(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 055 377
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 81109163.6

(22) Date of filing: 29.10.81

(51) Int. Cl.[3]: C 25 D 3/56
H 01 F 10/14

(30) Priority: 31.12.80 US 221598

(43) Date of publication of application: 07.07.82 Bulletin 82/27

(84) Designated Contracting States: DE FR GB

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(54) Method of depositing nickel-iron-boron alloy magnetic films.

(57) Nickel-iron-boron alloy magnetic films containing from 0.1 to 2.0% boron by weight and from 17 to 27% iron by weight are electrolytically deposited using a bath having a pH of 2.5 or less, and containing a borane reducing agent. The films have a high resistance to corrosion and a coercivity less than 0.1 Oe in films 3000Å thick.

EP 0 055 377 A2

METHOD OF DEPOSITING NICKEL-IRON-BORON ALLOY MAGNETIC FILMS

This present relates to methods of depositing nickel-iron-boron alloy magnetic films.

U.S. patent specification 3,483,029 entitled "Method and Composition for Depositing Nickel-Iron-Boron Magnetic Films" describes in the Example an NiFeB electrolessly deposited alloy with 0.8% B, 19.3% Fe and the remainder Ni. The film was 12,550 Å thick and had a coercivity of H_O = 1.0e. The magnetostriction was near zero. The anisotropic field was about 4.8 Oe. The pH of the bath was above 8.

A process for depositing a nickel-iron-boron alloy magnetic film which contains from 0.1 to 2 per cent boron by weight is characterised according to the invention, by being an electrolytic deposition process employing a bath having a pH at or below 2.5 and containing a borane reducing agent.

The present invention provides nickel-iron-boron alloy magnetic films having extremely low coercivity and very high resistance to corrosion. Magnetic films 3000Å thick or thicker deposited according to the present invention, have a coercivity and a bubble collapse field of less than 0.1 Oe. They also have excellent magnetic anisotropy.

In accordance with the present invention, magnetic films are electrodeposited from an acid (pH below 2.5) bath containing small amounts of a borane reducing agent such as Dimethylamine borane. Table I below gives one specific bath formulation and a range of bath formulations.

TABLE I

	Specific	Range
$NiCl_2 \cdot 6H_2O$	109.0 g/l	25 to 218 g/l
H_3BO_3	25.0 g/l	15 to 50 g/l
Na saccharin	1.0 g/l	0.8 to 3.0 g/l
Na lauryl SO_4	0.6 g/l	0.2 to 1.0 g/l
adjust to pH 1.5, then add		
$FeCl_2 \cdot 4H_2O$	1.9 g/l	1.0 to 3.0 g/l
Dimethylamine borane (DMAB)	1.6 g/l	0.9 to 2.0 g/l

The dimethylamine borane (DMAB) is predissolved in 100 cc H_2O. 1.6 g/l of DMAB is near maximum solubility in the specific bath in Table I. The sodium lauryl SO_4 is a surfactant, which improves plating. The sodium saccharin serves to reduce stress in the plated film. The boric acid serves as a pH regulator and deposit brightener.

$\lambda = 0$ at 16.5 mA/cm^2 when $FeCl_2 \cdot 4H_2O$ = 1.9 g/l. Agitation rate anywhere from 0.5 cycle per second to 2 cycles per second can be utilized. Agitation of 1 cycle/second in a paddle cell is the equivalent of 200 rpm on a rotating disc electrode.

After the addition of DMAB solution to the bath, the pH rises for a few minutes. After readjusting the pH to 2.5 the bath is usable. If the concentration of $FeCl_2 \cdot 4H_2O$ is higher than 1.9 g/l, the current will have to be raised in order to maintain the λ = 0 composition. For example, if the $FeCl_2 \cdot 4H_2O$ is increased to 5.0 g/l, λ=0 is obtained at 49.6 mA/cm^2 when plating onto a cathode in a continuous sheet form. At this high current density the DMAB seems to have a smaller effect on the film. When plating is conducted at low density, the resulting films incorporate 2% boron. Despite this small quantity of boron, the magnetic behaviour of the film is markedly improved. The films also have excellent anisotropy.

A NiFeB film 5400Å thick deposited in accordance with the present invention on a substrate comprising 1000Å platinum/100Å titanium on glass had a value for H_o of 0.1 or less. The instrument commonly used to measure the magnetic properties of NiFe films is not sufficiently sensitive to measure values at this very low level.

When NiFeB films are deposited in accordance with the present invention on T and I bars, or when a sheet film is shaped by ion milling or sputter etching, the superiority in coercivity of NiFeB over NiFe is still apparent. This makes the NiFeB quite useful for bubble memory applications. When plating through masks, we have also discovered to our surprise that the deposits of NiFeB are smoother and the thickness of individual features over a large area are considerably more uniform than for NiFe. This suggests that in addition to providing boron incorporated in the film, DMAB acts as a smoothing agent and a levelling agent.

While the above example employed dimethylamine borane, it should be apparent to those skilled in the art that other borane containing compounds, particularly borane reducing agents, may be used to obtain similar results. Other useful compounds include, for example, amine boranes such as trimethylamine borane, and other aliphatic heterocyclic, arylamine and heteroaromatic boranes and borohydrides.

I <u>Examples of films plated onto a continuous sheet metal cathode</u>

Films were electroplated at room temperature in a >40 Oe magnetic field from the bath as shown in Table I onto a cathode in a continuous sheet form except for the following changes:

(a) $FeCl_2 \cdot 4H_2O$ was 1.6 g/l
DMAB 1.2 g/l
and current density was 5.0 ma/cm^2

The resulting 4000Å thick film had a coercivity H_c <0.1 Oe and a very square B-H loop. The film composition was 19% Fe, 0.6%B; 80.2% Ni. The film was zeromagnetostrictive (λ=0).

(b) $FeCl_2 \cdot 4H_2O$ was 1.8 g/l
DMAB was 1.5 g/l
current density was 10 ma/cm^2

The composition of the 4000Å film was 19.4%Fe, 0.4%B and 80.2%Ni. Magnetic results were substantially the same as in (a) above.

(c) $FeCl_2 \cdot 4H_2O$ was 1.8 g/l
DMAB was 1.5 g/l
current density was 21.6 ma/cm^2

The composition of the 4000Å film was 21.6%Fe, 0.3%B and 78.1%Ni. Magnetic properties were substantially the same as in (a) above. Film was slightly off from zero magnetostriction.

II Examples of films plated through photoresist masks

(a) Discrete features were plated onto a continuous thin metallizing starter sheet cathode on top of a garnet coated with 3000Å of SiO_2 spacer and on top of Si wafer with 3000Å SiO_2 masked by Shipley 1350 resist with 2µm wide features exposed in resist to define the bubble memory C- and I-bar and chevron pattern.

The bath composition was:

$NiCl_2 \cdot 6H_2O$	109 g/l
H_3BO_3	25 g/l
Na saccharin	1 g/l
Na lauryl sulfate	0.1 g/l
$FeCl_2 \cdot 4H_2O$	1.5 g/l
DMAB	was varied from 0 to 2 g/l

the overall current density id varied from 3.48 to 5 ma/cm^2.

The film compositions were:

	DMAB g/l	id ma/cm^2	%Fe	%B	%Ni
(a)	0	5.0	21	0	79
(b)	1.0	5.0	25	0.4	74.6
(c)	1.0	3.5	27	0.4	72.6

In both cases where the DMAB was added to the solution the films were smoother; the thickness of various features showed less variation from spot to spot on the wafer; the coercive force of the features was much lower than in the features plated without the Boron, and the garnet devices showed lower operative margins of the magnetic field. The operative margin was much lower than in devices plated in the absence of DMAB in the bath (a). When DMAB was added (baths (b) and (c)), the percentage of iron in the features, plated through a mask, was always higher than in the absence of DMAB.

(b) Discrete features were plated onto a continuous thin film metallizing starter sheet on SiO_2 on a garnet and on 3000Å of SiO_2 on Si wafers through 2μ openings in shipley 1350 resist.

The bath composition was:

$NiCl_2 \cdot 6H_2O$	109 g/l
H_3BO_3	25 g/l
Na Saccharin	1.0 g/l
Na Lauryl Sulfate	0.6 g/l
$FeCl_2 \cdot 4H_2O$	1.1 g/l
DMAB	varied from 1.6 to 2.2 g/l

Overall current density varied from 5 to 7.0 ma/cm^2.

Film Compositions were:

DMAB	id	%Fe	%B	%Ni
1.6	5	17	0.4	82.6
1.6	7	19	0.4	80.6
2.2	7	22	0.4	77.6

Films were plated 3500Å thick.

In all cases the films have shown superior surface smoothness, superior uniformity of thickness from feature to feature, very low closed loop coercive force and the bubble devices plated on garnets operated at much lower minimum operating bias field.

The minimum bias field in the absence of the Boron in the 3500Å film plated in 2µm wide features is of the order of 25 to 30 Oe, while for the same thickness film plated from the above bath containing Boron the minimum bias field is consistently 15Oe or lower.

(c) Discrete features were plated onto a continuous thin film metallizing starter sheet on SiO_2 on a garnet and on 3000Å SiO_2 on top of Si wafers through 2µm openings of the C- and I-Bar bubble pattern in Shipley 1350 resist mask.

The bath composition was:

$NiCl_2 \cdot 6H_2O$	109 g/l
H_3BO_3	25 g/l
Na Saccharin	1.0 g/l
Na Lauryl Sulfate	0.6 g/l
$FeCl_2 \cdot H_2O$	1.2 g/l
DMAB	varied from 0 to 1.2 g/l

overall current density id varied from 3.6 to 7.2 ma/cm^2.

The resulting 3500Å plated features had the following characteristics:

DMAB g/l	id ma/cm^2	%Fe	%B	%Ni
0.0	5.0	18 (varied 18.3 to 19.5)	0	82
0.4	7.2	20	~0.4	79.6
1.0	3.6	24	~0.4	75.6
1.2	5.0	25	~0.4	74.6

All films in which DMAB was used showed superior smoothness, superior thickness uniformity from feature to feature and superior magnetic characteristics. The bubble memory devices plated with these films on garnet showed much lower value of the lower operating margin of the bubble devices.

Corrosion testing of all films plated from the bath containing DMAB, and hence containing B in addition to Ni and Fe, showed 4 to 10 times higher corrosion resistance than the films plated from the above bath in absence of DMAB.

CLAIMS

1. A process for depositing a nickel-iron-boron alloy magnetic film, the boron being present in an amount from 0.1 to 2 per cent by weight, characterised by the process being an electrolytic deposition process employing a bath having a pH at or below 2.5 and containing a borane reducing agent.

2. A process as claimed in claim 1, in which the borane reducing agent is dimethylamine borane.

3. A process as claimed in claim 1 or claim 2, in which the bath also contains a pH regulator, a surfactant and sodium saccharin.

4. A magnetic film deposited by a process as claimed in any preceding claim, the film containing 0.1 to 2 per cent boron by weight, 17 to 27 per cent iron by weight and the balance nickel.

5. A magnetic film as claimed in claim 4, which is at least 3000Å thick and has a coercivity less than 0.1 oersted (π/25 ampere turns per cm).