

NB SEMIPLATE CU 150

Copper electroplating process

INTRODUCTION

The NB SEMIPLATE CU 150 process is an acid copper plating formulation engineered for wafer plating applications including copper bump plating, interconnects or MEMS. The NB SEMIPLATE CU 150 process provides excellent throwing power, improved levelling characteristics, ductile low stress deposits and offers unique flexibility in its operation.

This product is specially designed for the operation with **inert anode** systems without negative impact on plating quality or sensitive compounds such as organic additives. However, the operation using soluble anodes is not excluded.

The solution is shipped as ready-to-use solution.

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 150	203150-00	<ul style="list-style-type: none"> • Ready-to-use solution; contains copper, additives and sulphuric acid in nominal values
CU 150 ADD CP	203150-20	<ul style="list-style-type: none"> • Brightening Carrier • concentrations of this additive can be varied in working solutions based on specific operating preferences
CU 150 ADD AP	203150-30	<ul style="list-style-type: none"> • Brightening Agent • concentrations of this additive can be varied in working solutions based on specific operating preferences
CU 150 REPLENISHER	203150-10	<ul style="list-style-type: none"> • Replenisher used for replenishing copper metal and additives (refill or bleed and feed modus); contains 125% of the NB SEMIPLATE CU 150 contents
CU 150 P CONC	203150-40	<ul style="list-style-type: none"> • Consists of CU 150 REPLENISHER plus high concentrated inert anode conditioner (IAC) for operation with inert anode system
CU 150 COPPER SULPHATE	203150-60	<ul style="list-style-type: none"> • used to replace copper metal 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 (H₂SO₄) and hydrochloric acid (HCl 1N or 1M).
(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	<p>Boron Doped Diamond anodes (BDD anodes) are preferred as inert anode system. As an alternative, platinated titanium can be used, however, gas evolution and protective additive consumption may be higher. Inert anodes must be degreased and clean.</p> <p>If soluble anodes are used, copper anodes with a certified uniform phosphorous content of 0.045% to 0.06% must be used. Soluble anodes must be conditioned (refer to next section). 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.</p>

MAKE-UP PROCEDURE

The product is delivered ready-to-use, use the following installation 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 sulphuric acid heated to 50°C for 8 hours. Again flush tank with water.
3. Empty the tank.
4. **If soluble anodes are used, follow the instruction further below.**
5. Inert anodes may be installed after degreasing with NaOH, short soak in 5% sulphuric acid and thorough cleaning with DI-water.
6. 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 10 ml/l of CU 150 Add CP 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.
7. Install leached filter cartridges.
8. Carefully pour or pump recommended amount of NB SEMIPLATE CU 150 solution (or 80% CU 150 REPLENISHER plus 34 g/l sulphuric acid (19.3 ml/l sulphuric acid 96%) plus 20% DI-water) into the tank and start filtering the solution. The solution is now ready for production operation.
9. Take a sample of the solution to check for final additive concentrations, optionally send to NB Technologies GmbH for analysis.

Soluble anodes:

- a) 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. 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.
- b) 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 1 minute up to 20 minutes, followed by a thorough water rinse.
- c) Soak in 10% by volume sulphuric acid for 30 to 60 sec with a final rinse in DI-water.
- d) 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.
- e) Rinse the anodes with DI-water and install into plating tool.
- f) Pre-leached anode bags may be used in some applications where installation is recommended by the equipment vendor.
- g) 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 150 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.
- h) 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.

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	50	45	40	35	30
Sulphuric acid (H ₂ SO ₄)	X	g/l	225	200	170	160	150
Chloride Ion	X	mg/l	50	45	40	35	30
CU 150 ADD CP	X	ml/l	35	30	25	20	15
CU 150 ADD AP	X	ml/l	25	20	15	12.5	10
Inert anode conditioner (IAC)	X	ml/l	100	75	50	37.5	25

PLATING CONDITIONS

Parameter	Optimum	Range
Cathode current density [A/dm ²] (ASD)	3	1 - 4
Flow (depending on tool) [l/h]	-	500 - 1000
Anode to cathode area ratio BDD/platinated titanium soluble anode	4:1 2:1	3:1 or bigger 1:1 or bigger
Anode to cathode spacing (depends on tool and wafer size) [cm]		5 - 15
Temperature [°C]	24	10 - 27

DEPOSITION RATES:

The bath yields 1.18g Cu per Ah. The efficiency is 99.9% up to 3ASD.

Current density [A/dm ²]	Layer thickness per 1minute plating time [µm]	Time needed for 1µm deposit [min]
1 ASD	0.22	4:32
2 ASD	0.44	2:16
3 ASD	0.66	1:30

OPERATION

CU 150 REPLENISHER

CU 150 REPLENISHER is a replenishing solution with higher concentration of copper metal and all additive contents, so that it can be used for replenishing the copper metal and additives in a bleed and feed modus. The CU 150 REPLENISHER contains 125% of the NB SEMIPLATE CU 150 solution (50 g/l copper, 25 ml/l CU 150 ADD CP, 15 ml/l CU 150 ADD AP, 62.5 ml/l inert anode conditioner (IAC)).

NOTE: There is no increased content of sulphuric acid in the CU 150 REPLENISHER. Sulphuric acid content is at nominal value of 170g/l.

CU 150 P CONC / inert anode additive (IAC)

The inert anode conditioner (IAC) is needed for the operation with inert anode systems. The IAC normally is sufficiently replenished with the replenishments using CU 150 REPLENISHER. CU 150 P CONC contains 500 ml/l IAC and is added only upon analysis result, when heavy consumption of the IAC was not compensated with regular replenishments.

CU 150 COPPER SULPHATE

Copper sulphate is used in the NB SEMIPLATE CU 150 process to provide the proper concentration of copper ions. In operation, copper has to be replenished by adding Cu 150 COPPER SULPHATE or by bleed and feed with high concentrated make-up solution unless soluble anodes are used.

Add only specially pre-purified copper sulphate or CU 150 COPPER SULPHATE to the solution.

Copper concentration when using soluble 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 (soluble anodes only)

Chloride ions are essential to the electron transfer mechanism independent of anode type. The process requires a nominal concentration of 40 mg/l (ppm) of chloride ion. Excess of 60 mg/l is detrimental to the process operation and must be avoided.

Additives

CU 150 ADD CP and CU 150 ADD AP are the additives and addition agent replenishment solutions for the process and are consumed during process. The CU 150 ADD AP is the brightening agent and is consumed at the rate of 0.1 ml to 0.5 ml per Ah. CU 150 ADD CP is the brightening carrier and is consumed at the rate of 1 to 3 ml/l per Ah. The addition rate depends on the specific plating conditions.

Following the initial addition of CU 150 ADD CP and CU 150 ADD AP 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

The bath may be operated between 10 and 27 °C. The recommended 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 may be useful for achieving low stress films at higher current densities. Heating may not be required if ambient temperature is within the range as indicated. Still, temperature control is recommended, as the solution may be heated without control from power dissipations of the pump.

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 agents 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 in the indicated ratio to the cathode area (wafer). Lower anode to cathode area ratios may effect undesired gas generation and may cause defects especially in fountain plater arrangements. 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 are only 85% anodically effective of their full surface area.

Soluble anodes:

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 additive consumption, poor levelling and rough deposits.

Anode-to-Cathode Spacing

Normal anode-to-cathode spacing for wafer plating is 5 to 15 cm 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 or for achieving better thickness uniformity of the deposit.

REPLENISHMENT & MAINTENANCE

Cu concentration

When inert anodes are used, the copper concentration needs to be replenished according to the amount of metal plated or Ah processed.

There are two options to replenish the solution:

Option 1: Replenish by bleed and feed using CU 150 REPLENISHER

After plating certain Ah and depositing the corresponding mass of copper, a pre-calculated volume is removed from the bath and replaced by the same amount of CU 150 REPLENISHER.

The volume V_R of the bath, which has to be replenished at a chosen level of reduced concentration c_R , at which the replenishment is performed, is given by:

$$V_R = V_N * c_N * (1 - z) / (c_R - z * c_N), \quad \text{where } V_N \text{ is the nominal bath volume, } c_N \text{ is the nominal concentration, } c_R \text{ the concentration of the replenishing solution CU 150 REPLENISHER and } z \text{ the ratio of the concentration at depletion level } c_{depl} \text{ to the nominal concentration } c_N$$

This ratio can be chosen depending on the desired level of stability of the concentration.

$$z = c_{depl} / c_N, \quad (\text{e.g. } z = 0.97)$$

The corresponding mass of metal plated is:

$$m_p = V_N * c_N * (1 - z) = I * t \ddot{A}_e, \quad \text{where } \ddot{A}_e \text{ is the electrochemical equivalent.}$$

Example: Replenishment of the bath at a depletion concentration of copper at 97% of the nominal concentration of 40 g/l and a nominal bath volume of 40 litres.

The volume to be replenished is:

$$V_R = (40 \text{ l} * 40 \text{ g/l} * (1 - 0.97)) / (50 \text{ g/l} - 0.97 * 40 \text{ g/l}) = 4.29 \text{ l}$$

The mass of copper metal plated up to this point is: $m_p = 40 \text{ l} * 40 \text{ g/l} * (1 - 0.97) = 48 \text{ g}$

The electrochemical equivalent \ddot{A}_e is 1.19 g/Ah, so the replenishment has to be performed after:

$$Q = m_p / \ddot{A}_e = 48 \text{ g} / 1.19 \text{ g/Ah} = 40.33 \text{ Ah}$$

As a result in this example: After plating 40.33 Ah, the copper concentration has dropped to 97% of the nominal value of 40 g/l. The bath is replenished by taking out 4.29 litres of the depleted bath and refilling 4.29 litres from CU 150 REPLENISHER.

Option 2: Replenish plated metal using CU 150 COPPER SULPHATE

The depleted amount of copper is replenished with solid copper sulphate according the molar mass ratio:

$$m_{\text{CuSO}_4} = m_{\text{Cu}} * 249.69 \text{ mol g}^{-1} / 63.55 \text{ mol g}^{-1} = 3.93 m_{\text{Cu}}$$

Example: For replenishing 48 g copper to the bath (without bleed and feed), fill

$$m_{\text{CuSO}_4} = 3.93 * 48 \text{ g} = 188.59 \text{ g} \quad \text{from CU 150 COPPER SULPHATE into the bath.}$$

The procedure of option 2 is only recommended, when the complete dissolution of the copper sulphate can be assured, which implies a separated plating volume circulation from a storage or make up tank system.

CU 150 ADD CP and CU 150 ADD AP additives

The additives are added along with the CU 150 REPLENISHER solution.

The assumed consumption rate of CU 150 ADD CP resp. CU 150 ADD AP is 1.2 ml/Ah (1 ml per g copper) resp. 0.12 ml/Ah (0.1 ml per g copper).

If the consumption of additives is higher than these values, separate dosage of the additives can be performed additionally. Especially in new tool setup situations, the consumption rate may be higher due to the absorption of the additives in filter units and other plastic materials.

Inert anode conditioner (IAC)

For the replenishment of the inert anode conditioner (IAC), substitute with the corresponding amount of CU 150 P CONC needed for proper IAC concentration from the volume of CU 150 REPLENISHER to be replenished as described in option 1. (1 litre Cu 150 P CONC contains 500 ml IAC.)

Example: 40 litres nominal bath volume, IAC level has dropped to 37.5 ml/l

$$\text{IAC amount needed: } 40 \text{ l} * (50 \text{ ml/l} - 37.5 \text{ ml/l}) = 500 \text{ ml}$$

CU 150 P CONC needed: 1 litre (containing 500 ml IAC)

Cu 150 REPLENISHER needed for replenishing Cu and additives according to option 1 above: 4.29 litres.

Replenish the bath nominal volume of 40 litres with 4.29 litres bleed and feed:

1. Take out 4.29 litres depleted solution.
2. Replenish 3.29 litres CU 150 REPLENISHER
3. Replenish 1.00 litres CU 150 P CONC

Sulphuric acid

Sulphuric acid is replenished upon analysis according to the nominal values.

For increasing the concentration of sulphuric acid by 1g/l add 0.63 ml/l H₂SO₄ (96%).

For increasing the concentration of sulphuric acid the following formula applies:

$$V_R = V_N * (C_N - C_{depl}) / (C_R - C_N) = V_N * \Delta C / (C_R - C_N)$$

- V_R: volume to add from sulphuric solution
- V_N: nominal volume of the bath
- C_N: nominal concentration
- C_{depl}: depleted or actual concentration
- C_R: concentration of replenishing solution (e.g. H₂SO₄ 96%)
- ΔC: increase of concentration

Example: Bring sulphuric acid concentration from 160 g/l back to 170 g/l in a bath of 40 litres

$$V_R = 40 \text{ l} * (170 \text{ g/l} - 160 \text{ g/l}) / (0.96 * 1840 \text{ g/l} - 170 \text{ g/l}) = 0.251 \text{ l}$$

(setting V_N to 1 liter, the result V_R = 6.3ml represents the value for increasing by Δc = 10 g/l per liter)

As a result, 251 ml of H₂SO₄ (96%) are needed to restore the nominal concentration of 170 g/l sulphuric acid in a bath of 40 liters. Note, that while the acid concentration per liter is accurate, the total volume has increased by the volume replenished.

Sulphuric acid replenishment may also be anticipated, if drag out loss data is consistent.

Example: Assuming 3 ml bath drag out per wafer, 0.5 g sulphuric acid is dragged out per wafer processed. After 100 wafers processed, 50g sulphuric acid needs to be replenished, corresponding to 28.3ml H₂SO₄ (96%) replenishment.

Chloride ion concentration

The chloride content is easily increased, when necessary according to analysis data, by the addition of reagent grade hydrochloric acid. For increasing 1 mg/l chloride add 0.028 ml/l HCL (1N/1M solution).

SPECIFIC PROCEDURES

- Oxygen plasma treatment of substrates 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.

STORAGE

NOTE: NB SEMIPLATE CU 150 and CU 150 REPLENSHER are sensitive especially to cool temperatures such as less than 15°C. If stored at less than 10°C, copper sulphate may precipitate, however, which can be dissolved again under agitation at elevated temperatures.

Make sure to store these products between 15°C and 30°C !

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 or 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.

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