NB SEMIPLATE BI 100

Pure Bi plating process

INTRODUCTION

NB SEMIPLATE BI 100 is a high-purity electroplating process which produces fine-grained, matte, pure bismuth deposits. It is especially formulated for use in the fabrication of micro patterns on semiconductor wafers. The solution is available as ready-to-use solution.

"NB SEMIPLATE BI 100" is shipped **ready-for-use**, while the "BI **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	Comment
NB SEMIPLATE Bi 100	• Ready-to-use solution; contains bismuth, additives and methanesulfonic acid in nominal values
BI 100 REFINER	• grain refiner to produce fine grained, matte deposits
BI 100 ACID	• high purity solution containing 942 g/l free methanesulfonic acid. It provides acid for the operating solution and is necessary for solution stability and conductivity.
BI 100 CONC	• is a high purity concentrate containing 100 g/l bismuth. It provides the bismuth ion concentration for replenishment.

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

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.
Acidic 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	Platinated titanium anodes are preferred as inert anode system. Inert anodes must be degreased and clean.

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 BI 100 ACID heated to 50°C for 8 hours. Again flush tank with water.
3. Empty the tank.
4. Inert anodes may be installed after degreasing with NaOH, short soak in 10% by volume BI 100 ACID and thorough cleaning with DI-water.
5. 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 BI 100 ACID to which 20 ml/l of BI 100 REFINER 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.
6. Install leached filter cartridges.
7. Carefully pour or pump recommended amount of NB SEMIPLATE BI 100 solution into the tank and start filtering the solution. The solution is now ready for production operation.
8. Take a sample of the solution to check for final additive concentrations, optionally send to NB Technologies GmbH for analysis.

BATH PARAMETERS

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

	NB analysis	Units	Max. upper limit	Upper action limit	Optimum	Lower action limit	Lowest limit
Bi^{3+} concentration	X	g/l	50	45	40	35	30
BI 100 ACID	X	ml/l	120	110	100	90	80
BI 100 REFINER	X	ml/l	50	40	30	25	20

PLATING CONDITIONS

Parameter		**Optimum**	**Range**
Cathode current density	[A/dm²] (ASD)	1	0.5 - 3
Flow (depending on tool)	[l/h]	-	500 - 1000
Anode to cathode area ratio platinated titanium		3:1	1:1 or higher
Anode to cathode spacing (depends on tool and wafer size)	[cm]		5 - 15
Temperature	[°C]	20	20 - 40

DEPOSITION RATES:

The efficiency is >99% up to 3 ASD.

The bath yields

Bi	Unit
0.721	mg / As
43	mg / Amin
2.596	g / Ah

Current density [A/dm²]	Layer thickness per 1minute plating time [µm]	Time needed for 1µm deposit [min]
0.5 ASD	0.16 µm	6:16
1 ASD	0.32 µm	3:08
2 ASD	0.64 µm	1:34
3 ASD	0.96 µm	1:04

OPERATION

BI 100 REFINER
The consumption rate of BI 100 REFINER will be a function of the type of plating equipment used. However, the replenishment rate will normally be 0.2 to 0.5 ml per Ah. If deposits start to show coarse grain, BI 100 REFINER may be added in 5 ml/l to 10 ml/l increments. A slight overdose is not critical.

BI 100 ACID
The acid concentration should not fall below 80ml/l. For replenishment add the correspondent volume of BI 100 ACID.
Low levels of acid concentrations effect higher anode potential and poorer uniformity. Higher levels of acid concentration reduce the maximum plating current density, but do not impact the plating quality in general.

BI 100 CONC
The Bi concentration of the electrolyte will fall corresponding to the work out of the metal ions. The metal concentration can be increased to nominal value using the BI 100 CONC containing 100g/l Bi.

Temperature
The bath can be operated at room temperature. Elevated temperatures may take effect on uniformity.
Control the temperature of the solution between 20 and 40 °C. The optimum operating temperature is 20 °C. Lower temperature effects better thickness uniformity, but limits the maximum current density to be used and effects bigger grain size. Higher temperature enables higher plating currents and finer grains, but effects poorer uniformity.

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 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.

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 5 to 30 mA/cm² (0.5 to 3.0 ASD) is recommended for most applications. Lower current densities yield more shiny surface conditions.

CONTAMINATION PRECAUTIONS

Make sure to prevent sulfuric acid to enter the bath. The bath will be destabilized at small concentrations, such as 0.4g/l H_2SO_4 or 4ml per liter H_2SO_4 (10%).

REPLENISHMENT & MAINTENANCE

Bi^{3+} concentration

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

The depleted amount of bismuth is replenished from the concentrated bismuth concentrate BI 100 CONC:

The BI 100 CONC contains 100 g/l Bi^{3+}.

Example: For replenishing 1g/l Bi^{3+} add 10ml/l BI 100 CONC.
Please note that the volume is increased by 5% from the nominal volume and the concentration per is approximated only.

Please also note that the concentration of BI 100 REFINER needs to be replenished separately.

BI 100 REFINER

The BI 100 REFINER is added upon analysis or according to Amin. The assumed consumption rate of BI 100 REFINER is 0.2 ml/Ah (or 0.08 ml per g Bi deposited).
Especially in new tool setup situations, the consumption rate may be higher due to the absorption of organic compounds in filter units and other plastic materials.

Methanesulfonic acid

Methanesulfonic acid is replenished upon analysis according to the nominal values using the BI 100 ACID.

For increasing the concentration of BI 100 ACID the following formula applies:

$$V_R = V_N * (c_N *- c_{depl}) / (c_R – c_N) = V_N * \triangle c / (c_R – c_N)$$

V_R:	volume to add from BI 100 ACID
V_N:	nominal volume of the bath
c_N:	nominal concentration
c_{depl}:	depleted or actual concentration
c_R:	concentration of replenishing solution
$\triangle c$:	increase of concentration

Example: Bring BI 100 ACID concentration from 90 ml/l back to 100 ml/l in a bath of 3 litres

V_R = 3 l * (100 ml/l – 90 ml/l) / (1000ml/l – 100ml/l) = 0.033 l
(setting V_N to 1 liter, the result V_R = 11ml represents the value for increasing by $\triangle c$ = 10 ml/l per liter)

As a result, 33ml of BI 100 ACID are needed to restore the nominal concentration of 100 ml/l in the bath of 3 liters. Note, that while the acid concentration per liter is accurate, the total volume has increased by the volume replenished.

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

Example: Assuming 3 ml bath drag out per wafer, 0.3 ml BI 100 ACID is dragged out per wafer processed. After 100 wafers processed, 30 ml BI 100 ACID need to be replenished, corresponding to 28.26g methanesulfonic acid

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.

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