INNOVATIVE HIGH THROW COPPER ELECTROPLATING PROCESS FOR METALLIZATION OF PCB

Maria Nikolova, Ph.D. and Jim Watkowski
MacDemid, Inc.
Waterbury, CT, USA
mnikolova@macdermid.com and jwatkowski@macdermid.com

ABSTRACT

Copper electroplating is widely used in the electronic industry for fabrication of electronic devices. It is particularly explored for fabrication of printed circuit boards and semiconductors. High throwing power copper electrolytes are becoming increasingly important due to the electronic industry requirements for manufacturing of high aspect ratio circuit boards.

Utilizing an innovative DC plating technique a reliable copper metallization of through holes can be achieved. The parameters of this plating technique have been studied and are presented in this paper. Excellent Throwing Power in PCB through holes, and blind micro-vias are achieved. Two formulas are developed. The copper distribution is superior across the PCB for the two formulations. Plated copper is bright, smooth, and leveled, especially inside the through holes, including at low CD, 5ASF. Plated copper exhibits excellent ductility and tensile strength. The process is easily controlled be CVS analysis and Hull cell tests and can be applied to both panel and pattern plate.

Key words: Copper electroplating, PTH, PCB metallization.

INTRODUCTION

Electronic industry mass production utilizes acid copper plating in fabrication of printed circuit (PCB) boards and semiconductors. A uniform deposition of copper is required for the development of complex conductor structure, especially for the high aspect ratio through hole plating. With smaller diameter holes and thicker panels more difficult task is faced with respect to plating distribution. If the deposited copper is insufficient at the walls of the through holes, the result will be rejection of the entire PCB. Organic compounds are added to copper plating bath during the production of PCBs, chip carriers, and semiconductors [1-2]. They act as levelers and brighteners enabling as uniform a deposition of copper as possible on different regions of the PCB including through holes and BMVs. 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.

It is shown in this paper that utilizing an innovative DC copper plating system a reliable copper metallization of high aspect ratio PCB can be achieved. Two high throw formulas have been developed. The first one allows for plating in the CD operating range of 10 – 45 ASF. The MD measured is = > 85% for the AR 8:1. This formula in particular is suitable for VCP applications where the plating times are restricted. The second formula is developed for plating especially at low CD to meet the requirement for high AR PCB using a DC process. The operating CD range is 5 – 25 ASF. MD of = >90% for AR 8:1 is achievable. Various plating parameters were 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 and the thermal characteristics of the deposits were examined. Panel and pattern plate were tested.

ACID COPPER PLATING PROCESS

Sulfuric acid copper bath are now dominating the industry. A plating solution contains copper sulfate, sulfuric acid, chloride ions, and organic additives that control the deposition process and the quality of the plated coatings. Typically the organic additives include brightener (grain refiner), suppressor, and leveling agents [3-8]. Throwing power of an electroplating bath depends on solution conductivity, electro-deposition kinetics (the slope of the polarization curve), cell geometry, and temperature. The plating uniformity is influenced by the solution chemistry and solution agitation conditions.

The purpose of this work was to determine the effect of various organic additive species and their concentration on the throwing power. The suppressors (high molecular weight polyether compounds and polyoxyalkylene glycols) in the presence of chloride ion have a strong polarizing influence producing a large decrease in the exchange current density. Addition of brightener such as sulfopropyl sulfides to an acid copper electrolyte acts as a depolarizer producing an increase in exchange current density. As an example, the maximum depolarization effect for SPS (disodium bis (sulfopropyl) disulfide) was observed at a concentration of 5 ppm. Above this concentration of the brightener, the surface blocking effect of the adsorbed brightener mitigates the depolarizing effect to some degree. The brightener spices are much smaller molecules than the wetter molecules and so the adsorption of the wetter does not appear to significantly interfere with the adsorption of the brightener.

Leveler adsorbs preferentially near the most negatively charged sites of the cathode (PCB), thus slowing down the plating rate at high current density areas. The organic additives affect the secondary current distribution and control the physical mechanical properties of the metal deposits considerably important being tensile strength and elongation.

In this study a low organic additive system was combined with a high free acid to copper ratio electrolyte.

TEST VEHICLES

The test vehicles used in the process evaluation were 1.6 mm, 2.4 mm, and 3.5 mm thick boards with various sized through holes. The through holes diameters were 0.2 mm, 0.25 mm, 0.35 mm and 0.5 mm. The through holes AR varied from 3.2 to 17.5. All geometries incorporated in the test vehicles were simultaneously plated.

The process flow includes the following operations:

- Acid cleaner: Wets the hole and removes light soils.
- Rinse
- Micro-etch: Etches undercuts and remaining debris and ensures excellent copper to copper adhesion.
- Rinse
- Acid dip: Acidifies copper surface prior to plating.
- Deposition of copper in acid copper bath

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.

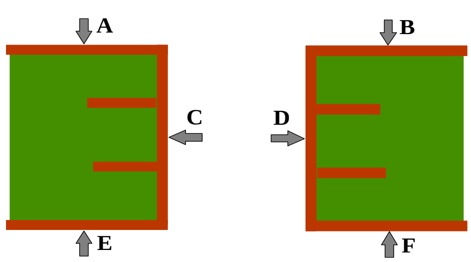


Figure 1. Cross Section of Plated Panel

BATH CONSTITUENTS

The bath constituents for the two formulas studied and the plating parameters are given in Tables 1 for MacuSpec HT 100 and in Table 2 for MacuSpec HT 200. The process can be used at varying basic electrolyte compositions to optimize performance. The best results were achieved with a low copper, high acid concentration solution. Plating at low current densities allowed for reliably plating of higher AR through holes.

Table 1. High Throw 100 Bath Constituents

COMPONENT	MacuSpec HT 100 Target	MacuSpec HT 100 Range
$CuSO_4 x 5H_2O$	50 g/l	45 – 80 g/l
Sulfuric Acid	250 g/l	220 – 300 g/l
Chloride	60ppm	45ppm – 85ppm
Wetter	10 ml/l	8 - 20 ml/l
Brightener	0.6 - 1.0 ml/l	0.5 – 1.2 ml/l
Leveler	1.5 ml/l	1.2 – 2.0 ml/l
Temperature	72 – 73 F (22 - 23^{o}C)	68 – 80 F (20 – 27^{o}C)
Current Density	10 ASF – 45 ASF (1.1 ASD – 4.9 ASD)	

Table 2. High Throw 200 Bath Constituents

COMPONENT	MacuSpec HT 200 Target	MacuSpec HT 200 Range
$CuSO_4 x 5H_2O$	30 - 50 g/l	30 – 75 g/l
Sulfuric Acid	270 - 250 g/l	220 – 300 g/l
Chloride	60ppm	45ppm – 85ppm
Wetter	6 ml/l	5.5 - 8 ml/l
Brightener	1.0 ml/l	0.8 – 1.2 ml/l
Leveler	6 ml/l	5.5 – 8 ml/l
Starter	2.5 ml/l	2.0 – 3.5 ml/l
Temperature	72 – 73 F (22 - 23^{o}C)	68 – 80 F (20 – 27^{o}C)
Current Density	5 ASF – 25 ASF (0.5 ASD – 2.7 ASD)	

RESULTS

Micro-Distribution Measurements

The difficulties for plating through holes depends not only on the aspect ratio but on the particular board thickness and hole vehicle design (thickness & hole diameters). The graphs show diameter, e g. at the same aspect ratio it would be easier to plate the thinner board with a smaller diameter, than a thicker board with a larger diameter. The difficulty of plating (IR drop in the hole) is influenced by the thickness of the board or length of the hole by a squared term and it is inversely proportional to the though hole size (diameter).

We included in our study plating at various current densities, CD depending on test the data obtained from the Microdistribution measurements.

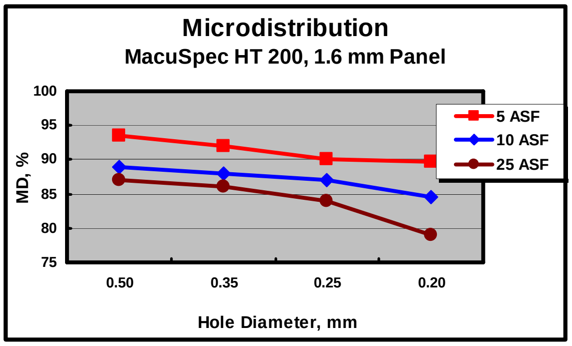


Figure 2. Microdistribution for 1.6 mm Thick Panel Aspect Ratio: 3.2, 4.6, 6.4, and 8

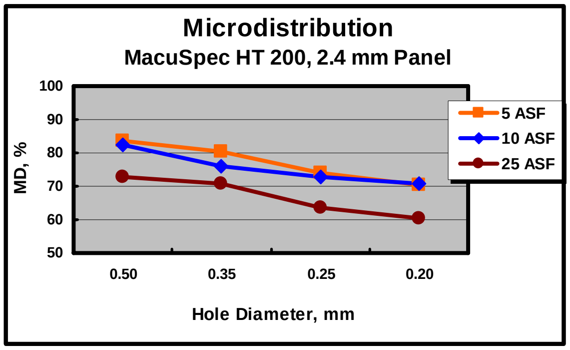


Figure 3. Microdistribution for 2.4 mm Thick Panel Aspect Ratio: 4.8, 6.9, 9.6, and 12

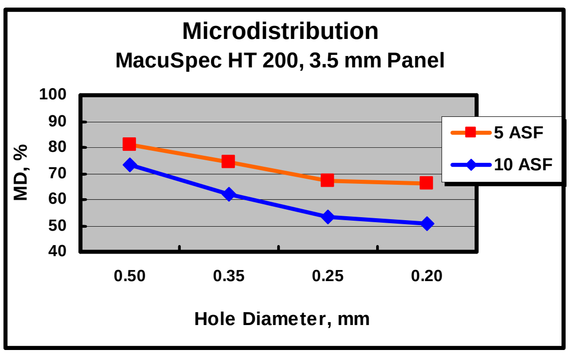


Figure 4. Microdistribution for 3.5 mm Thick Panel Aspect Ratio: 7, 10, 14, and 17.5

Process Features

Surface Appearance and Structure

Under plating condition shown in Table 1 and Table 2 MacuSpec HT 100 and MacuSpec HT 200 processes produce bright, smooth, and uniform metal deposit on the panel surface. Plated copper is leveled inside the holes. No thin copper at the knee of the holes is observed. Plating thickness is consistent throughout the barrel.

Figures 5 through 9 show pictures of cross sections taken from test vehicles plated under various conditions.

Figure 5. Cross Section of 0.20 mm Through Hole in 1.6 mm Panel Plated at 10 ASF, AR = 8

Figure 6. Cross Section of 0.50 mm Through Hole in 1.6 mm Panel Plated at 10 ASF

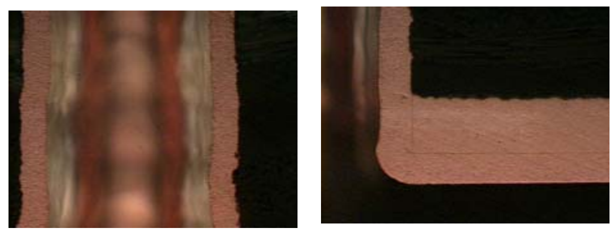
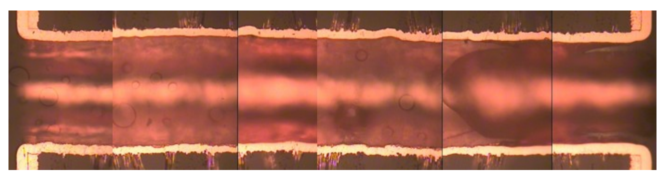
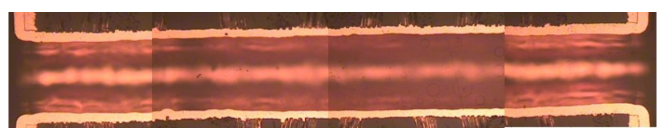


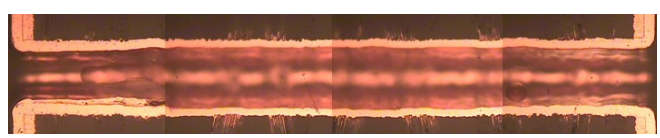
Figure 7. Cross Section of 0.25 mm Through Hole in 1.6 mm Panel Plated at 15 ASF



a)



b)



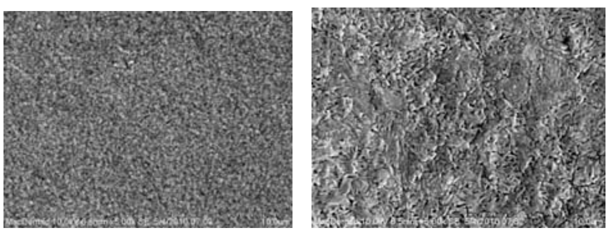
c)

Figure 8 - Cross Sections Through Holes with diameter **a)** 0.35 mm ; **b)** 0.25 mm; **c)** 0.20 mm; 2.4 mm Test Panel Plated at 10 ASF

Figure 9. Cross sections of 0.20 mm Through Hole in 3.5 mm Panel Plated at 5 ASF

SEM Study

Fine grained deposits were obtained from these electrolytes. SEM study of plated copper surface was performed before and after etching to examine the surface morphology. It revealed small equiaxial grain size structure. No particular texture was determined (Figure 10).



a) **b)**

Figure 10. SEM **a)** Panel surface; **b)** Panel Surface after Etching; Plating at 15 ASF.

SEM pictures were taken from cross sections of the panel surface (higher current density regions) and from the inside of the through holes (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 11 through 14. They show a uniform grain orientation.

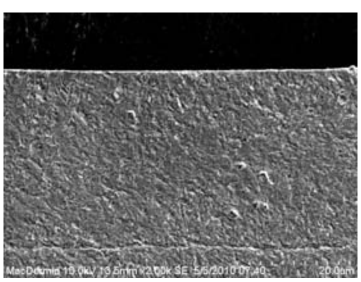


Figure 11. SEM 2000x
Cross Sections of the Surface; 1.6mm Thick Panel Plated at 15 ASF.

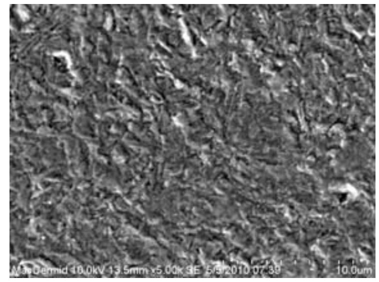


Figure 12. SEM 5000x
Cross Sections of the Surface; 1.6mm Thick Panel Plated at 15 ASF.

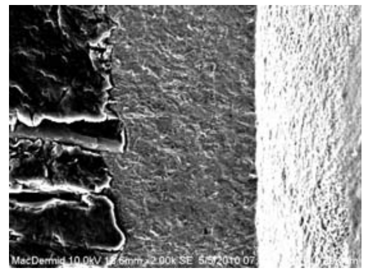


Figure 13. SEM 2000x
Cross Sections of 0.2 mm Through Hole; 1.6mm Thick Panel Plated at 15 ASF

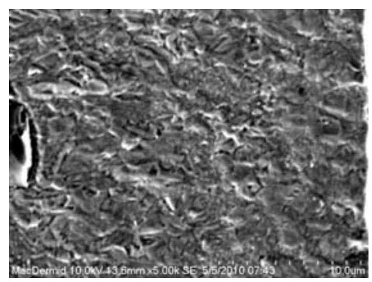


Figure 14. SEM 5000x
Cross Sections of 0.2 mm Through Hole; 1.6mm Thick Panel Plated at 15 ASF

Properties

The physical mechanical properties of electroplated metals are function of solution composition, including nature of the organic additives, plating current density, operating temperature, impurities. Fine-grained copper is usually stronger and harder than columnar or fibrous copper.

Tensile Strength and Elongation of plated copper were measured in accordance with IPC TM-650, 2.4.18.1. Plated copper foils are baked for 4 hours at 125^{o}C then tested on an Instron pull tester. The values of Tensile strength and elongation were calculated according to the equations:

Tensile Strength =
Maximum load (lbs) / Mean cross sectional area (in^2)

Elongation =
(Length at break – Original gage length) x 100 / Original gage length

Vertical and horizontal pulls were measured. The values for the two high throw formulas HT 100 and HT 200 were very close. The results from the measurements are demonstrated for Macuspec HT 200 in Figures 15 and Figure 16. Increasing plating over-potential increases the nucleation rate and leads to formation of deposits with higher Tensile Strength. This is shown in Figure 15: increasing the deposition current densities from 5 ASF up to 25 ASF increases the values of the Tensile Strength measured. Plating at all conditions met or exceeded IPC specifications.

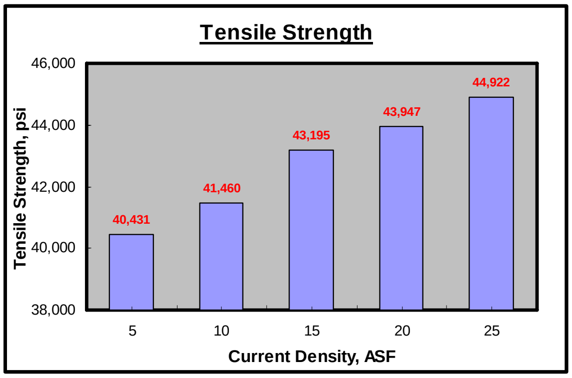


Figure 15. Tensile Strength versus Current Density

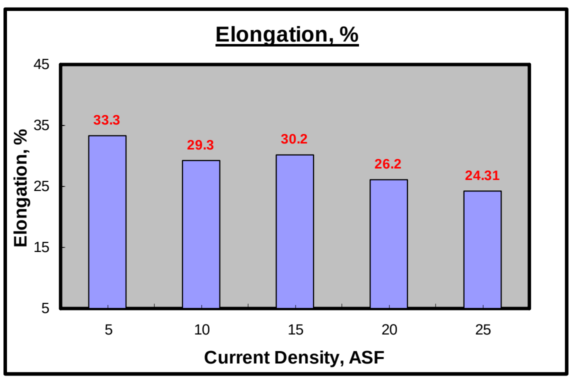


Figure 16. Elongation versus Current Density

Thermal Characteristics

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 5, 10, 15, 20, and 25 ASF. The thermal integrity was excellent for all of the through hole sizes plated. Neither corner cracks nor barrel cracks were observed across the current densities range studied as shown in Figure 17. Plated copper deposits met industry standards for Solder shock resistance.

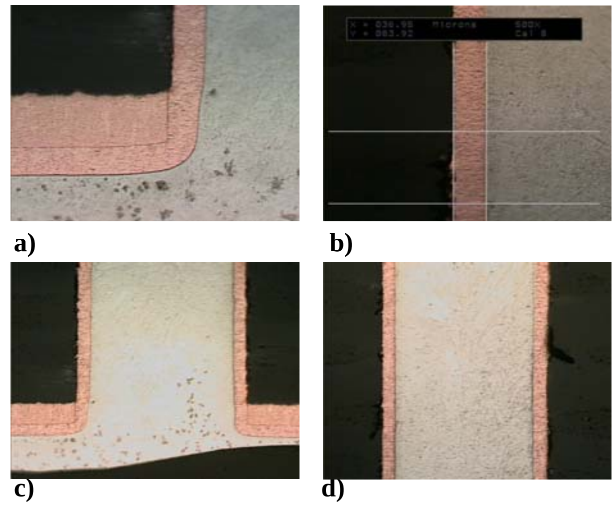


Figure 17. Cross Section of 0.5 mm Through Hole After 6x Solder Shock; Panel Plate at 10 ASF; Bath at 153 Ah/L; **a)** Corner, 500x; **b)** Middle of the Barrel, 500x; **c)** Corners, 200x; **d)** Middle of the Barrel, 200x

Pattern Plate

The High Throw copper plating process is suitable for Pattern Plate.

Customer 2.2 mm thick pattern boards were plated at 10 ASF and 15 ASF. The surface copper was bright, smooth, and no flares around the through holes were observed. Deposited metal was uniform and Microdistribution met the customer requirements. The measured MD values corresponded to the MD values shown in the Figures 3.

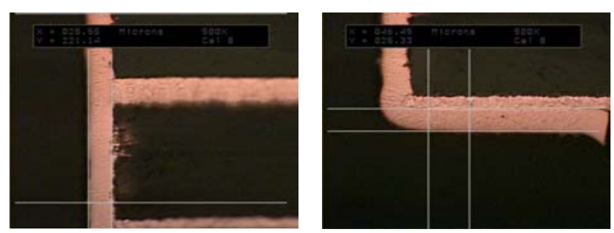


Figure 18. Pattern Plate, Current Density 10 ASF

Figures 19 through 21 illustrate Pattern plate of 1mm thick customer panel, 0.3 mm diameter through holes, 100 µm and 140 µm traces. Plating was performed at 15 ASF for 75 minutes and at 20 ASF for 50 minutes. Microdistribution was measured to be >100%.

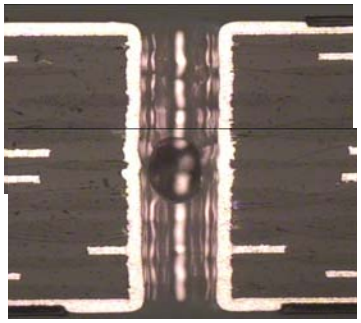


Figure 19. Pattern Plate; Current Density 20 ASF; 50 minutes

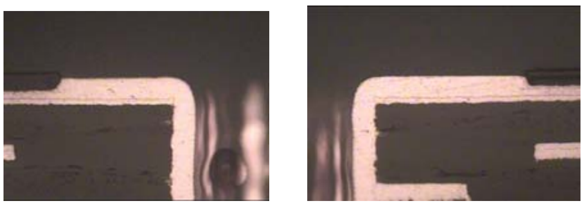
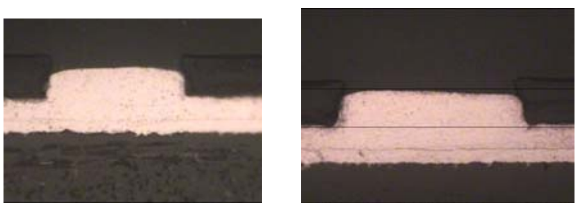


Figure 20. Pattern Plate; Current Density 15 ASF; 75 minutes



a) **b)**

Figure 21. a) 4 mil Trace; **b)** 5.5 mil Trace

BATH CONTROL

The bath performance can easily be monitored by using CVS analysis. Hull cell tests also can be used for bath control and solution chemistry adjustment.

CONCLUSIONS

Two formulas MacuSpec HT 100 and MacuSpec HT 200 for direct current (DC) copper electroplating were developed to meet the need of high throwing power baths for reliable metallization of electronic devices. Throwing Power is excellent in through holes and blind micro-vias at relatively high effective CDs. It exceeds the throwing power of conventional acid copper processes.

MacuSpec HT 100 and MacuSpec HT 200 processes represent low organic additive systems, combined with a high free acid to copper ratio electrolytes. They have a wide operating window.

MacuSpec HT 100 allows for plating in the CD operating range of 10 – 45 ASF (1.1 – 4.9 ASD). The micro-distribution measured is = > 85% for aspect ratio 8:1. This formula in particular is suitable for VCP applications where the plating times are restricted.

MacuSpec HT 200 is developed for plating at low CD to meet the requirement for high aspect ratio PCB. The operating CD range is 5 – 25 ASF (0.5 – 2.7 ASD). Micro-distribution of = > 90% for aspect ratio 8:1 is achievable.

The copper distribution is superior across the PCB for the two formulas. Plated 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 and can be applied to both panel and pattern plate.

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, January 1998, pp. 405-411.

[3] Yung, Edward K., "Plating of Copper into Through-Holes and Vias," J. Electrochem. Soc., 136, 1989, pp. 206-215.

[4] J.J. Kelly, C. Tian, A.C. West, J. Electrochem. Soc., 146, 1999, pp. 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, pp. 103.

[6] T. Pearson, Transaction of Institute of Metal Finishing, vol. 83, No 4, 2005, pp. 171-180.

[7] J.P. Healy, D. Pletcher, M. Goodenouth , J. Electroanal. Chem., 338, 1992, pp. 179.

[8] Wei Wang and Ya-Bing Li, J.Electrochem. Society, 155 (4) 2008, D263-D269.