

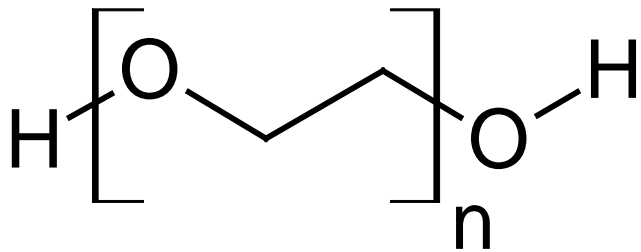
Plating Components Inorganic

- **Sulfuric acid**
 - Principal function is to provide conductivity of the solution
- **Copper sulfate**
 - The source of copper ions that are plated out onto the cathode
- **Chloride**
 - Enhances the adsorption and inhibition effect of the wetter.
 - Act as binding sites for the polyglycols.
 - Helps the corrosion of copper phosphorous anode

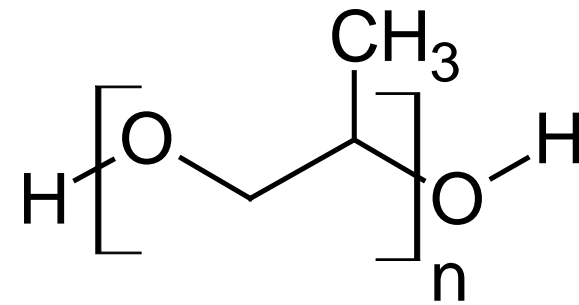
Plating Components Organic

Wetter (suppressor)

- High molecular weight polyglycols
- Form a complex with chloride and are adsorbed onto the cathode and inhibit transfer of brightener and leveler.
- Increase activation energy and slow the plating rate.



Polyethylene Glycol

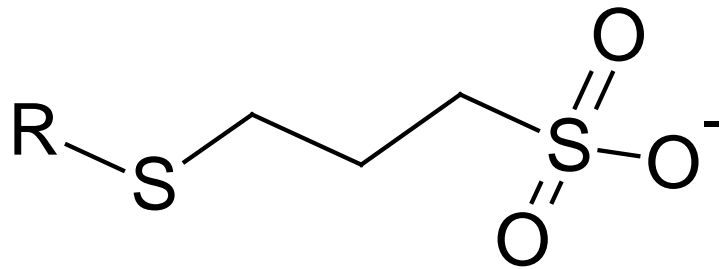


Polypropylene Glycol

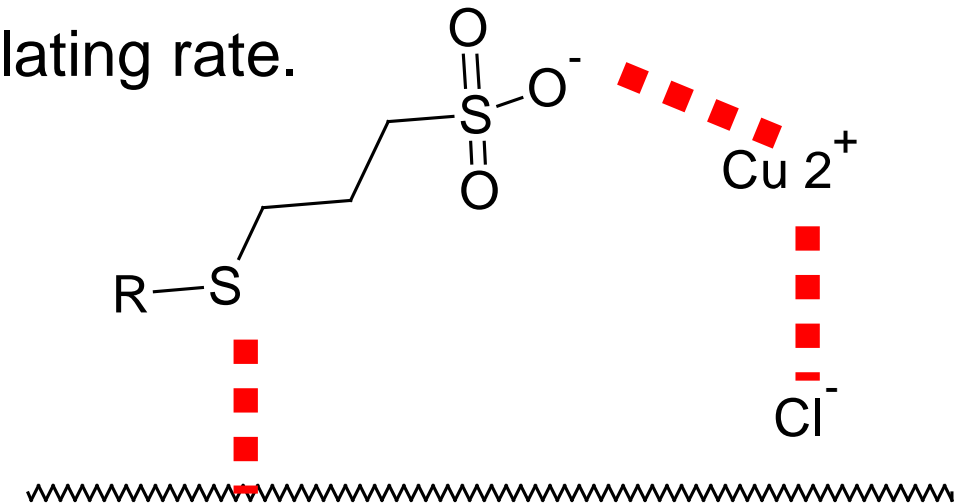
Plating Components Organic

Brightener

- Sulfur containing organic compounds
- Grain refiners
- Increases rate of nucleation versus build up of existing nuclei.
- Lower activation energy and allow increased plating rate.



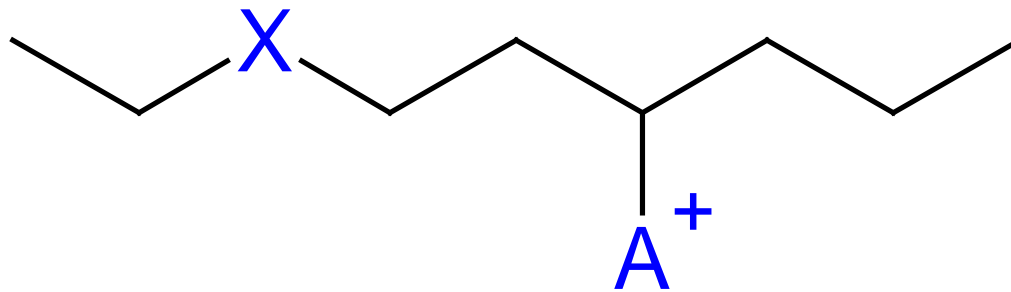
Sulfur Compound



Plating Components Organic

Leveler

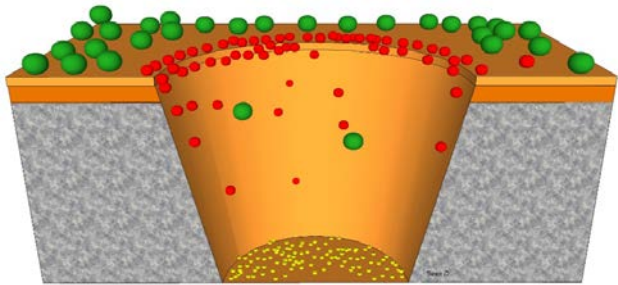
- Adsorbs onto specific locations such as corners and peaks of base materials.
- Act as suppressors, decrease plating rate
- Increase activation energy



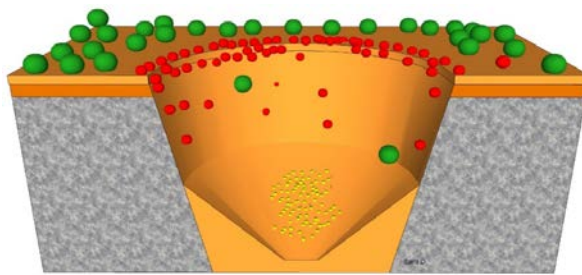
Leveler Compound

Filling Mechanism

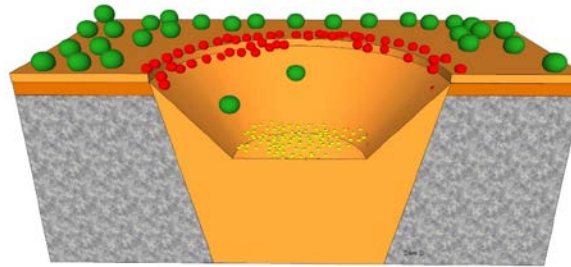
CURVATURE-ENHANCED-ACCELERATOR COVERAGE (CEAC) MECHANISM



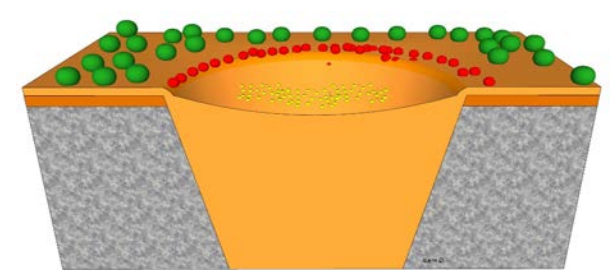
Preferential Adsorption of additives



Accelerator gets concentrated at the bottom of the via

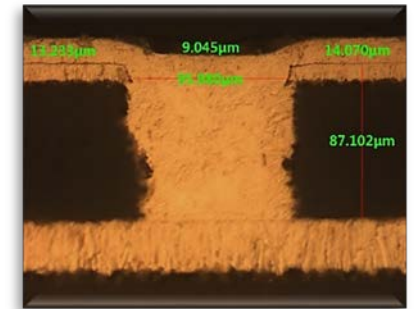
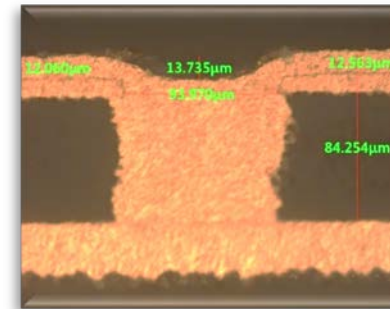
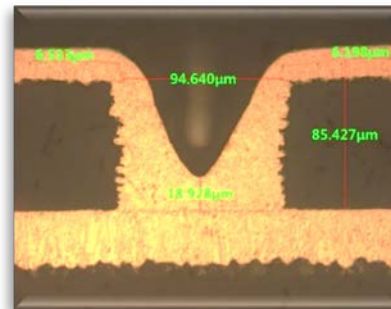
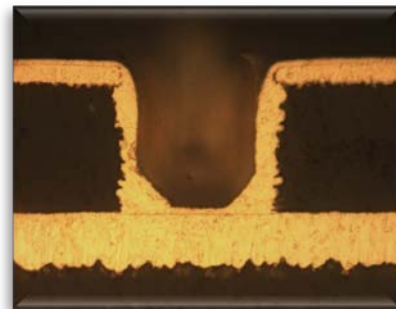


Accelerated bottom up growth

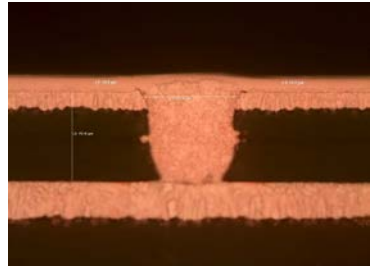
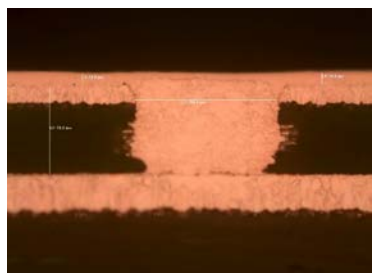
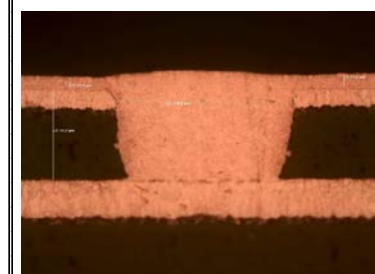
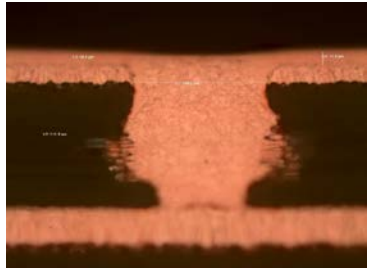
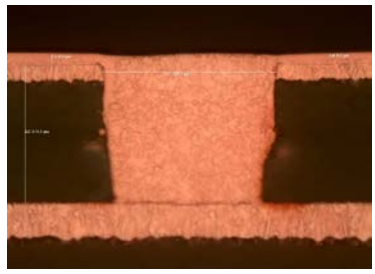
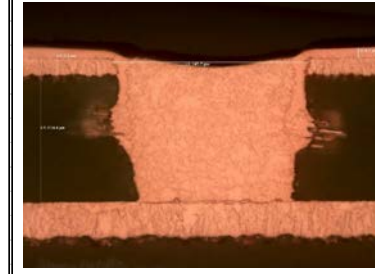


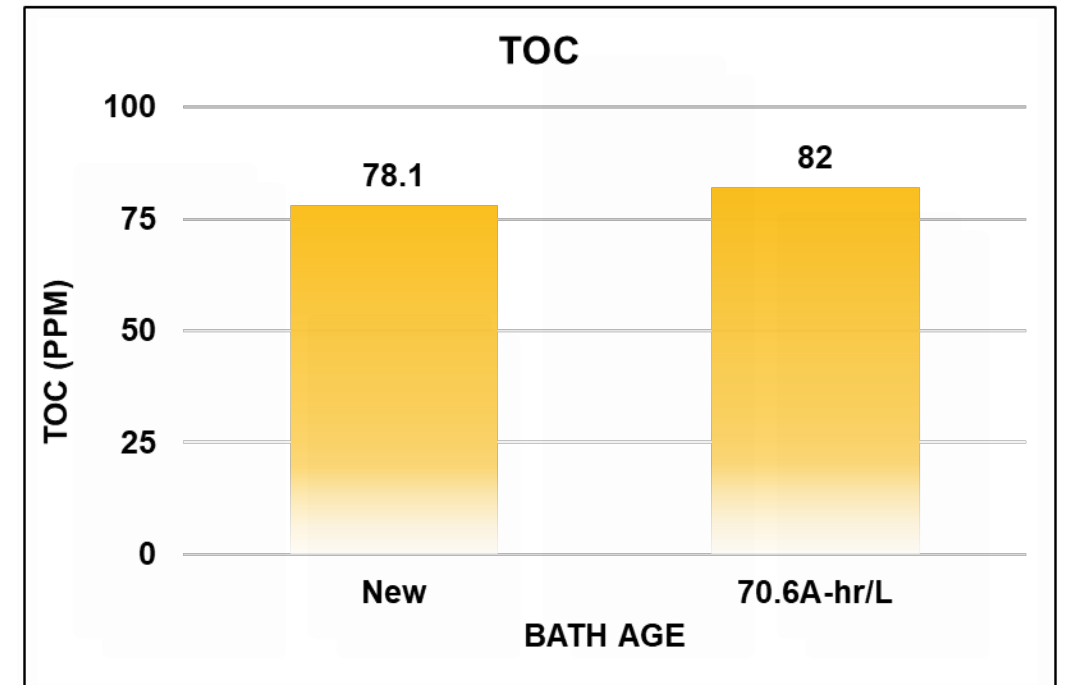
Accelerator diffuses out of the via

- Brightener
- Leveler
- Wetter



Performance

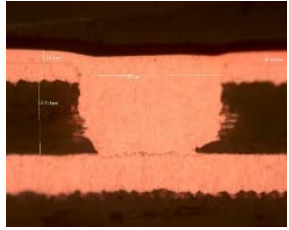
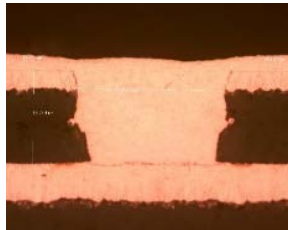
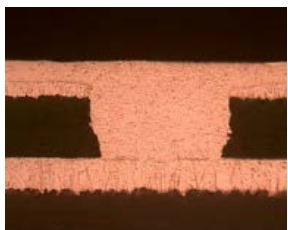
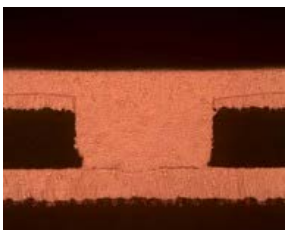
3X3	Dimple	Surface	4X3	Dimple	Surface	5X3	Dimple	Surface
		10.4			10.4			10.6
								
4X4	Dimple	Surface	5X4	Dimple	Surface	6X4	Dimple	Surface
		10.8			8.5			7.7
								



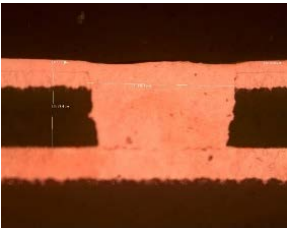
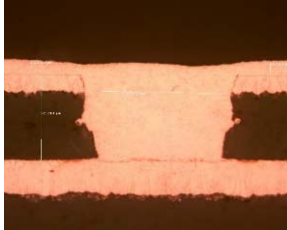
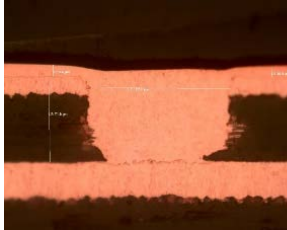
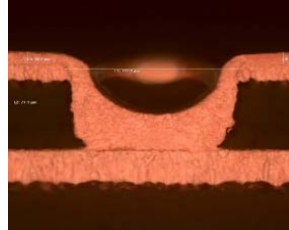
- Excellent fill at low surface Cu
- Low total organic content (TOC) after bath age

Via fill performance - 125 x 75 μm

At different surface Cu.

Surface Cu = 10 μm	Surface Cu = 12 μm	Surface Cu = 18 μm	Surface Cu = 22 μm
			

With different solution flow rates

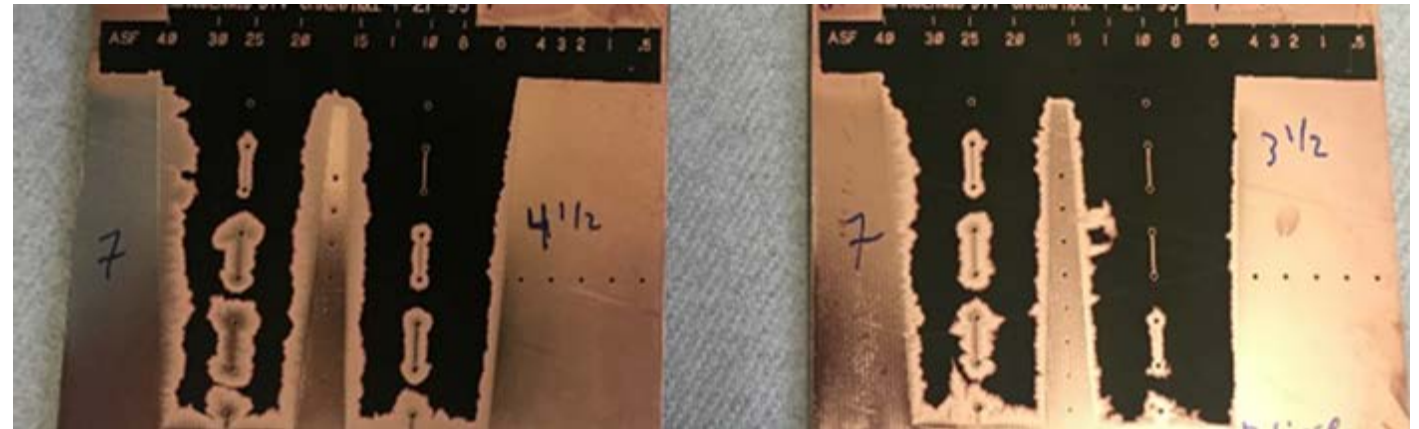
0.4 LPM	0.6 LPM	0.8 LPM	1.2 LPM
			

- Excellent fill, with different surface Cu
- Flat via top
- Wide range of flow rate

Compatibility with direct metallization

Propagation testing was run on four Direct Metallization processes, in Hull cell 1 A, for 10 min

Trial	Panel propagation	
	HCD	LCD
1	7/8	4.5/8
2	7/8	3.5/8



- Excellent propagation at high current density
- Compatible with direct metallization

Physical Properties

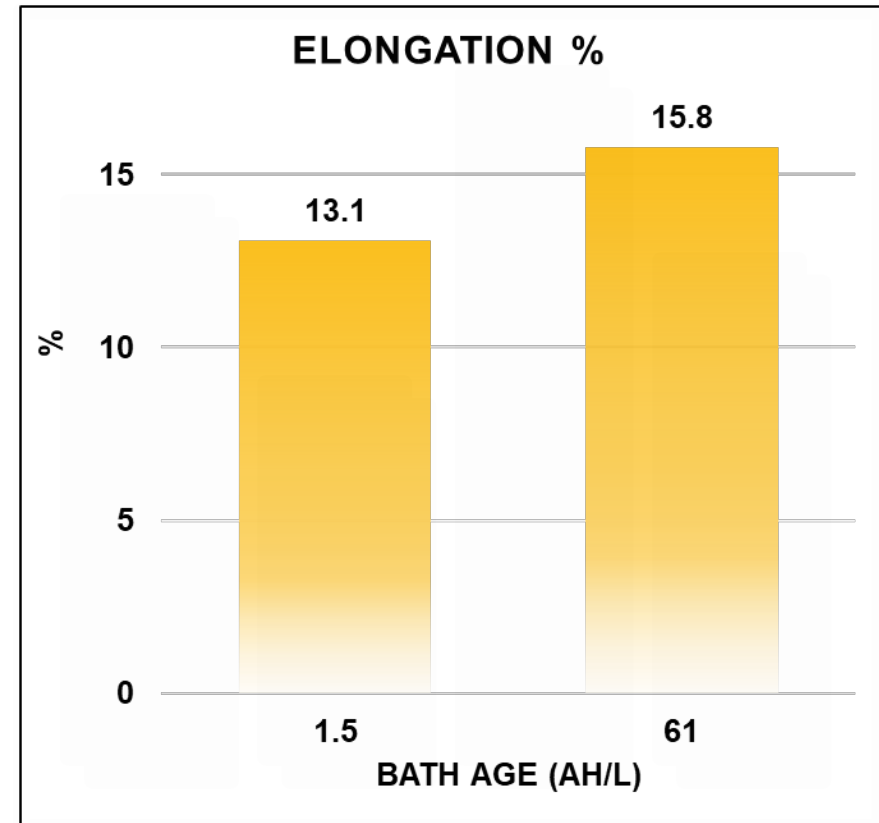
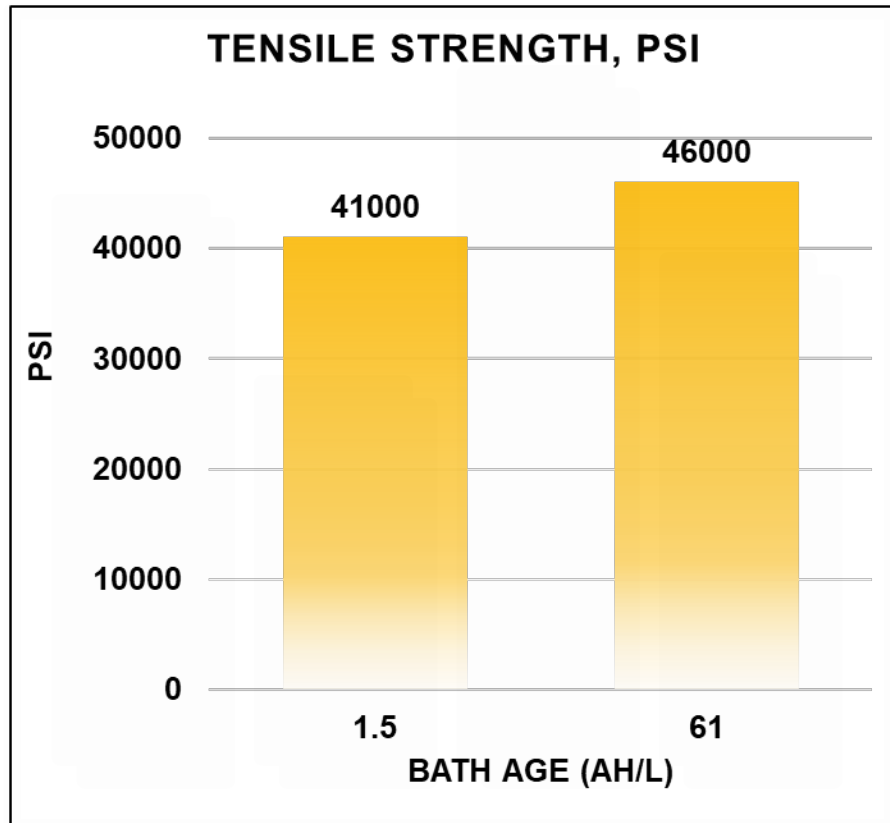
- Hardness of the deposit was approximately 105 HVN100



Load, g/f	Hardness, VHN			
	1st point	2nd point	3rd point	average
10	110	102	94.6	102.2
50	99	102	106	102.3
100	103	106	106	105.0

- Bright uniform deposit.
- Evenly etched if chemical reduction of copper thickness is necessary

Physical Properties – Tensile strength and Elongation



- Tensile strength and elongation passed minimum IPC standards

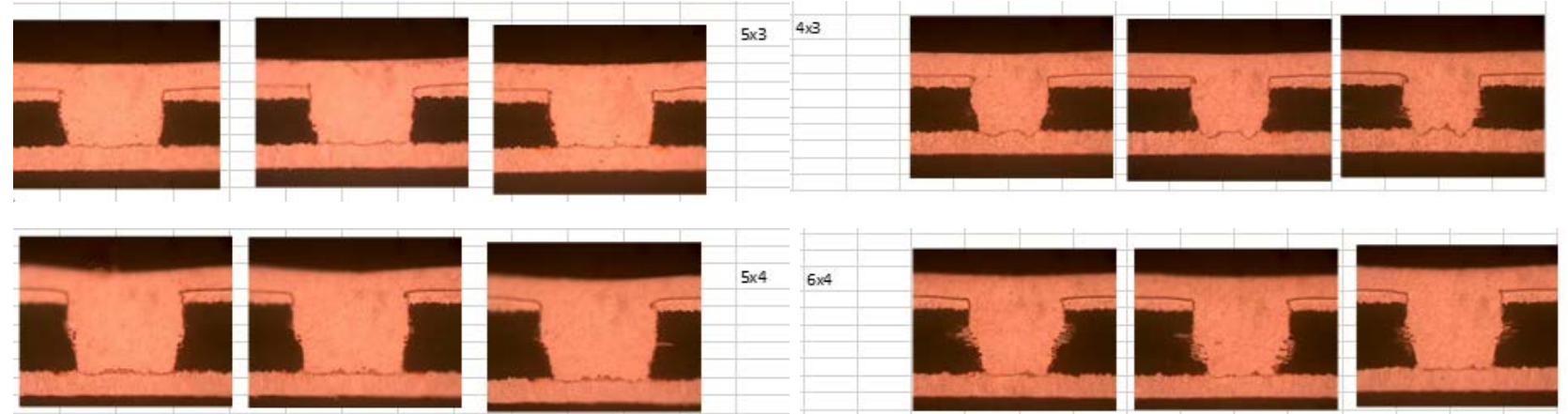
Thermal Properties – 15x Reflow and Solder Shock



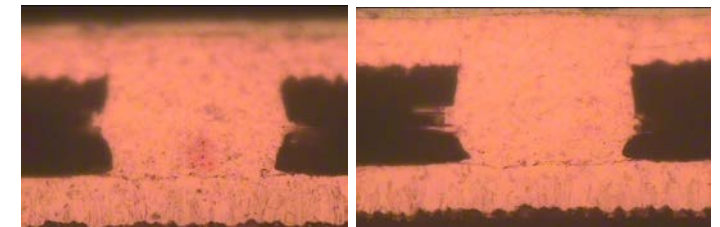
PW= 59%							
	Max Rising Slope	Soak Time 150-215C	Reflow Time 217C	Peak Temp			
3	2.1	19%	72.7	-6%	59.4	-4%	245.5
5	2.2	38%	72.2	-5%	57.1	-19%	245.1
7	2.1	29%	73.1	-6%	56.0	-26%	244.5
9	2.2	47%	73.1	-5%	51.1	7%	247.1
Delta	0.2		2.9		5.0		2.6

Process Window:			
Solder Paste: Keester EM907			
Statistic Name	Low Limit	High Limit	Units
Max Rising Slope (Target=2.0) (Calculate Slope over 20 Seconds)	0.0	2.5	Degrees/Second
Soak Time 150-215C	60	120	Seconds
Time Above Reflow - 217C	45	75	Seconds
Peak Temperature	235	255	Degrees Celsius

- 15x Reflow on full panel

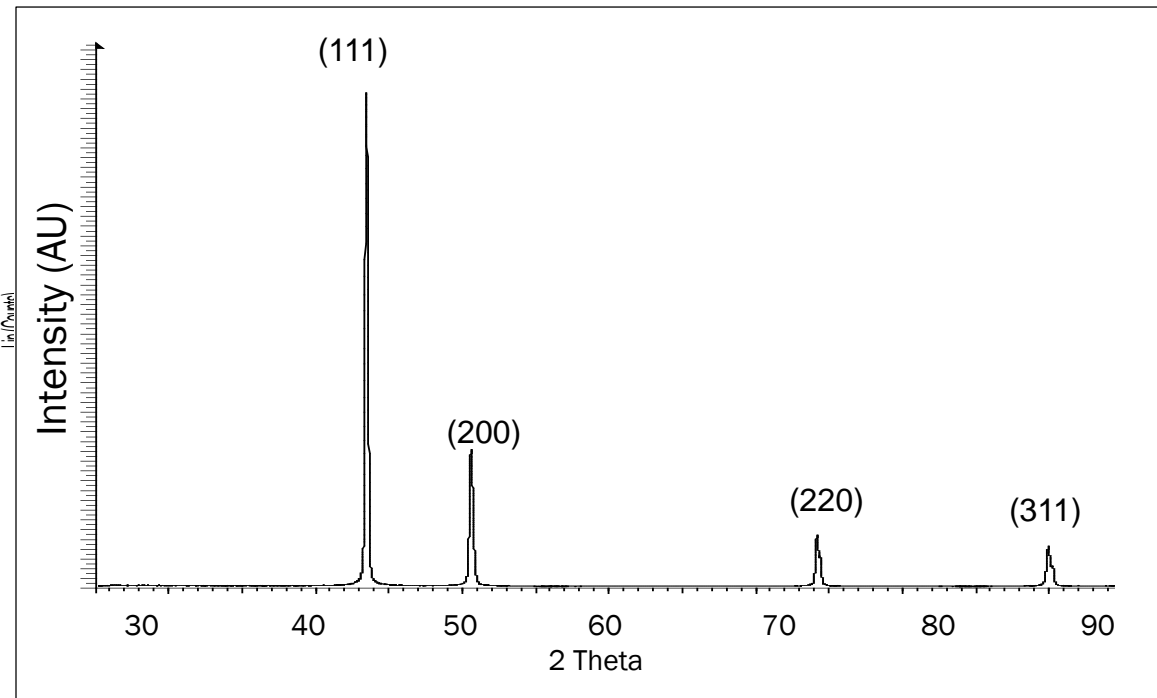


- 6 X Solder shock test @ 288 ° C



- No separation at target pad or via wall after 15X reflow or 6X Solder shock

Structural Properties -XRD



Data	Literature	0 Ah/L	50 Ah/L	100 Ah/L	150 Ah/L
(111)	100	100	100	100	100
(200)	46	28.4	45.7	38.4	35.2
(220)	20	10.4	12	14.6	10.5
(311)	17	8.4	9.9	8.3	7.6
Lattice Constant [Å]	3.615	3.613	3.611	3.613	3.613
Density [g/cm³]	8.92	8.953	8.963	8.952	8.948

- Typical XRD pattern for Cu, all the peaks matched with literature.
- No significant change in Lattice constant or Density with bath age

Structural Properties -XRD

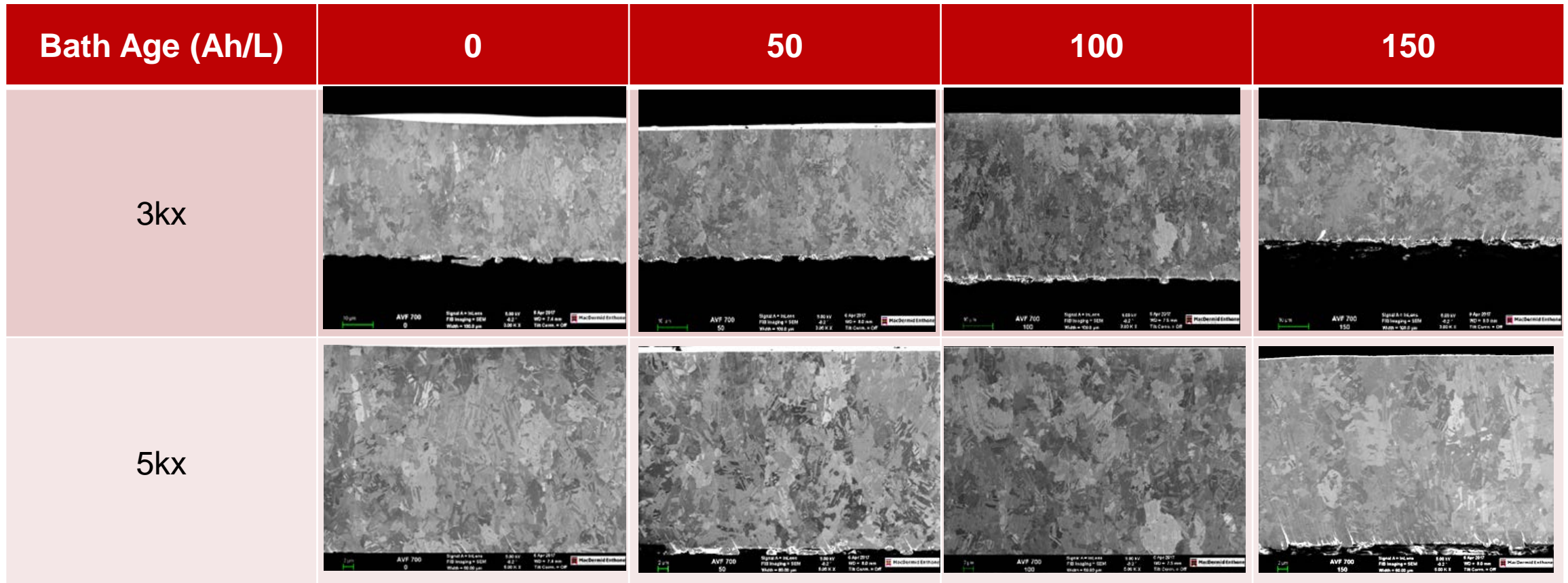
Crystal plane	Lotgering Factor			
	0 Ah/L	50 Ah/L	100 Ah/L	150 Ah/L
(111)	0.29	0.11	0.16	0.23
(200)	- 0.08	0.03	-0.02	-0.03
(220)	-0.04	-0.12	-0.02	-0.05
(311)	-0.04	-0.04	-0.05	-0.05

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

- Preferred (111) orientation - most dense plane

- No significant change in the Crystal size with bath age

Structural Properties – Scanning Electron Microscopy



- No change in the grain structure after bath age

Structural Properties – Scanning Electron Microscopy

Bath Age (Ah/L)	C [% w/w]	S [% w/w]	N [% w/w]	Cl [% w/w]
0	0.008	< 0.002	< 0.002	< 0.05
	0.005	< 0.002	< 0.002	< 0.05
50	0.005	< 0.002	< 0.002	< 0.05
	0.004	< 0.002	< 0.002	< 0.05
100	0.007	< 0.002	< 0.002	< 0.05
	0.007	< 0.002	< 0.002	< 0.05
150	0.006	< 0.002	< 0.002	< 0.05
	0.006	< 0.002	< 0.002	< 0.05

Impurity analysis –

C and S - combustion IR method (e.g. with production analysis equipment),
 N by using carrier gas hot extraction (CGHE)
 Cl X-ray fluorescence spectroscopy (XRF spectroscopy).

- Very low impurity incorporated in to the deposit
- Impurity amount did not increase as bath age

Summary



- Excellent via filling of vias up to 7 mils in diameter and 4 mils deep
- Minimum surface copper means less/no copper reduction necessary after plating



- Bright Even Appearance
- No Predip – Less pretreatment steps
- No Formaldehyde – Stress-free handling and waste treatment



- Compatible with direct metallization
- Low TOC and impurities



- Fine grain structure
- Fully analyzable by CVS and common analytical tools

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OF **TECHNOLOGY**

THANK YOU!

THANK YOU!