NB SEMIPLATE CU 100

Copper electroplating process

INTRODUCTION

The NB SEMIPLATE CU 100 process is an acid copper plating formulation engineered for wafer plating applications including copper bump plating, interconnects for VLSI/ULSI or MEMS. The NB SEMIPLATE CU 100 process provides excellent throwing power, improved levelling characteristics, ductile low stress deposits and offers unique flexibility in its operation.
This product is formulated, packaged, and quality controlled according to the needs of the semiconductor industry. The solution is made up with CU 100 MAKE UP and the CU 100 additives described below.

"NB SEMIPLATE CU 100" is shipped **ready-for-use**, while the "**CU 100** xxx" are compounds and used for mixture and maintenance.

READ ENTIRE TECHNICAL DATA SHEET BEFORE USING THIS PRODUCT.

MATERIALS REQUIRED

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

Product Name	Product code	Comment
NB SEMIPLATE CU 100	203100-00	• ready-for-use solution
CU 100 MAKE UP	203100-10	• supplied pretested and ready to use to make up the initial operating solution.
CU 100 MD	203100-20	• Brightening Carrier • Concentrations of this additive can be varied in working solutions based on specific operating preferences.
CU 100 LO	203100-30	• Brightening Agent • Concentrations of this additive can be varied in working solutions based on specific operating preferences.
CU 100 COPPER SULPHATE	203100-60	• used to replace copper in heavy drag-out situations

Materials are purified and packaged for semiconductor applications in clean room compatible packages

In addition, there might be needed sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) needed for maintenance (use only reagent or semiconductor grade).

EQUIPMENT REQUIRED

The following section is a guide for usual operation conditions. The specific conditions and requirements may depend on tool vendor specifications and application.
Acid copper sulphate 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.
Leaching	Tanks, filter cartridges, anode bags, and peripheral equipment must be leached prior to installation. Depending on tool status, this may include degreasing, base solution treatment, DI water rinse, acidic treatment and final DI-water rinse.
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.
Heating and Cooling	Cooling coils may be considered 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 woven Dynel or polypropylene filter cartridges (with a polypropylene core) with a 5 micron or less retention. Cotton filters must not be used. Filter cartridges must be leached before installation in the tool (refer to next section).
Ventilation	Ensure sufficient exhaust (acidic mists) and check with local regulations.
Rectifiers	Direct current or pulse rectifiers (direct or reverse mode) may be used. Make sure to use power supply without current ramping and ripple less than 2%. Consult NB Technologies GmbH for specific application recommendations.
Anodes	Anodes must be degrease and conditioned (refer to next section). Copper anodes with a certified uniform phosphorous content of 0.045% to 0.06% must be used. Copper anodes with a certification of phosphorous content are available from NB Technologies GmbH. 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 cannot be used.

MAKE UP PROCEDURE

1. Proper leaching and cleaning of the tank is mandatory. Depending on the tool status (used or first time of use), 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 CU 100 MAKE UP into tank.
5. Copper anodes: new copper anodes must be cleaned of oils, organic materials, dirt, oxides and sulfides. If vapours degreasing is possible, this is the preferred first step toward removing grease and oil and soils bound by these materials. As an alternative to vapour degreasing, the anodes may be totally immersed in a hot, alkaline soak cleaner for at least one hour, followed by thorough rinsing.
6. 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 sulphuric acid. Etch the anodes for at least 1minute up to 20 minutes, followed by a thorough water rinse
7. Soak in 10% by volume sulphuric acid for 30 to 60 sec with a final rinse in DI-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/sulphuric 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 sulphuric acid and rinse once again as would be done with the ammonium persulfate etch procedure.
9. Rinse the anodes with DI-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 mA/cm² (1.0 ASD) while filming the anode at 10 to 15 mA/cm² (1.0 to 1.5 ASD) anode current density. Plate the dummy cathode for ½ to 1 hour before adding CU 100 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 supplier recommendation. During this time a black continuous film will form on the anodes. 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 DI-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 sulphuric acid, to which 2.5 ml/l of CU 100 MD has been added. The cartridges must be allowed to soak for 1 hour. For sub-micron filters follow the manufacturer recommendation for preparation prior to installation.
15. Add CU 100 MD and CU 100 LO starting dosages. 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.
17. Take a sample of the solution and send to NB Technologies GmbH to check for final additive concentrations.

BATH PARAMETERS

The following table shows the bath parameters, which should be maintained and checked with regular sample analysis.

	NBT analysis	Units	Max. upper limit	Upper action limit	Optimum	Lower action limit	Lowest limit
Cu	X	g/l	24	22	20	17	15
Copper sulphate (pentahydrate)	X	g/l	94	86	79	67	59
Sulphuric acid	X	g/l	225	200	170	160	150
Chloride Ion	X	mg/l	50	45	40	35	30
CU 100 MD	X	ml/l	16	12	8	6	4
CU 100 LO	X	ml/l	4	3	2	1,5	1

PLATING CONDITIONS

Parameter		**Optimum**	**Range**
Cathode current density	[mA/cm²]	20	10 - 40
Flow (depending on tool)	[l/h]	-	500 - 1000
Anode to cathode area ratio		1:1	1:1 to 2:1
Anode to cathode spacing (depend on tool and wafer size)	[cm]		5 - 15
Temperature	[°C]	24	21 - 27

OPERATION

Copper sulphate
Copper sulphate is used in the NB SEMIPLATE CU 100 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 CU 100 COPPER SULPHATE or bleeding solution as necessary. Add only specially pre-purified copper sulphate, CU 100 COPPER SULPHATE to the solution or CU 100 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, DI-water. If left in the electrolyte, the high free acid will dissolve the copper.

Sulphuric Acid
Sulphuric 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 45 mg/l (ppm) of chloride ion. Excess of 60mg/l 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. For increasing 1mg/l chloride add 0,0023ml/l HCL (37%).

Replenisher
CU 100 MD and CU 100 LO are the addition agent replenishment solutions for the process and are consumed during process. CU 100 LO is the brightening agent and is consumed at the rate of 0,2 to 0,8 ml per ampere-hour. CU 100 MD is the brightening carrier and is consumed at the rate of 1 to 3 ml/l per ampere-hour. The addition rate depends on the specific plating conditions.
Following the initial addition of CU 100 MD and CU 100 LO at start up, it may be determined that the higher replenishment figure 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. The optimum operating temperature is 24 °C. Temperatures above 27 °C cause clouding of the bright deposit. Temperatures below 21 °C lower the conductivity of the solution and cause graininess in the high current density areas. However, cooling or heating may not be required if ambient temperature is within the range as indicated.

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. 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 0.5 to 2.0 times (1:1 optimum) the cathode plating area (wafer) for NB SEMIPLATE CU 100 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 levelling and rough deposits.

Anode-to-Cathode Spacing
Normal anode-to-cathode spacing for wafer plating is 5 to 15cm depending on wafer size and anode shape.

Current Density
The normal current density range of 10 to 40 mA/cm² (1.0 to 4.0 ASD) is recommended for most applications. Lower currents may be desirable during filling of damascene structure.

SPECIFIC PROCEDURES

- Oxygen plasma before plating
- chemical pre-treatment not recommended/normally not needed
- Cleaning of all items with DI before insertion in electrolyte
- Wetting of wafer surface with DI water before insertion into bath (check for wetting)

CUSTOMER SUPPORT

Further customer support on the process with this product is available by contacting NB Technologies GmbH.

BATH ANALYSIS SERVICE

NB Technologies supports the bath analysis and provides special shipping kits including shipping box, sample bottles and labels.

DATA LOGGING

Keep a record of ampere-hours of use to determine replenishment volumes. Examples of process log sheets are available by contacting NB Technologies GmbH.

HANDLING AND SAFETY INSTRUCTIONS

For detailed information consult the material safety data sheets for this product.
Please read material safety data sheets carefully before using this product.

DISCLAIMER

All recommendations and suggestions in this bulletin concerning the use of our products are based upon tests and data believed to be reliable. Since the actual use by others is beyond our control, no guarantee expressed or implied, is made by NB Technologies GmbH, its subsidiaries of distributors, as to the effects of such use or results to be obtained, nor is any information to be construed as a recommendation to infringe any patent.

ADDRESS

NB Technologies GmbH
Fahrenheitstr. 1
28359 Bremen
Tel. +49 421 2445810
Fax. +49 421 22379787
info@nb-technologies.de