

## MICROFAB<sup>®</sup> MP2500

Acid Copper Electroplating Process for Advanced Packaging Applications

Limited Release

Product Code: 251651

### DESCRIPTION

The **MICROFAB MP2500** is a **high-speed copper** process engineered for mega pillars applications. It provides exceptional within-wafer (WIW), within-die (WID), and within-feature uniformity (WIF, TIR). The product is formulated, packaged, and quality controlled, according to the needs of the semiconductor industry. A series of electrolyte conditions may be used based on specific process requirements. In addition, **MICROFAB MP 2500-A, MICROFAB MP 2500-S, and MICROFAB MP 2500-L are the necessary additives** used to ensure superlative performance for high speed copper electrochemical deposition (ECD).

READ ENTIRE TECHNICAL DATA SHEET BEFORE USING THIS PRODUCT

### PROCESS COMPONENTS REQUIRED

The following material is normally recommended for a typical start up and operation of deposition rates up to 6  $\mu\text{m}/\text{min}$ . Where higher throughput is necessary, ECD around 8  $\mu\text{m}/\text{min}$ , the copper concentration should be adjusted.

- **COPPER VMS concentrations will vary by tool, pattern, and rate. Please consult the tool vendor for choice and MacDermid Enthone representative for settings.**

Additives that are also included in the **MICROFAB MP 2500** processes are as follows:

- **MICROFAB MP 2500-A**
- **MICROFAB MP 2500-S**
- **MICROFAB MP 2500-L**

Each product is pretested and ready to use to make up an initial operating solution for its respective plating applications. It is purified, performance tested, and packaged for semiconductor applications in 1, 4, and 20 liter clean room compatible packages. Consultation with the tool vendor can help determine the advantages of high metal/high speed formulations.

Other solution chemistries available for minor adjustments include:

- **MICROFAB SC COPPER SULFATE** contains 270 g/L copper sulfate (equal to 69 g/L of copper metal). It is used to replace copper in heavy drag-out situations.

### MAKE UP PROCEDURE

1. Proper leaching and cleaning of the tank is mandatory. The tank must be leached with a solution containing 45 g/L trisodium phosphate and 7.5 g/L sodium hydroxide heated to 60 °C for 4 to 8 hours. Scrub tank lining with solution to remove any dirt, oils or surface soils. Be careful to flush thoroughly with several rinses to remove all residues of sodium (filled and drained).
2. Then leach with 10% by volume sulfuric acid heated to 50 °C for 8 hours. Again, flush tank with water.
3. Empty the tank.
4. Carefully pour or pump recommended amount of **Concentrated Copper, Sulfuric Acid, and Hydrochloric Acid** into tank.
5. Copper anodes: new copper anodes must be cleaned of oils, organic materials, dirt, oxides and sulphides. If vapours degreasing is possible, this is the preferred first step toward removing grease and oil, and soils bound by these materials.
6. As an alternative to vapor degreasing, the anodes may be totally immersed in a hot, alkaline soak cleaner for at least one hour, followed by thorough rinsing. The anode skin must then be etched to uniform, matte pink copper in a solution of 120 g/L ammonium persulfate and 5 mL/L of concentrated sulfuric acid.
7. Etch the anodes for 10 to 20 minutes, followed by a thorough water rinse and a soak in 10% by volume sulfuric acid with a final rinse in deionized water.
8. Evidence of any smooth, shiny areas on the anodes at this point indicates an incomplete etch. Etch the anodes once again in a fresh persulfate solution or use a more aggressive etchant. Etchants of the peroxide/sulfuric type act well in removing copper anode skins due to their aggressive nature. Most of the commercially available stabilized etchants are suitable when prepared and used according to the manufacturer's recommendations. Follow the safety precautions given in the supplier's literature because these solutions are strongly acidic and are oxidizers. Rinse the anodes, treat in 10% by volume sulfuric acid and rinse once again as would be done with the ammonium persulfate etch procedure.
9. Rinse the anodes with deionized water and install into plating tool.
10. Pre-leached anode bags may be used in some applications where installation is recommended by the equipment vendor.
11. MP2500 system was designed for insoluble anodes. If using please skip step 12
12. Clean, prepare and use a copper "dummy" cathode panel or copper blanket seeded wafer for anode filming. Prepare enough cathode area to provide a cathode current density no greater than 1.0 ASD while filming the anode at 1.0 to 1.5 ASD anode current density. Plate the dummy cathode for ½ to 1 hour before adding **MICROFAB MP 2500** additives as described in the start-up section of this manual. Continue electrodeposition for approximately 4 hours maintaining additive concentrations by ampere-hour or by tool supplier's recommendation. During this time a black continuous film will form on the anodes.
13. When a uniform film on the anodes is achieved, remove the dummy cathode panels. The panels should have a uniform, satin, to bright pink deposit of copper.

14. Inspect each individual anode for the presence of the black film, taking care not to disturb the film. If there are any anodes which do not have the proper film overall, repeat the above filming procedure.
15. Leach string wound polypropylene filter cartridges at this time by immersing in boiling deionized water for 30 minutes, followed by thorough rinsing with deionized water. This process must be repeated until there is no evidence of foam or turbidity of the boiling water.
16. Install leached filter cartridges and start filtering the solution. The solution is now ready for production operation. Keep a record of ampere hours of use to determine replenishment volumes. Examples of process log sheets are available by contacting your local representative.

### EQUIPMENT

**Follow instructions from the tool manufacturer.**

**MICROFAB MP 2500** has a wide operating window. The optimum plating recipe will vary significantly depending on the tool platform (agitation, anode/cathode configuration, flow rate), open area on the wafer, and the complexity of the die pattern

Please consult with your Field Service Sales & Engineers for assistance in developing specific plating recipes for a given tool platform and wafer layout.

### OPERATING PARAMETERS

Parameter	Range	Optimum
Copper Concentration	58 to 70 g/L	*Consult Representative
Sulfuric Acid	95 to 105 g/L	100 g/L
Chloride Ion	45 to 100 ppm	Consult Representative
Temperature	27 to 48 °C	Consult Representative
Current Density	30 to 45 ASD	40 ASD
Anode to Cathode Ratio	~	2:1
<b>MICROFAB MP 2500-A</b>	2 to 4 mL/L	3 mL/L
<b>MICROFAB MP 2500-S</b>	5 to 7 mL/L	6 mL/L
<b>MICROFAB MP 2500-L</b>	2 to 4 mL/L	3 mL/L

\*It is strongly recommended that process optimization is performed on the customer's preferred tool platform using their wafers prior to establishing the Process of Record (POR).

\*The copper concentration will vary by pattern, rate and tool platform. Please consult your local representative.

## SOLUTION MAINTENANCE

### Copper Sulfate

**MICROFAB SC COPPER SULFATE** is used in the **MICROFAB MP2500** process to provide the proper concentration of copper ions. In operation, copper is replenished from the anodes. Fluctuations in the copper content of the solution may be compensated by adding **MICROFAB SC COPPER SULFATE** or bleeding solution as necessary. Add only specially pre-purified copper sulfate, **MICROFAB SC COPPER SULFATE** to the solution if bleed-and-feed process control is used.

### Copper Concentration and Anodes

The copper concentration of the electrolyte will change slightly with use and time. If there is an excessively high anode to cathode ratio, or if the solution is infrequently used, the concentration of copper in the electrolyte will rise steadily. When a solution is used infrequently and/or is taken out of service for longer than 1 week, remove all anodes and store in a tank of clean, deionized water. If left in the electrolyte, the high free acid will dissolve the copper.

### Sulfuric Acid

Sulfuric acid performs the principal function of maintaining high solution conductivity. Add only reagent or semiconductor grade acid to adjust the solution.

Note: Use only Reagent or Semiconductor Grade

### Chloride Ions

Chloride ions are essential to the promotion of proper anode corrosion characteristics. The process requires a nominal concentration of 45 to 105 mg/L (ppm) of chloride ion. The chloride content is easily increased, when necessary, by the addition of reagent grade hydrochloric acid.

Note: 0.024mL/L of 12N hydrochloric acid will increase the chloride concentration by about 10 mg/L (10 ppm).

### Additives

**MICROFAB MP 2500-A**, **MICROFAB MP 2500-S** and **MICROFAB MP 2500-L** are the additive solutions for the process. Additive consumption rate varies with different tool platforms, with or without membrane/anode bag on anode side, and various photoresists on wafer. Temperature does not show considerable impact on additive consumption rate. Below numbers are estimations based on historical data. Actual consumption rate needs to be determined for each installation.

### Maintaining Additives

**MICROFAB MP 2500-A**, **MICROFAB MP 2500-S**, and **MICROFAB MP 2500-L** are replenished based on a specific customer requirement or as provided by a specific tool supplier's feed algorithm. Additionally, the additive concentrations can be analyzed by CVS methodology.

#### Plating Consumption

- **MICROFAB MP 2500-A** is usually consumed at the rate of approximately 0.080 to 0.2 mL per ampere-hour.
- **MICROFAB MP 2500-S** is usually consumed at the rate of approximately 0.1 to 0.2 mL per ampere-hour.
- **MICROFAB MP 2500-L** is usually consumed at the rate of approximately 0.050 to 0.250 mL per ampere-hour.
- Additive consumption rate varies with different tool platforms. Temperature does not show a considerable impact on the additive consumption rate. The showing numbers are from field record as a reference. Actual consumption rate needs to be determined for each installation.

Following the initial addition of the **MICROFAB MP 2500 Additives** at start up, it may be determined that the higher replenishment figure (3 mL per ampere hour) will be required. Leached tanks and filter cartridges will have a tendency to absorb the additive until a saturation equilibrium is reached.

### Temperature

Control the temperature of the solution between 27 to 48 °C. The nominal operating temperature is process dependent. Temperatures above 42 °C increase the conductivity of the solution and result in high limiting current.

### Filtration

Continuous filtration for the removal of particulate matter is strongly recommended. Clean and leach cartridges or filter bags prior to use according to the solution make-up section of this document. Do not operate continuously with carbon filter cartridges, or addition agent will be removed from the solution.

Capacity of the pump and filter must be sufficient to turn over the complete volume of solution at least once per hour, preferably two or more times per hour. Pumps, fittings, pipes, valves, connections and filter must be of inert acid resistant materials. Duriron, plastic and hard rubber are recommended for pumps. PVC, PVDC, polypropylene and approved grades of rubber are suitable materials of construction for filter chambers and baffles.

### Anodes

Maintain the anode area between 2.0 to 3.0 times (2:1 nominal) the cathode plateable area (wafer) for the **MICROFAB MP 2500** process. Exercise care in the original determination of the anode area and take into consideration the increase in area due to fine features including vias and trenches. Anodes facing tank walls have only 85% of their full surface area anodically effective. Establish a maintenance program to replace anodes as consumed to keep the anode

to cathode ratio within the operating limits. A black film is formed on the anodes when the solution is plating. This film will remain on the anode when the solution is not in use. Take care not to disturb this film as it plays a major role in the performance of the solution. Properly filmed anodes effectively prevent the addition agents from being consumed at the surface of the anode and thereby decrease brightener consumption. If the film is disturbed, small copper fines will be set free causing roughness of the deposit and higher brightener consumption until a new film is formed. The use of incorrect anodes will result in an inadequate film formation, high brightener consumption, poor leveling and rough deposits.

### **Anode-to-Cathode Spacing**

Normal anode-to-cathode spacing for wafer plating is 2 to 5 inches depending on wafer size and anode shape.

### **Current Density**

The normal current density range is 30.0 to 45.0 ASD. Higher current density may be accomplished depending on the type of plating cell, solution flow, total copper metal content and total sulfuric acid content, as well as wafer pattern complexity.

## **ANALYTICAL PROCEDURES**

### **I. ANALYSIS FOR COPPER**

#### **A. REAGENTS NEEDED**

1. Concentrated Ammonium Hydroxide (NH<sub>4</sub>OH)
2. Glacial Acetic Acid (CH<sub>3</sub>COOH)
3. 20% Potassium Iodide (KI) - Dissolve 200 grams KI in about 500 mL of water and dilute to one liter in a volumetric flask.
4. 0.1N Sodium Thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) Solution - Dissolve 24.8 grams of AR grade Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O and 3.8 grams of AR Grade sodium borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) in 600 mL of deionized or distilled water. Dilute to one liter in a volumetric flask. Standardize periodically against a potassium dichromate or potassium iodate solution of known normality; 0.1N sodium thiosulfate solutions deteriorate with time.
5. 0.5% Starch Indicator Solution - Stir 10.5 gram of starch in 100 mL of cold deionized water. Bring to a boil. The solution should be clear. Remove from heat and store in a cool place.

#### **B. PROCEDURE**

1. Pipet accurately a 5 mL sample into a 500 mL Erlenmeyer flask and add 20 mL of distilled water.
2. Add concentrated ammonium hydroxide (NH<sub>4</sub>OH) dropwise until the solution turns a permanent deep blue color. Dilute to 150 mL with distilled water.
3. Add 10 mL glacial acetic acid (CH<sub>3</sub>COOH).

4. Add 20 mL of 20% potassium iodide (KI) solution. Swirl to mix.
5. Titrate with 0.1N sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution until the solution turns pale yellow.
6. Add 2 mL of 0.5% starch indicator solution and continue to titrate with 0.1N sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution to a white end point.

**C. CALCULATION**

1. g/L copper = mL of 0.1N sodium thiosulfate solution titrated x 1.27
2. oz/gal copper = mL of 0.1N sodium thiosulfate solution titrated x 0.17

**II. ANALYSIS FOR SULFURIC ACID****A. REAGENTS NEEDED**

1. 1.0N Sodium Hydroxide (NaOH) Solution - Weigh 40 grams NaOH, AR grade, and dissolve in water. Dilute to one liter in a volumetric flask. Standardize against a  $\text{H}_2\text{SO}_4$  acid solution of known concentration.
2. 0.2% Methyl Orange Indicator - Dissolve 2.0 grams of methyl orange salt in one liter of deionized water.

**B. PROCEDURE**

1. Pipet accurately a 5 mL sample into a 250 mL Erlenmeyer flask.
2. Add 150 mL distilled water and 5 drops of 0.2% methyl orange solution. Swirl to mix.
3. Titrate with standard 1.0N sodium hydroxide solution until the color changes from orange to pale yellow-green.

**C. CALCULATION**

1. g/L sulfuric acid = mL of 1.0 N NaOH titrated x 9.8
2. oz/gal sulfuric acid = mL of 1.0 N NaOH titrated x 1.31

**III. ANALYSIS FOR CHLORIDE****A. REAGENTS NEEDED (This procedure requires the use of a spectrophotometer and the following solutions)**

1. MICROFAB SC matrix without chloride - Use MICROFAB SC COPPER SULFATE and sulfuric acid, mix to target copper and acid concentrations.
2. Standard Chloride Solution (1 mL = 0.1 mg Cl) - Dissolve 0.165g reagent grade solution chloride ( $\text{NaCl}$ ) in distilled water. Dilute to 1 liter.
3. 0.1N Silver Nitrate ( $\text{AgNO}_3$ ) Indicator Solution - Weigh out exactly 17 grams of AR grade silver nitrate on an analytical balance. Dissolve in 500 mL of distilled or deionized water and dilute to one liter. No standardization is required. Store in

brown bottle in a cool place out of direct light. Or purchase as a ready-to-use solution.

4. Ethylene Glycol
5. Concentrated Nitric Acid (HNO<sub>3</sub>)

NOTE: All glassware must be washed with deionized water.

## B. PROCEDURE

1. Pipet two 5 mL aliquots of sample into 25 mL volumetric flasks.
2. Using a graduate, add 5 mL concentrated nitric acid (HNO<sub>3</sub>) to each flask and mix.
3. Using a graduate, add 10 mL ethylene glycol to each flask and mix.
4. Using an eye dropper or the dispensing buret add 1 mL 0.1N silver nitrate to one aliquot only. Dilute to volume with distilled water. Mix well. Allow to stand approximately 15 minutes. Dilute the other sample to volume. This is the blank.
5. Read on a spectrophotometer in 1 cm cells at about 440 nm after setting the zero with water.
6. Find the amount of chloride present from the calibration curve in both the sample and the blank. Correct for the blank.

## C. PREPARATION OF CALIBRATION CURVE

1. Pipet 5 mL of the MICROFAB SC matrix without chloride into each of 5 separate 25 mL volumetric flasks.
2. Using clean grade A pipets and 0, 1.0, 2.0, 3.0 and 4.0 mL standard chloride solution to the flasks to obtain 0, 20, 40, 60 and 80 ppm chloride.
3. Using a graduate, add 5 mL concentrated nitric acid (HNO<sub>3</sub>) to each flask. Mix.
4. Using a graduate, add 10 mL ethylene glycol to each flask. Mix.
5. Using an eye dropper or the dispensing buret, add 1 mL 0.1N silver nitrate to all flasks except that one containing no chloride. Dilute to 25 mL volume with distilled water. Mix well. Allow to stand about 15 minutes.
6. Read on a spectrophotometer in 1 cm cells at about 440 nm using water to set the zero.
7. Prepare a calibration curve by plotting a linear graph paper absorbance versus the concentration of chloride.
8. Repeat the calibration curve on 2 different days; it should be reproducible. Recalibrate about once or twice a year.

## IV. ANALYSIS FOR ADDITIVES

CVS (cyclic voltametric stripping) analysis can be used to monitor **MICROFAB MP 2500-A**, **MICROFAB MP 2500-S** and **MICROFAB MP 2500-L**. Please contact your local sales or technical support representative for further instruction.



### SAFETY & WARNING

It is recommended that the company/operator read and review the Safety Data Sheets for the appropriate health and safety warnings before use.

**Safety Data Sheets are available.**

### WASTE TREATMENT

Prior to using any recommendations or suggestions for waste treatment, the user is required to know the appropriate local/state/federal regulations for on-site or off-site treatment which may require permits. If there is any conflict regarding our recommendations, local/state/federal regulations take precedent.

### ORDER INFORMATION

Product	Code
MICROFAB SC COPPER SULFATE	400133
MICROFAB MP 2500-A	251651
MICROFAB MP 2500-S	258159
MICROFAB MP 2500-L	251814

### CONTACT INFORMATION

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Also read carefully warning and safety information on the Safety Data Sheet. This data sheet contains technical information required for safe and economical operation of this product. READ IT THOROUGHLY PRIOR TO PRODUCT USE. Emergency safety directory assistance: US 1 202 464 2554, Europe + 44 1235 239 670, Asia + 65 3158 1074, Brazil 0800 707 7022 and 0800 172 020, Mexico 01800 002 1400 and (55) 5559 1588

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