

## MICROFAB<sup>®</sup> SC

### Acid copper electroplating process for semiconductor applications

#### INTRODUCTION

The MICROFAB<sup>®</sup> SC acid copper plating formulation provides excellent throwing power, improved leveling characteristics, and ductile low stress deposits. The MICROFAB SC process is specifically engineered for wafer plating applications including interconnects for VLSI and ULSI technologies. By modifying the operating parameters the MICROFAB SC may be used for wafer plating applications including copper bump or post plating at higher current densities. These products are formulated, packaged, and quality controlled according to the needs of the semiconductor industry. The solutions are made up with MICROFAB SC MAKE-UP and MICROFAB SC-32 MAKE-UP and the MICROFAB additives described below. Normal additive replenishment is accomplished through the use of a combination of MICROFAB SC MD and MICROFAB SC LO 70/30. READ ENTIRE TECHNICAL DATA SHEET BEFORE USING THIS PRODUCT.

#### MATERIALS REQUIRED

The following materials are normally recommended for a typical start up and operation:

1. MICROFAB SC MAKE-UP is supplied at a copper metal concentration of 17 gpl, is pretested and ready to use to make up an initial operating solution for plating of VLSI and ULSI technologies at lower current densities. It is purified, performance tested, and packaged for semiconductor applications in 20 and 200 liter clean room compatible packages.
2. MICROFAB SC-32 MAKE-UP is supplied at a copper metal concentration of 32 gpl, is pretested and ready to use to make up the initial operating solution for plating of posts and bumps at higher current densities. It is purified, performance tested, and packaged for semiconductor applications in 20 and 200 liter clean room compatible packages.
3. MICROFAB SC MD is an addition agent which when used in a typical ratio of 4:1 with MICROFAB SC LO 70/30 is designed to provide for via and trench filling in copper damascene applications. Concentrations of this additive can be varied in working solutions from 4 to 16 mL/L based on specific operating preferences. It is available in 1, 4, and 20 liter containers.
4. MICROFAB SC LO 70/30 is an addition agent which when used in a typical ratio of 1:4 with MICROFAB SC MD is designed to provide for via and trench filling in copper damascene application. Concentrations of this additive can be varied in working solutions from 1 to 4 mL/L based on operating preferences. It is available in 1, 4, and 20 liter containers.

Other solution chemistries available for minor adjustments include:

1. MICROFAB SC COPPER SULFATE contains 250 g/L (33.5 av oz/gal) copper sulfate (equal to 64 g/L or 8.5 av oz/gal of copper metal). It is used to replace copper in heavy drag-out situations.
2. The former CUBATH SC REPLENISHER has been discontinued. An acceptable alternative for special replenishment purposes is to use MICROFAB SC MD and MICROFAB SC LO 70/30 in a 1:1 ratio. To prepare a one liter equivalent of the former CUBATH SC REPLENISER, add 500 mL of each MICROFAB SC MD and MICROFAB SC 70/030.
3. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) maintains high solution conductivity. Use only reagent or semiconductor grade.
4. Hydrochloric acid (HCl, reagent grade) is used to adjust the chloride ion concentration of the electrolyte.
5. Evaporative losses may be replaced with deionized or distilled water.

**EQUIPMENT REQUIRED**

Acid copper sulfate solutions are highly corrosive; therefore, exposed metal materials in the fab area should be protected from the effects of these solutions. Several coats of a vinyl coating can provide adequate protection.

|                     |   |
|---------------------|---|
| Tanks               | PVC, PVDC, polypropylene or Teflon tanks can be used. Have available a lined storage tank of at least equal capacity to the plating tank equipped with a means of heating to 60 °C (140 °F) for carbon treatment.   |
| Leaching            | Tanks, filter cartridges, anode bags, and peripheral equipment must be leached prior to installation. Refer to technical bulletin: "Leaching Procedures for New and Used Plating Tanks" available from Enthone Inc.   |
| Heating and Cooling | Cooling coils may be necessary for temperature adjustment. Cooling and heating coils made of titanium or Teflon-coated copper may be used. Teflon tube bundles, immersion type heat exchangers or external heat exchangers are preferred.   |
| Filtration          | Continuous filtration is necessary for maintaining low particle counts of the solution. Use properly leached woven Dynel or polypropylene filter cartridges (with a polypropylene core) with a 5 micron or greater retention. Cotton filters must not be used.  |
| Agitation           | Solution agitation is necessary to achieve the best results. Solution agitation, without air, is recommended. Increased solution flow rate can be important for uniform plate distribution and plating rate.  |
| Rectifiers          | Direct current or pulse rectifiers (direct or reverse mode) may be used. Consult Enthone Inc. for specific application recommendations.   |
| Anodes              | Copper anodes with a certified uniform phosphorous content of 0.045% to 0.06% must be used. If copper anodes, other than phosphorized copper anodes are to be used, obtain certification verifying that phosphorous content is uniform and within the specified range. Pure electrolytic or OFHC copper <u>cannot be used</u> . |
| Ventilation         | Consult the American Conference of Industrial Hygienists book entitled, "Industrial Ventilation, A Manual of Recommended Practice."   |

**OPERATING CONDITIONS**

|   | <u>Nominal</u>          | <u>Range</u>                        |
|---|-------------------------|-------------------------------------|
| Copper Concentration (low current density)  | 17 g/L (2.25 av oz/gal) | 15 to 20 g/L (2.0 to 2.7 av oz/gal) |
| Copper Concentration (high current density) | 32 g/L (4.24 av oz/gal) | 25 to 35 g/L (3.5 to 4.7 av oz/gal) |
| Copper Sulfate                              | 67 g/L (9 av oz/gal)    | 59 to 75 g/L (8.5 to 10 av oz/gal)  |
| Sulfuric Acid                               | 175 g/L (24 av oz/gal)  | 150 to 250 g/L (22 to 33 av oz/gal) |
| Chloride Ion                                | 40 mg/L (ppm)           | 35 to 55 mg/L (ppm)                 |
| Temperature                                 | 24 °C (75 °F)           | 21 to 27 °C (70 to 80 °F)           |
| Current Density MICROFAB SC                 | 15 ASF (1.5 ASD)        | 10 to 25 ASF (1.0 to 2.5 ASD)       |
| Current Density MICROFAB SC-32              | 25 ASF (2.0 ASD)        | 15 to 40 ASF (1.5 to 4.0 ASD)       |
| Anode to cathode ratio                      | 2:1                     | 2:1 to 3:1                          |

**Standard Process Make Up**

|                                   |             |              |
|-----------------------------------|-------------|--------------|
| MICROFAB SC MAKE UP (low c/d)     | As Supplied | --           |
| MICROFAB SC-32 MAKE UP (high c/d) | As Supplied | --           |
| MICROFAB SC MD                    | 8 mL/L      | 4 to 16 mL/L |
| MICROFAB SC LO 70/30              | 2 mL/L      | 1 to 4 mL/L  |

## **OPERATING CONDITIONS (Cont.)**

### **Maintaining Additives:**

By dosing the individual MICROFAB SC MD or MICROFAB SC LO 70/30 components based on a specific customer requirement or as provided by specific tool supplier's feed algorithm (see the section on PROCESS CONTROL for further discussion).

## **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 (6 oz/gal) trisodium phosphate and 7.5 g/L (1 oz/gal) sodium hydroxide heated to 60 °C (140 °F) 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 (120 °F) for 8 hours. Again flush tank with water.
3. Empty the tank.
4. Carefully pour or pump recommended amount of MICROFAB SC MAKE-UP or MICROFAB SC-32 MAKE-UP into tank.
5. Copper anodes: new copper anodes must be cleaned of oils, organic materials, dirt, oxides and sulfides. If vapors 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 (16 oz/gal) ammonium persulfate and 5 mL/L (0.6 fl oz/gal) 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. 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 10 ASF (1.0 ASD) while filming the anode at 10 to 15 ASF (1.0 to 1.5 ASD) anode current density. Plate the dummy cathode for ½ to 1 hour before adding MICROFAB SC addition agents 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 suppliers recommendation. During this time a black continuous film will form on the anodes.

### **MAKE UP PROCEDURE (Cont.)**

12. 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.
13. 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.
14. 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. The cartridges must then be immersed in a solution of 10% by volume reagent grade sulfuric acid, to which 2.5 mL/L of MICROFAB SC MD has been added. The cartridges must be allowed to soak for 1 hour. For sub-micron filters follow the manufacturers recommendation for preparation prior to installation.
15. Add MICROFAB SC MD and MICROFAB SC LO 70/30 starting dosages as described under the start up procedure earlier described in this technical data sheet. Dispense the additives throughout the tank and allow for proper mixing while running the agitation pumps. Air agitation may be used in some applications as recommended by your tool supplier.
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 Enthone Inc.

### **OPERATION**

#### **Copper Sulfate**

MICROFAB SC COPPER SULFATE is used in the MICROFAB SC 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 or MICROFAB SC MAKE-UP or MICROFAB SC-32 MAKE UP 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 2 weeks, 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.

#### **Chloride Ions**

Chloride ions are essential to the promotion of proper anode corrosion characteristics. The process requires a nominal concentration of 40 mg/L (ppm) of chloride ion. Excess of 60 ppm is detrimental to the process operation and must be avoided. The chloride content is easily increased, when necessary, by the addition of reagent grade hydrochloric acid. Note: 10 mL of reagent hydrochloric acid per 100 gallons of plating solution will increase the chloride concentration by about 10 mg/L (10 ppm).

Evaporative losses may be replaced with deionized or distilled water

## **OPERATION (Cont.)**

### Additives

MICROFAB SC MD and MICROFAB SC LO 70/30 are the addition agent replenishment solutions for the process. They are consumed at the rate of approximately 1.0 to 3.0 mL per ampere-hour. The addition rate depends on the specific plating conditions.

Following the initial addition of 8 mL/L of MICROFAB SC MD and 2 mL/L of MICROFAB SC LO 70/30) 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 21 and 27 °C (70 and 80 °F). The nominal operating temperature is 24 °C (75 °F). Temperatures above 27 °C (80 °F) cause clouding of the bright deposit. Temperatures below 21 °C (70 °F) lower the conductivity of the solution and cause graininess in the high current density areas.

### 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 SC 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 for the MICROFAB SC MAKE-UP is 10 to 25 ASF (1.0 to 2.5 ASD) and is recommended for most low speed applications. The normal current density range when using the MICROFAB SC-32 MAKE-UP is 15 to 40 ASF (1.0 to 4.0 ASD) and is recommended for most high speed applications. Higher current density for each formulation may be accomplished depending on type of plating cell, solution flow, total copper metal content and total sulfuric acid content.

## **SAFETY AND HANDLING INSTRUCTIONS**

**DANGER!** MICROFAB SC MAKE-UP, MICROFAB SC-32 MAKE-UP, MICROFAB SC MD, MICROFAB SC LO 70/30, MICROFAB SC COPPER SULFATE AND THE OPERATING SOLUTION CONTAIN SULFURIC ACID WHICH MAY CAUSE SEVERE SKIN AND EYE BURNS.

**HAZARDS:** MICROFAB SC MAKE-UP, MICROFAB SC-32 MAKE-UP, MICROFAB SC MD, MICROFAB SC LO 70/30, MICROFAB SC COPPER SULFATE and the operating solution contain sulfuric acid which may cause severe burns to skin and eyes, possible blindness. Sulfuric acid is also a possible carcinogen. Inhalation of vapors or mist from the operating solution may cause severe irritation or burns to respiratory tract. Ingestion may cause severe burns of mouth, throat, esophagus and stomach. Contact with most metals will generate hydrogen, a highly flammable and explosive gas. May react violently with water. Do not get in eyes, on skin, or on clothing. Do not inhale or take internally.

CONSULT SUPPLIERS MSDS FOR INFORMATION ON pH ADJUSTERS

**FIRST AID:** In case of contact with MICROFAB SC MAKE-UP, MICROFAB SC-32 MAKE-UP, MICROFAB SC MD, MICROFAB SC LO 70/30, MICROFAB SC COPPER SULFATE, pH adjusters, or the operating solution with skin or eyes, flush with plenty of clean, cool water for 15 minutes; for eyes get immediate medical attention. Remove contaminated clothing and shoes.

**HANDLING INFORMATION:** When preparing or maintaining solutions, always add MICROFAB SC MAKE-UP, MICROFAB SC-32 MAKE-UP, MICROFAB SC MD, MICROFAB SC LO 70/30, MICROFAB SC COPPER SULFATE and sulfuric acid (may cause heat and spattering) slowly and cautiously. Do not get in eyes, on skin, or on clothing. Avoid breathing vapors or mists. When handling MICROFAB SC MAKE-UP, MICROFAB SC-32 MAKE-UP, MICROFAB SC MD, MICROFAB SC LO 70/30, MICROFAB SC COPPER SULFATE, pH adjusters, or the operating solution, wear protective clothing, chemical safety goggles, respirator, face shield and rubber gloves. Avoid contact with alkalis or any other foreign materials. Exhaust ventilation is recommended to remove vapors or mist that may be generated during make-up and operation.

**CONTAINER INFORMATION:** Keep containers tightly closed. Store indoors in a cool, dry area away from alkalis. Loosen closure cautiously when opening. Wash thoroughly after handling. Do not reuse containers, wash before disposal. Improper disposal or reuse of container may be dangerous and illegal.

REFER TO MSDS FOR FURTHER SAFETY AND HANDLING INFORMATION

## **CONTROL**

Procedures for determining copper, sulfuric acid, and chloride content of the operating solution are available from Enthone Inc. on request.

The MICROFAB SC process may be controlled by bleed-and-feed methods as recommended by your tool supplier. Typically 8 to 12% are removed and replaced daily when operating in full production. Specific feed algorithm have been developed by tool suppliers and customers to meet the desired performance demands for their products.

An alternative approach is based on feeding dosages determined by amp-time and idle-time as specified by the tool supplier. In this approach specific limits are set for solution life. At the end of this period the product is replaced with fresh starting solution.

CVS (cyclic voltametric stripping) analysis can be used to monitor addition agents. Procedure for MICROFAB SC MD and MICROFAB SC LO 70/30 may be obtained from ECI Technologies in Rutherford, New Jersey, e-mail address [info@ecitechnology.com](mailto:info@ecitechnology.com)

## MATERIAL SAFETY DATA SHEETS

For more detailed information on the toxicological properties of the products described herein, reference can be made to the Material Safety Data Sheet (MSDS) for each product. If you do not have the proper MSDS, it can be requested from: Enthone Inc., attention: Regulatory Affairs Department, 350 Frontage Road, West Haven, CT 06516. For emergency assistance call CHEMTREC (800) 424-9300.

### WARRANTY AND DISCLAIMER

The information presented herein is to the best of our knowledge true and accurate and all recommendations and suggestions appearing in this bulletin covering the use of our products are based upon information believed to be reliable. However, since the conditions of use are beyond our control, this information is given on the express condition and agreement that Enthone Inc. will not be liable to any person in contract, tort (including negligence), strict liability or otherwise for any claims, damages or losses whatsoever. Nothing herein shall be deemed a recommendation to use any product or process in violation of any existing patent rights and no warranties, expressed or implied, are made regarding the information, product, processes, recommendations, description and safety notations contained herein. The above includes proprietary information of Enthone Inc. and is furnished to you for your use solely on products or processes supplied by us to you.

### CUSTOMER ORDER CENTERS

#### UNITED STATES

West Haven, Connecticut (800) 496-8326  
Precious Metal Products (800) 560-7214  
Fax (203) 933-0249  
[ctchemorders@cooksonelectronics.com](mailto:ctchemorders@cooksonelectronics.com)

PWB Chemistry (U.S. and Canada) (800) 657-0240

#### MEXICO

Mexico, D.F. (011-52-55) 5078-3904  
Fax (011-52-5) 567-6326



**Cookson Electronics**  
[www.cooksonelectronics.com](http://www.cooksonelectronics.com)

® Registered Trademark of Enthone Inc. ™ Trademark of Enthone Inc.