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(54) **ELECTROLESS NICKEL PLATING BATH COMPOSITION**
STROMLOSE VERNICKELUNGSBADZUSAMMENSETZUNG
COMPOSITION DE BAIN DE NICKELAGE AUTOCATALYTIQUE

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Description

Field of the invention

5 [0001] The present invention relates to an aqueous plating bath composition for the electroless deposition of nickel phosphorous alloys.

Background of the invention

10 [0002] Electroless plating of nickel-phosphorous alloys is used in various industries. The deposits derived are used e.g. as wear resistant coatings and barrier layers.

[0003] Such plating bath compositions generally comprise a source of nickel ions, a hypophosphite compound as the reducing agent, at least one complexing agent and at least one stabilizing agent.

15 [0004] The at least one stabilizing agent present is required in order to provide a sufficient bath lifetime, a reasonable deposition rate and to control the phosphorous content in the as deposited nickel phosphorous alloy. Often, plating baths for deposition of nickel-phosphorous alloys known in the art comprise more than one stabilizing agent.

[0005] Common stabilizing agents are selected from heavy metal ions such as cadmium, thallium, bismuth, lead and antimony ions, inorganic ions such as SCN- and various organic compounds such as thiourea.

20 [0006] The patent document US 2,830,014 discloses plating bath compositions for electroplating of nickel which comprise thioalkane sulfonic acids or salts thereof such as mercaptopropane-1-sodium sulfonate as brightening and ductility-improving agents.

[0007] The patent application US 2005/0013928 A1 discloses an electroless plating pre-treatment solution which comprises 3-mercaptopropanesulfonic acid. The pre-treatment solution reduces the incubation time (time from the start of the supply of an electroless plating solution to the start of the plating reaction) of nickel plating from an electroless plating bath on a copper surface.

25 [0008] The patent application US 2006/024043 A1 discloses an alkaline aqueous plating bath for deposition of nickel phosphorous alloys which optionally comprises further additives such as thiourea and/or 3-mercapto-1-propane sulfonic acid. Such plating bath compositions are not acceptable for industrial applications (see Examples 2 to 5). Furthermore, thiourea is a carcinogenic substance.

30 [0009] CH620710 discloses an acidic electroless nickel plating bath comprising hypophosphite, complexing agent and a sulfur containing stabilising agent, namely thiourea, whereby a deposition of a nickel phosphorous alloy having a phosphorous concentration in the range between 7 and 10 wt.% is given.

[0010] The main disadvantages of known stabilizing agents are

35 a) the toxic behaviour of heavy metal ions such as cadmium, thallium, lead and antimony ions and

b) in case more than one stabilizing agent is present in an electroless nickel plating bath, the control of the mixture of stabilizing agents during use of such a plating bath is complex.

Objective of the Invention

[0011] Therefore it is the objective of the present invention to provide a bath composition for electroless deposition of nickel phosphorous alloys which is free of toxic heavy metal ion based stabilizers.

45 [0012] It is a further objective of the present invention to provide a bath composition for electroless deposition of nickel phosphorous alloys which allows deposition of a nickel phosphorous alloy having a phosphorous concentration in the range of 5 to 12 wt.-%.

Summary of the Invention

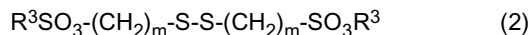
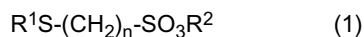
50 [0013] These objectives are solved by an aqueous plating bath composition according to claim 1 for electroless plating of a nickel phosphorous alloy, the plating bath comprising

(i) a water soluble source of nickel ions

55 (ii) a hypophosphite compound

(iii) at least one complexing agent and

(iv) a stabilizing agent selected from the group consisting of compounds according to formulae (1) and (2):



wherein

R^1 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,

n ranges from 1 to 6,

R^2 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,

R^3 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium and m ranges from 1 to 6

and having a pH value in the range of 3.5 to 6.5.

[0014] From such a plating bath composition, a nickel phosphorous alloy having a phosphorous content in the range of 5 to 12 wt.-% of phosphorous is derived by electroless plating.

Detailed Description of the Invention

[0015] The aqueous plating bath composition according to the present invention comprises a water soluble source of nickel ions such as nickel sulfate, a reducing agent such as sodium hypophosphite, at least one complexing agent and a stabilizing agent selected from compounds according to formulae (1) and (2).

[0016] The concentration of nickel ions ranges from 1 to 18 g/l, more preferably from 3 to 9 g/l.

[0017] The reducing agent is selected from hypophosphite compounds such as hypophosphorous acid or a bath soluble salt thereof such as sodium hypophosphite, potassium hypophosphite and ammonium hypophosphite. The amount of the reducing agent employed in the plating bath ranges from 2 to 60 g/l, more preferably from 12 to 50 g/l and most preferably from 20 to 45 g/l. As a conventional practice the reducing agent is replenished during the reaction.

[0018] The complexing agents are employed in amounts of 1 to 200 g/l, more preferably from 15 to 75 g/l.

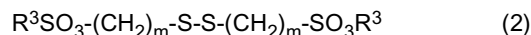
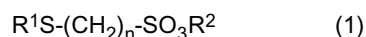
[0019] In one embodiment of the present invention, carboxylic acids, polyamines or mixtures thereof are selected as complexing agents. Useful carboxylic acids include mono-, di-, tri- and tetra-carboxylic acids. The carboxylic acids may be substituted with various substituent moieties such as hydroxy or amino groups and the acids may be introduced into the plating solutions as their sodium, potassium or ammonium salts. Some complexing agents such as acetic acid, for example, may also act as a buffering agent, and the appropriate concentration of such additive components can be optimised for any plating solution in consideration of their dual functionality.

[0020] Examples of such carboxylic acids which are useful as the complexing agents include: monocarboxylic acids such as acetic acid, hydroxyacetic acid, aminoacetic acid, 2-amino propanoic acid, 2-hydroxy propanoic acid, lactic acid; dicarboxylic acids such as succinic acid, amino succinic acid, hydroxy succinic acid, propanedioic acid, hydroxybutanedioic acid, tartaric acid, malic acid; tricarboxylic acids such as 2-hydroxy-1,2,3 propane tricarboxylic acid; and tetra-carboxylic acids such as ethylene diamine tetra acetic acid (EDTA).

[0021] The most preferred complexing agents are selected from the group consisting of mono-carboxylic acids and di-carboxylic acids.

[0022] In one embodiment, mixtures of two or more of the above complexing agents are utilized.

[0023] The stabilizing agent is selected from compounds according to formulae (1) and (2):



wherein

R^1 is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,

n ranges from 1 to 6,

R² is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,

R³ is selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium and

m ranges from 1 to 6.

[0024] More preferably, R¹ is selected from the group consisting of hydrogen, sodium and potassium.

[0025] More preferably, n ranges from 2 to 4.

[0026] More preferably, R² is selected from the group consisting of hydrogen, sodium and potassium.

[0027] More preferably, R³ is selected from the group consisting of hydrogen, sodium and potassium.

[0028] More preferably, m ranges from 2 to 4.

[0029] The concentration of the stabilizing agent according to formulae (1) and (2) in the plating bath composition ranges from 1 to 100 ppm, more preferably from 2 to 50 ppm and most preferably from 3 to 30 ppm.

[0030] Since the plating solution has a tendency to become more acidic during its operation due to the formation of H₃O⁺ ions, the pH may be periodically or continuously adjusted by adding bath-soluble and bath-compatible alkaline substances such as sodium, potassium or ammonium hydroxides, carbonates and bicarbonates. The stability of the operating pH of the plating solutions can be improved by the addition of various buffer compounds such as acetic acid, propionic acid, boric acid, or the like, in amounts of up to 30 g/l, more preferably from 2 to 10 g/l.

[0031] The pH value of the aqueous plating bath according to the present invention preferably ranges from 3.5 to 6.5, more preferably from 4 to 6.

[0032] Other materials may be included in the nickel plating solutions such as buffers and wetting agents. These materials are known in the art.

[0033] The nickel plating solutions optionally may employ one or more wetting agents of any of the various types heretofore known which are soluble and compatible with the other bath constituents. In one embodiment, the use of such, wetting agents prevents or hinders pitting of the nickel phosphorous alloy deposit, and the wetting agents can be employed in amounts up to about 1 g/l.

[0034] The substrate to be plated is contacted with the plating bath at a temperature of at least 40°C up to 95 °C. The electroless nickel plating baths according to the present invention are employed, in one embodiment, at a temperature of from 70°C to 95°C, and more often, at a temperature of from 80°C to 90°C.

[0035] The duration of contact of the electroless nickel plating bath with the substrate being plated is a function which is dependent on the desired thickness of the nickel phosphorus alloy. Typically, a contact time can range from 1 to 30 min.

[0036] The substrate to be coated with a nickel phosphorous alloy can be contacted with the plating bath according to the present invention by dipping the substrate into the plating bath or by spraying the plating bath onto the substrate.

[0037] During the deposition of the nickel phosphorous alloy, mild agitation may be employed. Agitation may be a mild air agitation, mechanical agitation, bath circulation by pumping, rotation of a barrel plating, etc. The plating solution may also be subjected to a periodic or continuous filtration treatment to reduce the level of contaminants therein. Replenishment of the constituents of the bath may also be performed, in some embodiments, on a periodic or continuous basis to maintain the concentration of constituents, and in particular, the concentration of nickel ions and hypophosphite ions, as well as the pH level within the desired limits.

Examples

[0038] The invention will now be illustrated by reference to the following non-limiting examples.

Examples 1 (comparative)

[0039] An electroless nickel plating bath comprising 6 g/l nickel ions as nickel sulfate; hypophosphite as reducing agent, a mixture of lactic acid and malic acid as complexing agents (overall concentration: 150 mmol/l) and lead ions as stabilizing additive was tested. The pH value of this plating bath was 4.8. The plating results are summarised in Table 1.

Table 1: plating results obtained for an electroless nickel plating bath known from prior art (MTO = metal turn over).

Sample No.	MTO	Lead concentration / ppm	P concentration in deposited layer / wt.-%	Plating rate / μm/h
1	1	0.9	7.0	11.8
2	2	1.2	7.7	11.9

(continued)

Sample No.	MTO	Lead concentration / ppm	P concentration in deposited layer / wt.-%	Plating rate / $\mu\text{m/h}$
3	3	1.3	8.3	11.0

[0040] The phosphorous concentration in the deposited nickel phosphorous alloys increases from 7.0 wt.-% at 1 MTO to 8.3 wt.-% at 3 MTO.

Example 2 (comparative)

[0041] The same plating bath as described for example 1 was used. Instead of lead ions, 0.6 g/l of a stabilizing agent according to formula (1) with R^1 = hydrogen, R^2 = sodium and $n = 3$ (600 ppm, as disclosed in US 2006/0264043 A1) was added to said plating bath. The pH value of this plating bath composition was adjusted with an aqueous solution of ammonia to 9.25. The plating bath temperature was held at 85 °C in presence of the substrate.

[0042] No nickel phosphorous alloy layer was deposited onto the substrate. Accordingly, the plating rate of this plating bath is 0 $\mu\text{m/h}$.

Examples 3 (comparative)

[0043] The same plating bath as described for example 1 was used. Instead of lead ions, 0.6 g/l of a stabilizing agent according to formula (1) with R^1 = hydrogen, R^2 = sodium and $n = 3$ (600 ppm, as disclosed in US 2006/0264043 A1) was added to said plating bath. The pH value of this plating bath composition was adjusted with an aqueous solution of ammonia to 4.8. The plating bath temperature was held at 85 °C in presence of the substrate.

[0044] No nickel phosphorous alloy layer was deposited onto the substrate. Accordingly, the plating rate of this plating bath is 0 $\mu\text{m/h}$.

Example 4 (comparative)

[0045] The same plating bath as described for example 1 was used. Instead of lead ions, 0.6 g/l of thiourea (600 ppm, as disclosed in US 2006/0264043 A1) were added to the plating bath as stabilizing agent. The pH value of this plating bath composition was adjusted with an aqueous solution of ammonia to 9.25. The plating bath temperature was held at 85 °C in presence of the substrate.

[0046] No nickel phosphorous alloy layer was deposited onto the substrate. Accordingly, the plating rate of this plating bath is 0 $\mu\text{m/h}$.

Example 5 (comparative)

[0047] The same plating bath as described for example 1 was used. Instead of lead ions, 0.6 g/l of thiourea (600 ppm, as disclosed in US 2006/0264043 A1) were added to the plating bath as stabilizing agent. The pH value of this plating bath composition was adjusted with an aqueous solution of ammonia to 4.8. The plating bath temperature was held at 85 °C in presence of the substrate.

[0048] No nickel phosphorous alloy layer was deposited onto the substrate. Accordingly, the plating rate of this plating bath is 0 $\mu\text{m/h}$.

Example 6 (present invention)

[0049] The same plating bath as described for example 1 was used. Instead of lead ions, a stabilizing agent according to formula (1) with R^1 = hydrogen, R^2 = sodium and $n = 3$ was added to said plating bath. The pH value of this plating bath was 4.8. The plating results are summarized in Table 2.

Table 2: plating results obtained for an electroless nickel plating bath known from prior art (MTO = metal turn over).

Sample No.	MTO	Stabilising agent concentration / ppm	P concentration in deposited layer /wt.-%	Plating rate / $\mu\text{m/h}$
1	1	5	8.2	12.3
2.	2	5	7.9	12.3

(continued)

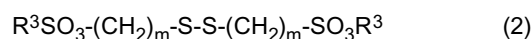
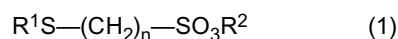
Sample No.	MTO	Stabilising agent concentration / ppm	P concentration in deposited layer /wt.-%	Plating rate / μm/h
3.	3	5	8.2	11.2

[0050] The stabilizing agent according to the present invention shows the desired properties in respect to the stable phosphorous concentration in the deposited nickel phosphorous alloy layers when using the plating bath. Furthermore, the plating rate is sufficient for industrial application.

Claims

1. An aqueous plating bath composition for electroless plating of a nickel phosphorous alloy, the plating bath comprising

- (i) a water soluble source of nickel ions
- (ii) a hypophosphite compound
- (iii) at least one complexing agent selected from the group comprising carboxylic acids, polyamines and mixtures thereof and
- (iv) a stabilizing agent selected from the group consisting of compounds according to formulae (1) and (2):



wherein

R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, lithium, sodium, potassium and ammonium,
 n ranges from 1 to 6
 and
 m ranges from 1 to 6

and having a pH value in the range of 3.5 to 6.5

wherein the concentration of the stabilizing agent according to formulae (1) and (2) ranges from 1 to 100 ppm.

2. The aqueous plating bath according to claim 1 wherein the concentration of nickel ions ranges from 1 to 18.g/l.

3. The aqueous plating bath composition according to any of the foregoing claims wherein the hypophosphite compound is selected from the group comprising phosphorous acid, sodium hypophosphite, potassium hypophosphite and ammonium hypophosphite.

4. The aqueous plating bath according to any of the foregoing claims wherein the concentration of the hypophosphite compound ranges from 2 to 60 g/l.

5. The aqueous plating bath according to any of the foregoing claims wherein the concentration of the at least one complexing agent ranges from 1 to 200 g/l.

6. The aqueous plating bath according to any of the foregoing claims wherein the plating bath composition is free of heavy metal ions selected from cadmium, thallium, lead and antimony.

7. The aqueous plating bath according to any of the foregoing claims having a pH value in the range of 4 to 6.

8. Method for depositing a nickel phosphorous alloy having a phosphorous concentration in the range of 5 to 12 wt.-%, the method comprising the steps of

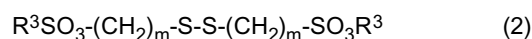
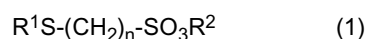
- (i) providing a substrate

(ii) contacting said substrate with an aqueous plating bath according to claims 1 to 7.

Patentansprüche

1. Wässrige Plattierungsbadzusammensetzung für die elektrolytische Plattierung einer Nickel-Phosphor-Legierung, wobei das Plattierungsbad umfasst:

- (i) eine wasserlösliche Quelle von Nickel-Ionen,
- (ii) eine Hypophosphit-Verbindung,
- (iii) wenigstens ein Komplettierungsmittel ausgewählt aus der Gruppe umfassend Carbonsäuren, Polyamine und Gemische davon und
- (iv) ein Stabilisierungsmittel ausgewählt aus der Gruppe bestehend aus Verbindungen der Formeln (1) und (2) :



wobei

R^1 , R^2 und R^3 unabhängig ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, Methyl, Ethyl, Propyl, Butyl, Lithium, Natrium, Kalium und Ammonium,
 n im Bereich von 1 bis 6 liegt
 und
 m im Bereich von 1 bis 6 liegt

und einen pH-Wert im Bereich von 3,5 bis 6,5 aufweist,
 wobei die Konzentration des Stabilisierungsmittels der Formeln (1) und (2) im Bereich von 1 bis 100 ppm liegt.

2. Wässriges Plattierungsbad gemäß Anspruch 1, wobei die Konzentration von Nickel-Ionen im Bereich von 1 bis 18 g/l liegt.

3. Wässrige Plattierungsbadzusammensetzung gemäß einem der vorstehenden Ansprüche, wobei die Hypophosphit-Verbindung ausgewählt ist aus der Gruppe umfassend phosphorige Säure, Natriumhypophosphit, Kaliumhypophosphit und Ammoniumhypophosphit.

4. Wässriges Plattierungsbad gemäß einem der vorstehenden Ansprüche, wobei die Konzentration der Hypophosphit-Verbindung im Bereich von 2 bis 60 g/l liegt.

5. Wässriges Plattierungsbad gemäß einem der vorstehenden Ansprüche, wobei die Konzentration des wenigstens einen Komplettierungsmittels im Bereich von 1 bis 200 g/l liegt.

6. Wässriges Plattierungsbad gemäß einem der vorstehenden Ansprüche, wobei die Plattierungsbadzusammensetzung frei von Schwermetall-Ionen ausgewählt aus Cadmium, Thallium, Blei und Antimon ist.

7. Wässriges Plattierungsbad gemäß einem der vorstehenden Ansprüche mit einem pH-Wert im Bereich von 4 bis 6.

8. Verfahren zum Abscheiden einer Nickel-Phosphor-Legierung mit einer Phosphor-Konzentration im Bereich von 5 bis 12 Gew. -%, wobei das Verfahren die Schritte

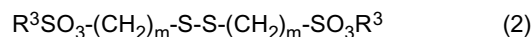
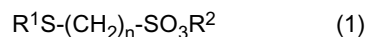
- (i) Bereitstellen eines Substrats,
- (ii) Inkontaktbringen des Substrats mit einem wässrigen Plattierungsbad gemäß Ansprüchen 1 bis 7

umfasst.

Revendications

1. Composition de bain aqueux de placage pour le dépôt autocatalytique d'un alliage de nickel-phosphore, le bain de placage comprenant

- (i) une source hydrosoluble d'ions nickel,
 (ii) un composé hypophosphite,
 (iii) au moins un agent complexant choisi dans le groupe comprenant les acides carboxyliques, les polyamines et les mélanges de ceux-ci et
 (iv) un agent stabilisant choisi dans le groupe constitué des composés répondant aux formules (1) et (2) :



dans lesquelles

R^1 , R^2 et R^3 sont indépendamment choisis dans le groupe constitué par l'atome d'hydrogène, le groupe méthyle, le groupe éthyle, le groupe propyle, le groupe butyle, l'ion lithium, l'ion sodium, l'ion potassium et l'ion ammonium,
 n va de 1 à 6 et
 m va de 1 à 6

et ayant une valeur de pH dans la plage de 3,5 à 6,5, dans laquelle la concentration de l'agent stabilisant répondant aux formules (1) et (2) va de 1 à 100 ppm.

2. Bain aqueux de placage selon la revendication 1 dans lequel la concentration d'ions nickel va de 1 à
3. Composition de bain aqueux de placage selon l'une quelconque des revendications précédentes dans laquelle le composé hypophosphite est choisi dans le groupe comprenant l'acide phosphoreux, l'hypophosphite de sodium, l'hypophosphite de potassium et l'hypophosphite d'ammonium.
4. Bain aqueux de placage selon l'une quelconque des revendications précédentes dans lequel la concentration du composé hypophosphite va de 2 à 60 g/l.
5. Bain aqueux de placage selon l'une quelconque des revendications précédentes dans lequel la concentration de l'au moins un agent complexant va de 1 à 200 g/l.
6. Bain aqueux de placage selon l'une quelconque des revendications précédentes dans lequel la composition de bain de placage est exempte d'ions de métaux lourds choisis parmi le cadmium, le thallium, le plomb et l'antimoine.
7. Bain aqueux de placage selon l'une quelconque des revendications précédentes ayant une valeur de pH dans la plage de 4 à 6.
8. Procédé pour le dépôt d'un alliage de nickel-phosphore ayant une concentration en phosphore dans la plage de 5 à 12 % en poids, le procédé comprenant les étapes consistant à
- (i) fournir un substrat et
 (ii) mettre en contact ledit substrat avec un bain aqueux de placage selon les revendications 1 à 7.

REFERENCES CITED IN THE DESCRIPTION

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