NB Semiplate NiMn 100

Nickel-Manganese sulfamate process

INTRODUCTION

NB Semiplate NiMn 100 is a nickelsulfamate electroplating process, which incorporates small amounts of Mn in the deposit. While properties of pure Ni deposits change dramatically during temperature treatments, the Mn content stabilises the hardness, ductility and yield strength under temperature treatments as high as 600°C. Secondly, such properties do not dramatically change in operation. Therefore, the process is well suited for Ni films used for micro-electromechanical functions, as required for sensors and actuators in microsystem technology.

The process can be operated

- for rather columnar growth **without grain refiner** and rather **rough surface condition**; this is the **ready-to-use product** status of **NB Semiplate NiMn 100**
- or for fine-grained films and semi-rough surface using the grain refiner Ni 100 ADD. AGENT

NB Semiplate NiMn 100 is manufactured to meet the requirements associated with the electroforming processes for the semiconductor industry and microsystem technology (MST).

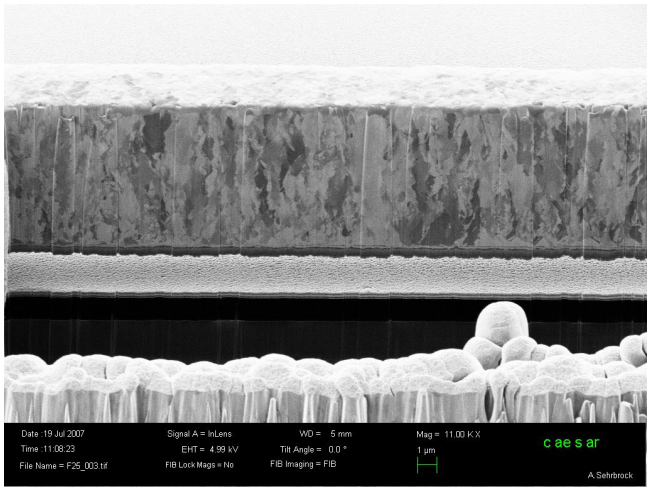
The NB Semiplate NiMn process contains an anode activating agent in controlled amounts to enhance anode corrosion and prevent anode passivation. Deposit properties are easy to control and maintain.

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

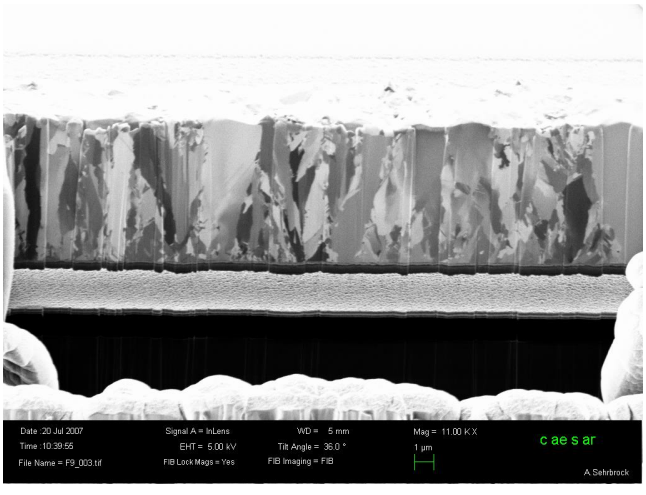
READ ENTIRE TECHNICAL DATA SHEET BEFORE USING THIS PRODUCT.

FEATURES/BENEFITS

- High purity nickel depositions
- High stability of mechanical properties under temperature and in operation
- High ductility
- High hardness
- Fine grained or large grained
- Medium mechanical stress impact of Mn incorporation (depending on operation condition)
- No anode passivation
- Good throwing power



Pure Ni film as plated showing fine columnar grain



NiMn film (200ppm Mn) showing medium size columnar grain growth

NiMn films from Mn sulfamate solution before and after tempering

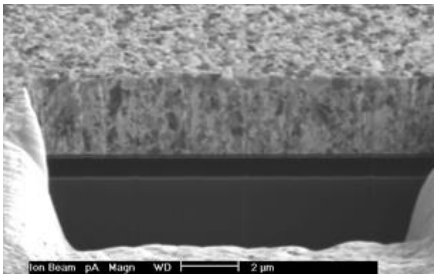
The cross section pictures below show a plated sheet film before and after temperature treatment.
There is no major increase in overall grain size from NiMn bath NB Semiplate NiMn 100 (from optical view).

The pure Ni films plated from a sulfamate bath (standard solution) show major change of the grain size after temperature treatment.

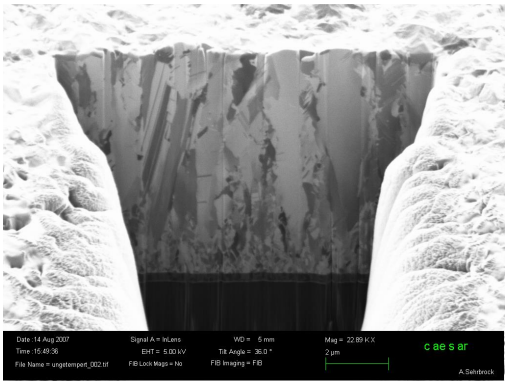
Parameters of NiMn plated films:
Sheet film plating on Cu seed from NB Semiplate NiMn 100 solution
(Solution: 4g/l Mn, Ni 70g/l, ph 3.8, 42°C; current density: 1ASD)

Mn film concentration: 1200ppm (XRF)

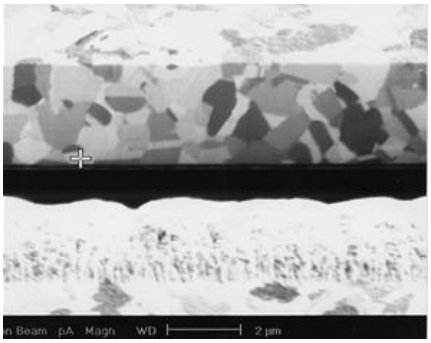
Tempering: 400°C, 15min holding time (excluding ramp up and ramp down)



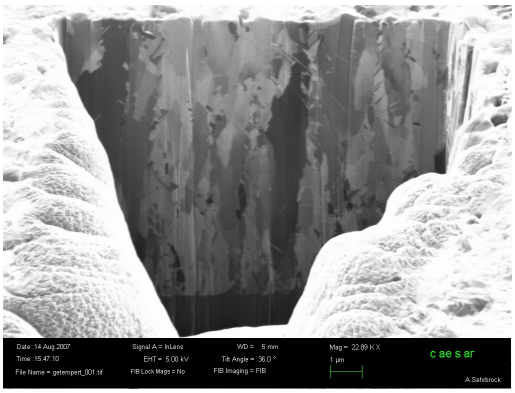
pure Ni film from sulfamate bath as plated (standard bath)



NiMn film from NB Semiplate NiMn 100 as plated (conditions as above)



pure Ni film from sulfamate bath after anneal at 350°C (standard bath)



NiMn film from NB Semiplate NiMn 100 after anneal at 400°C (conditions as above)

The table below shows mechanical data from indentation tests.
NiMn as plated with 670ppm Mn shows a higher Young's Modulus and a lower hardness than as plated Ni.

After temperature treatment at 400C° for 15 minutes, the hardness of both materials decreases, however, the change is more dramatic for Ni.

	Hardness [Vickers]	**Hardness [MPa]**	**Young's Modulus [GPa]**
NiMn 670ppm as plated	350	3780	205
NiMn 670ppm, annealed 15min@400C	250	2690	146
Ni as plated	480	5195	125
Ni annealed 15min@400C	190	2025	98

NB Semiplate NiMn 100 DELIVERY PROGRAMME

Product Name	**Comment**
NB SEMIPLATE NiMn 100	• ready-for-use solution (contains NO grain refiner NI 100 ADD. AGENT)
NI 100 ANODE ACTIVATOR	• anode activating agent for proper anode solubility
NI 100 ADD. AGENT	• grain refiner and smoothing agent for shiny surface
NICKELSULFAMATE SOLN 185 G/L NI	• nickelsulfamate concentrate for mixture and nickel replenishment
MANGANESESULFAMATE SOLN 20g/l MN	• manganesesulfamate concentrate for mixture and manganese replenishment
BORIC ACID	• boric acid for pH-buffering and conductivity
SULPHAMIC ACID	• used to lower the pH

Ready for use solution

The NB SEMIPLATE NiMn 100 is shipped as ready-for-use solution. Due to the high boric acid content, the boric acid falls out at room temperature.

NOTE
The ready-for-use solution contains **NO** grain refiner NI 100 ADD. AGENT.

NOTE
When filling the solution into the plating tank, make sure to drag out all precipitated boric acid. The boric acid will re-dissolved when heated to operating temperature.

EQUIPMENT

Tanks
Tanks made of temperature resistant polymers such as PP, PE, PTFE or glass are recommended materials. First they have to be leached, the best overnight or over the weekend with ca. 5-10% caustic soda solution at approx. 50°C, rinse with deionised water and neutralised with ca. 5% sulphamic acid.

Heating
Automatic temperature control recommended. Use porcelain-, quarz-, or glass heaters, do not use steel or stainless steel.

Anodes
Titanium baskets with new anode bags made of PP are recommended.
Anode material: S-Ni-Pellets (∅6-13 mm) or S-Ni-Rounds (∅21 mm).
New anode bags have to be leached out. Do not introduce anode bags used before.
New anodes have to be degreased and run in. For degreasing use 10 to 20% NaOH at 20°C to 50°C. Make sure to clean thoroughly with DI-water. Then do a slight etch witch sulphamic acid 10 to 20% for at least 1 hour at 20°C to 50°C, at best for a couple of hours until the solution shows slight green colour. For running in do dummy plating with varying current densities from 10 to 30mA/cm², e.g. for 1 hour each.

Filtration
Continuously, e.g. with filter cartridges (1-5 µm pores); filtration capacity at least 1 volume per hour. Tube connections should be made of fibre strengthened polymere.

Agitation
Use strong, uniform agitation or flow.

Rectifier
Sufficient to provide the necessary direct current with less than 5% ripple.

OPERATING CONDITIONS

	Optimum	**Range**
Nickel metal	90 g/l	80 – 110 g/l
Manganese metal	2g/l	depends on application
Boric acid	45 g/l	40 – 45 g/l
Ni 100 ANODE ACTIVATOR	160 ml/l	130 – 170 ml/l
Ni 100 ADD. AGENT	* 1)	depends on application
pH	3.5	3.0 – 4.0
Temperature	52°C	40 – 56°C
Cathodic current density	1 A/dm²	0.1 to 8.0 A/dm²
Anode to cathode surface		minimum 2 : 1
Agitation of the electrolyte	Vigorous	

* 1) e.g. 21ml/l corresponding to NB Semiplate Ni 100 process

COMPONENTS TO MAKE-UP A VOLUME OF 10 LITER

Nickelsulfamate SOLN 185 g/l Ni	4,9 l
Manganesesulfamate SOLN 20g/l Mn	1,0l
BORIC ACID	450 g
NI 100 ANODE ACTIVATOR	1,6 l
NI 100 ADD. AGENT	210 ml (if grain refiner is desired)

PREPARATION OF THE SOLUTION

1. All parts of the equipment, which are in direct contact with the electrolyte should be leached with 60 g/l tri-sodium phosphate solution for 8 hours at a temperature of 50°C. It should than be rinsed with clean water and leached with a 5% v.v. sulphamic acid solution for 8 hours at a temperature of 60°C. Again, it should be thoroughly rinsed with clean water.
2. Fill the tank to 35% (35 ltr) of the required volume with deionised water.
3. Add, with agitation, the Nickelsulfamate solution (185 g/l Ni metal) and stirr well.
4. Add, with agitation, the Manganesesulfamate solution (20g/l Mn metal) and stir well
5. Add, with agitation, the boric acid while heating the solution to 60-70°C. Make sure, that it is completely dissolved before you go to the next step
6. Add, with agitation, Ni 100 Anode Activator.
7. If desired: Add, with agitation, Ni 100 Add. Agent (
8. Adjust to final volume with deionised water.
9. Check and correct pH to 3.5 with sulphamic acid.
10. Analyse for the additive concentration and adjust if necessary.
11. Carry out internal stress measurement
12. The bath is then ready for use.

MAINTENANCE OF THE SOLUTION

Boric acid

Serves as a buffer to prevent variations in solution pH during the plating cycle. It also reduces the tendency toward burning at higher current densities and should be maintained at optimum for best results.

Temperature

Maintain the temperature of the plating solution between 32 and 54°C. For uniform results, keep the solution temperature near 50°C. Agitation or flow condition should be strong.

pH control

Maintain the pH of the solution between 3.0 and 4.0 to improve the solution conductivity and permit the use of higher current densities. High pH values result in less ductile deposits and lower pH values cause lowered plating efficiencies. The best results are obtained at pH 3.5. Use only reagent grade sulphamic acid to lower the pH and high purity nickel carbonate to raise the pH. Do not add nickel carbonate directly to the solution. Either make a slurry with a portion of the solution and add to sump or weir or fill an anode bag and hang it in the solution where solution movement is good.

Nickel concentration

Nickel sulfamate solution contains 185 g/l nickel metal. This solution is used for Make-up and compensation for drag-out losses.

Manganese concentration

The Mn concentration can be maintained with the Manganesesulfamate SOLN 20 g/l. The content depends on the incorporation target and current density of the process.

Ni 100 Anode Activator

Is used to improve solution conductivity, throwing power and anode corrosion.
For best results the anode activator should be maintained at the optimum range and added on the bases of analysis.

Ni 100 Add. Agent

NOTE: The ready-for-use solution contains **NO** grain refiner NI 100 ADD. AGENT.
If desired, the grain refiner can be added corresponding to the NB Semiplate Ni 100 process.

The grain refiner contains a wetting agent along with a stress reducer. This material serves the functions of keeping the deposit at a low internal stress (slightly compressive) as well as semi-bright and ductile, it increases also the hardness of the deposit up to 580 HV.
The semi-brightness is a side effect of the stress reducer in the addition agent, which should be maintained by use of an ampere hour meter, the rate of addition being 0.5 ml per ampere hour.

ANALYSIS

The electrolyte should be analysed routinely to control concentrations of its additives. NB Technologies GmbH offers analysis of the contents from 200 ml samples.

RATE OF DEPOSITION

Time required for plating different film thickness (in minutes)

µm A/dm²	2.5	7.5	12.5	17.5	25	50
1.1	12	36	60	84	120	240
2.2	6	18	30	42	60	120
3.2	4	12	20	28	40	80
4.3	3	9	15	21	30	60
5.4	2.4	7.2	12	16.8	24	48
10.8	1.2	3.6	6	8.4	12	24

Mn film concentration in (ppm) depending on current density and Mn content in the solution

A/dm²	Mn 1g/l	Mn 2g/l	Mn 4g/l
1.0	200	800	1250
1.5	1000	2700	3800
2.0	1700	4200	5300

CONTROL OF IMPURITIES

Control of contaminants, that may adversely affect the performance of the NB Semiplate NiMn 100 process solution, is best achieved through prevention methods, such as good rinsing and avoiding solution contact with acid soluble metals.

Metallic contaminants such as iron, tin and lead will alter both the efficiency of the solution and stress of the deposit if allowed to reach appreciable levels. Maintain the concentration of each of these metallic contaminants below 10 ppm. Frequent low current density “dummy” plating with a corrugated nickel (or nickel plated) cathode at 0.5 A/dm^2 will selectively remove these metals.

Organic contamination may be typically introduced to the solution in the form of lubricants, tape residues and plating resist breakdown products. Organic contaminants will affect the stress of the deposit by interaction with the brightening system of this process if allowed to reach appreciable levels. These materials can only be removed by the carbon treatment procedure.

Carbon filtering

In order to remove organic contaminations as per analysis or by suspect, organic cleaning and carbon filtering may be applied. After the procedure, analysis and replenishment of the additioners is required. Regular carbon filtering is not recommended. Contact NB Technologies for technical assistance.

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.

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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