MICROFAB DVF 200

Copper Electroplating Process for Through-Silicon Via Applications

Product Code: 414200

DESCRIPTION

The **MICROFAB DVF 200** is an acid copper plating process that fills Through-Silicon Vias (TSVs) without voids and other defects at high plating speeds. The process is specially formulated for vias with diameters that range from 5 to 100 µm, and with aspect ratios less than 10.1. **MICROFAB DVF 200** is a robust process that features on-line additive monitoring and control.

The following operating guidelines are recommendations based on customer production and in-house laboratory testing. Further optimization of operating parameters will be dependent upon tool platform, end user specifications and integration requirements. Factors such as seed process, tool hydrodynamics, use or non-use of anode membrane, as well as subsequent post plating integration steps will determine the final process parameters. Daily bleed-and-feed is recommended for maintaining a steady-state plating bath. Bleed rate needs to be established on a specific tool platform. Contact a sales representative prior to installing the **MICROFAB DVF 200** process at your facility.

READ ENTIRE TECHNICAL DATA SHEET BEFORE USING THIS PRODUCT

PROCESS COMPONENTS REQUIRED

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

* **MICROFAB DVF 200 MU** is supplied at a copper metal concentration of 80 g/L **MICROFAB DVF 200 MU** is shipped with Certificate of Analysis of critical specifications and is ready to use to make up an initial operating solution for its respective plating application. It is purified and packaged for semiconductor applications in 20 and 200 liter clean room compatible packages.
* This Make-Up solution does not include the organics needed to operate this system.

Organics:

MICROFAB DVF 200-B – Includes an accelerator component.

Concentrations of this additive can be varied in working solutions from 2 to 10 mL/L based on specific operating preferences. It is available in 4 and 20 liter containers.

MICROFAB DVF 200-C – Includes a primary suppressor component.

Concentrations of this additive can be varied in working solutions from 4 to 20 mL/L based on operating preferences. It is available in 4 and 20 liter containers.

MICROFAB DVF 200-D – Includes a secondary suppressor component.

Concentrations of this additive can be varied in working solutions from 2.5 to 20 mL/L based on operating preferences. It is available in 4 and 20-liter containers

Solution adjustment chemistries needed for adjustments:

MICROFAB CU MSA 128 CU CONCENTRATE contains 128 g/L of copper. It is used to replace copper in heavy drag-out situations.

MICROFAB NF ACID contains 952 g/L methanesulfonic acid. It is used to adjust the acid concentration of the plating solution.

Hydrochloric acid (HCl, reagent grade) is used to adjust the chloride ion concentration of the plating solution.

Evaporative losses may be replaced with deionized water.

ELECTROLYTE COMPOSITION

Parameter	Range	Target
Copper	78 to 82 g/L	80 g/L
MSA	18 to 22 g/L	20 g/L
Chloride Ion	45 to 55 ppm	50 ppm

MAKE UP PROCEDURE

For each liter of solution, add the following chemicals:

Order	Additive	Amount
1	MICROFAB DVF 200 MU	971 mL
2	MICROFAB DVF 200-B	6 mL
3	MICROFAB DVF 200-C	12 mL
4	MICROFAB DVF 200 D	11 mL

Note: Before initial bath make-up on a new tank, the tank must be cleaned / leached. Regular leaching is recommended to keep the equipment free of contaminants and to optimize process control when making up new baths (as needed for in conjunction with equipment maintenance.) Contact Representative for Tank Leaching Technical Bulletin.

EQUIPMENT

1. **Follow instruction from the tool manufacturer.**
2. **MICROFAB DVF-200** 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
3. Please consult with your equipment's Field Service Sales & Engineers for assistance in developing specific plating recipes for a given tool platform and wafer layout.
4. Optimization of equipment parameters will be required in establishing a Process of Record (POR).
5. The optimum copper concentration needed will vary based on product pattern, plating rate desired, and equipment platform characteristics.

RECOMMENED EXAMPLE OF OPERATING PARAMETERS

Parameter	Range	Optimum
Copper	75 to 85 g/L	80 g/L
MSA	15 to 25 g/L	20 g/L
Chloride	40 to 60 mg/L	50 mg/L
MICROFAB DVF 200-B	2 to 10 mL/L	6 mL/L
MICROFAB DVF 200-C	4 to 20 mL/L	12 mL/L
MICROFAB DVF 200-D	2.5 to 20 mL/L	11 mL/L
Temperature	22 to 28 °C	25 °C

CURRENT DENSITY WAVEFORM RAMP RECIPE EXAMPLE

The chart below provides a recommended recipe for complete fill for via size 10 to 50 micron wide by 175 micron deep. Please note that larger dimensions may require a longer plating period and vice versa. Pulse plating may also be used per tool maker recommendations.

ASD 1	Time 1	ASD 2	Time 2	ASD 3	Time 3	ASD 4	Time 4	Total Time
A/dm^2	minutes	A/dm^2	minutes	A/dm^2	minutes	A/dm^2	minutes	minutes
0.1	5	0.3	5	0.6	60	1.2	100	180

SOLUTION MAINTENANCE

Copper Sulfate

MICROFAB CONCENTRATE MSA 128 is used in the **MICROFAB DVF-200** 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 CONCENTRATE MSA 128 and /** or bleeding solution as necessary. Add only **MICROFAB CONCENTRATE MSA 128** to the solution if bleed-and-feed process control is used.

Sulfuric Acid

Sulfuric acid performs the principal function of maintaining high solution conductivity.

Note: 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 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).

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.

Anodes

Maintain the anode area between 2.0 to 3.0 times (2:1 nominal) the cathode plateable area (wafer) for the MICROFAB DVF-200 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. 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.

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.

Tanks PVC, PVDC, polypropylene or PTFE tanks can be used

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, connectors, and filters 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.

Rectifiers

The rectifier should be sized so that the average plating load utilizes more than 50% of the rated current load. The rectifier must have no more than 5% ripple (preferably with less than 2% ripple) at the amperage to be used.

Agitation / Flowrate

Uniform solution agitation from vigorous solution movement or low-pressure aeration is necessary for proper performance of the **MICROFAB DVF-200** process. When using low-pressure air, avoid using compressed air, no matter how strongly filtered. Air bubble impingement must primarily be upon work being plated, not on the anodes.

Ventilation

Consult the American Conference of Industrial Hygienists book entitled, “Industrial Ventilation, A Manual of Recommended Practice.”

Additives

MICROFAB DVF-200-B, **MICROFAB DVF-200-C** and **MICROFAB DVF-200-D** 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 DVF-200-B, **MICROFAB DVF-200-C** and **MICROFAB DVF-200-D** are replenished based on a specific customer requirement or as provided by specific tool supplier's feed algorithm. Additionally, the additive concentrations can be analyzed by CVS methodology.

Estimated Plating Consumption

- **MICROFAB DVF-200-B** is typically consumed at the rate of approximately 0.080 to 0.2 mL per ampere-hour.
- **MICROFAB DVF-200-C** is typically consumed at the rate of approximately 0.1 to 0.2 mL per ampere-hour.
- **MICROFAB DVF-200-D** is typically 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 considerable impact on additive consumption rate. The listed amp-hour data is an average of observed results from the field. Actual consumption rate needs to be determined for each installation.

Following the initial addition of the **MICROFAB DVF-200 Additives** at start up, it may be determined that the higher replenishment figure will be required. Leached tanks and filter cartridges tend to absorb additive until a saturation equilibrium is reached.

BATH COPPER, ACID, CHLORIDE, AND ADDITIVE ANALYSIS METHODS

Please contact a representative for Copper, MSA, and Chloride analysis at our West Haven, Connecticut Analytical Lab if you would prefer us to perform that analysis. We do not perform organic analysis of the organic additives. A web search for metallics lab analysis or plating bath analysis will help you find a service in your region. We also recommend searching for Cyclic Voltametric Stripping (CVS) equipment providers for researching into upgrading to real-time, internal / onsite analysis of your organic concentrations for optimum bath performance.

ANALYTICAL PROCEDURES

I. Analysis for Copper

A. Reagents Needed

1. Concentrated Ammonium Hydroxide (NH_4OH)
2. Glacial Acetic Acid (CH_3COOH)
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 ($Na_2S_2O_3$) Solution - Dissolve 24.8 grams of AR grade $Na_2S_2O3 \cdot 5H_2O$ and 3.8 grams of AR Grade sodium borate ($Na_2B_4O_7$) 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_4OH) 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_3COOH).
   Add 20 mL of 20% potassium iodide (KI) solution. Swirl to mix
4. Titrate with 0.1N sodium thiosulfate ($Na_2S_2O_3$) solution until solution turns pale yellow.
5. Add 2 mL of 0.5% starch indicator solution and continue to titrate with 0.1N sodium thiosulfate ($Na_2S_2O_3$) 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 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 (NaCl) in distilled water. Dilute to 1 liter.
3. 0.1N Silver Nitrate ($AgNO_3$) 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 ready-to-use solution.
4. Ethylene Glycol
5. Concentrated Nitric Acid (HNO_3)

B. NOTE: All glassware must be washed with deionized water.

C. 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_3) 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.

D. 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 (HNO3) 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.

III. Analysis for Methane Sulfonic Acid

Note: **Perform analysis in triplicate and report the average of three results**

1. Pipet 10 mL of CU-MSA Make-Up into a 250 mL Erlenmeyer flask.
2. Add approximately 100 mL of 3.5% ammonium oxalate solution and approximately 10 drops of methyl red indicator in alcohol. Swirl to mix.
3. Titrate with 0.1 N sodium hydroxide solution to a green end point.
4. Calculation: mL NaOH • N NaOH • 9.61 = g/L Methane Sulfonic Acid.

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 DVF 200 MU	414171
MICROFAB DVF 200 B	414200
MICROFAB DVF 200 C	414196
MICROFAB DVF 200 D	417317
MICROFAB CU MSA 128 CONCENTRATE	251870
MICROFAB NF ACID	208523

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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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