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(54) Beta-amino acid comprising electrolyte and method for the deposition of a metal layer

The present invention relates to an electrolyte for the electroless deposition of a metal layer on a substrate, wherein the electrolyte is free of heavy metal stabilizers, cyanides, selenium compounds and sulfur compounds comprising sulfur in an oxidation state between -2 and +5, and in which instead a β-amino acid is used as stabilizer. In particular, the inventive electrolyte can comprise 3-aminopropionic acid, 3-aminobutyric acid, 3-amino-4-methyvaleric acid, and 2-aminoethane-sulfonic acid. Furthermore, the invention is directed to a method for the electroless deposition of metal layers utilizing an inventive electrolyte as well as the use of β-amino acids as stabilizer in electrolytes for the electroless deposition of metal layers in general.
The present invention relates to an electrolyte as well as a method for the electroless deposition of metals, particularly layers of nickel, copper, cobalt, boron or gold, as well as layers of alloys comprising at least one of the aforementioned metals as alloying metal. Furthermore, the present invention relates to the use of \( \beta \)-amino acids as stabilizer in electrolytes for the electroless deposition.

Beneath electrolytic methods for the plating of substrates with metal layers, electroless plating methods are known from the state of the art for a long time. By electroless plating, also mentioned as chemical plating, the coating of almost every metal and a huge number of non-conductive substrate surfaces is possible. The electroless deposited metal layers differing from the galvanically deposited metal layers, i.e., those layers deposited by the use of an external current, in physical as well as mechanical aspects. Often, metal alloy layers with non-metal elements, like for example cobalt/phosphor, nickel/phosphor or boron carbide layers are deposited by means of electroless deposition methods. In this respect, electroless deposited layers in many cases differ also in their chemical nature from the galvanically deposited layers.

One major advantage of the electroless deposited metal layer is the outline accuracy of the layer thickness of the deposited layer independent from the substrate geometry, which feature makes the electroless methods the first choice in the area of printed circuit boards (PCB) manufacturing, and here especially for the metallization of through hole contacts, vias and trenches. Many times, electroless methods are also used for the coating of other non-conductive substrates, like for example plastic substrates, to render the surface of such substrates conductive and/or to change the appearance of the substrate in aesthetic respect. Furthermore, by the deposited layers, the material properties of the coated substrate can be improved or amended. Especially, the corrosion resistance or the hardness of the surface and/or the wear resistance of the substrate can be improved.

Electroless plating methods are based on an autocatalytic process, in which process the metal ions comprised in the electrolytes are reduced to the elemental metal by a reducing agent which is oxidized during this redox reaction.

A reducing agent commonly used in the field of electroless deposition of metals on substrate surfaces is sodium hypophosphite. However, also other reducing agents are used in dependency of the metals to be deposited.

The European patent application EP 1 413 646 A2 discloses, for example, an electrolyte for the electroless deposition of nickel layers having internal compressive stress. The electrolyte disclosed in this application comprises a metal salt of the metal to be deposited, a reducing agent, a complexing agent, an accelerator, and a stabilizer.

Here, the accelerator is used to increase the deposition rate of the metal on the substrate surface. The stabilizer is used to avoid the uncontrolled plateout (wild deposition) of the electrolyte, which means the unregulated wild deposition of metal on the substrate surface. Hitherto, in the state of the art, heavy metals like lead, bismuth, zinc or tin are used as stabilizers. According to common environmental regulations (ROHS (Restriction of the use of certain hazardous substances), WEEE (Waste electrical and electronic equipment), ELV (End of lifetime of vehicles)) prior to the disposal of expended electrolytes and the co-deposition of heavy metals such heavy metals have to be withdrawn from the aqueous solution used as electrolyte in an adequate treatment step. Also when the heavy metals are comprised in the electrolyte only in small amounts, such a treatment causes additional expenses for the disposal. Therefore, the use of heavy metal in electrolytes for the deposition of metal layers has to be avoided. In some other types of electrolytes, like for example electrolytes for the electroless deposition of copper, cyanides are used as stabilizers. Like heavy metal ions, such cyanides are subject to environmental regulations. The same is true for selenium compounds which are also commonly used as stabilizers.

Furthermore, there is an interest in the art of metal plating to avoid sulfur compounds which comprise sulfur in an oxidation state between -2 and +5, since these compounds are also subject to environmental regulations. However, by now such compounds are often needed in the electrolytes to gain good plating results.

It is therefore an object of the pending application to provide an electrolyte for the electroless deposition which is free of heavy metal stabilizers, cyanides; selenium compounds, and/or sulfur compounds comprising sulfur in an oxidation state between -2 and +5.

This object is solved by an electrolyte for the electroless deposition of a metal layer on a substrate, comprising a metal ion source for the metal to be deposited, a reducing agent, a complexing agent, an accelerator, and a stabilizer, characterized in that the electrolyte comprises as stabilizer a \( \beta \)-amino acid.

Surprisingly, it was found that \( \beta \)-amino acids are capable to replace heavy metal stabilizers, cyanides, selenium compounds as well as sulfur compounds comprising sulfur in an oxidation state between -2 and +5 in electrolytes for the electroless deposition of metal layers, totally.

While not being bound to this theory, the applicant believes that the \( \beta \)-amino acids due to their indirectly adjacent amino group and carboxyl group are capable to at least temporarily jam the active centers on the substrate surface which are responsible for the uncontrolled deposition. So the wild deposition of the metals can be avoided. Additionally, also the foreign ions comprised in the electrolyte which are responsible for the wild depo-
sition, too, are inactivated by the used β-amino acid.

[0015] A further benefit of the inventive electrolyte and the inventive use of β-amino acids is that an effect known as edge weakness can be avoided. When using electrolytes for the electroless deposition of metal layers which comprise heavy metal ions as stabilizers at high convection of the electrolyte a decreased deposition of metal at the edges of the substrate occurs. This is deemed to be related to an increased assembly of the heavy metal ions used as stabilizers in these areas. This effect deteriorates the outline accuracy of the plating. Surprisingly, by the use of β-amino acids as stabilizers in electroless plating methods this edge weakening effect can be avoided which significantly increases the overall outline accuracy of the plating especially when plating large substrates.

[0016] In particular, β-amino acids having a $pK_a$-value within a range of 4 to 8, preferably within a range of 5 to 7 seems to be suitable in this respect. In particular, 3-amino propionic acid (β-alanin), 3-aminobutyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (Taurin) are usable.

[0017] The β-amino acid can be comprised in the inventive electrolyte within a range of 1 mg/l to 2 g/l, preferably 100 mg/l to 1 g/l, and even more preferred 200 mg/l to 400 mg/l.

[0018] As reducing agent in the inventive electrolyte a reducing agent of the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, or other organic boranes can be comprised.

[0019] As a metal ion source in the inventive electrolyte, advantageously a metal compound of the group consisting metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbate can be used. Here, specially, the metal compounds having volatile ions, like for example metal acetate, metal nitrate, metal propionate, and metal formiate are preferred since the volatile character of the anion those anions leak out from the electrolyte in gaseous form which enables to reduce the amount of anions in the electrolyte. This enables to extend the lifetime of the electrolyte significantly, which under normal conditions is only limited. For example, by the use of volatile anions also at a metal turnover rate of 22 metal layers having internal compressive stress can be deposited.

[0020] As a complexing agent the inventive electrolyte comprises a compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, and amino acetic acid.

[0021] As an accelerator the inventive electrolyte comprises a compound of the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates.

[0022] As metal to be deposited the inventive electrolyte may comprise a metal of the group consisting of nickel, copper, cobalt, boron and gold. By an appropriate choice of the metal to be deposited also alloys like for example nickel-cobalt-alloys, nickel/phosphor-alloys, cobalt/phosphor-alloys, boron/phosphorus-alloys or the like can be deposited. Also, the deposition of nicket/PT-FE-layers or boron carbide/graphite-layers from dispersion bathes is possible by the inventive electrolyte.

[0023] The inventive electrolyte can have a pH-value within a range of pH 3 and pH 12, preferably within pH 3,9 and pH 6.

[0024] The temperature at which the electrolyte is used for deposition may vary between room temperature and 100° C.

[0025] The inventive electrolyte as well as the inventive method for the electroless deposition of metal layers on substrates are explained in terms of examples in the following, while the electrolyte as well as the method cannot be restricted to these embodiments only.

Examples

Example 1

At a temperature between 80° C and 94° C a substrate (steel sheet) was brought into contact with an electrolyte comprising:

- 12,5 g/l to 25,5 g/l nickel acetate-4-hydrate
- 30 g/l to 50 g/l sodium hypophosphite
- 32 g/l to 55 g/l lactic acid
- 0,5 g/l to 10 g/l malonic acid
- 2,5 g/l to 22 g/l sodium saccharin
- 0,1 g/l to 2 g/l potassium iodide and
- 200 mg/l to 400 mg/l β-alanin

Example 2

At a pH within a range of pH 4 to pH 5 from this electrolyte a semi glossy nickel layer was deposited on the substrate surface at a plating rate of 8 μm/h to 12 μm/h.

Example 3

At a temperature between 80° C and 94° C a steel sheet is brought into contact with an electrolyte comprising:

- 12,5 g/l to 25,5 g/l nickel acetate-4-hydrate
- 30 g/l to 70 g/l sodium hypophosphite
- 10 g/l to 30 g/l glycine
- 10 g/l to 40 g/l of an 25 % by weight aqueous ammonia solution
- 0,2 to 0,8 g/l potassium iodide and
- 200 mg/l to 400 mg/l β-alanin

Example 3

Plastic samples made from ABS etched with
chromosulfuric acid and activated with a Pd-activator system were brought into contact with an electrolyte comprising:

- 10 g/l copper sulfate
- 8 g/l sodium hydroxide
- 10 g/l formaldehyde (as 37% by weight solution in H₂O)
- 26 g/l quadrol (commercially available from BASF AG)
- 2.5 g/l sodium iodide
- 200 mg/l β-alanin

Example 4

Brass samples were degreased in an alkaline degreasing solution and activated in 10% sulfuric acid, rinsed and brought into contact with an electrolyte comprising:

- 5 g/l copper sulfate
- 4 g/l sodium hydroxide
- 14 g/l formaldehyde (as 37% by weight solution in H₂O)
- 400 mg/l β-alanin
- 11 g/l quadrol

Example 5

At a temperature of 80°C from this electrolyte within 20 min a copper layer having a thickness of about 0.5 μm was deposited on the brass surface.

Example 6

A at a temperature of 40°C, a copper substrate is brought into contact with an electrolyte having a pH-value of about 10 which comprises:

- 25 g/l nickelacetate-4-hydrate
- 30 g/l citric acid
- 30 g/l sodiumhypophosphite
- 1 g/l dimethylaminoborane
- 7 g/l glycine
- 200 mg/l β-alanine.

Example 7

At a temperature of about 85°C and a pH in the range between pH 4 - 5 a steel sheet was brought into contact with an electrolyte comprising:

- 10 g/l to 28 g/l nickel sulfate-6-hydrate
- 30 g/l to 50 g/l sodium hypophosphite
- 32 g/l to 55 g/l lactic acid
- 0.5 g/l to 10 g/l malonic acid
- 2.5 g/l to 22 g/l sodium saccharin
- 0.1 g/l to 2 g/l potassium iodide and
- 200 mg/l to 400 mg/l β-atanin

Example 8

Plastic samples made from ABS etched with chromosulfuric acid and activated with a Pd-activator system were brought into contact with an electrolyte comprising:

- 6.7 g/l copper(II)chloride dihydrate
- 23 g/l quadrol
- 8.9 g/l formaldehyde (as 37% by weight solution in H₂O)
- 8.2 g/l sodiumhydroxide
- 200 mg/l β-alanine

Example 9

From the above mentioned electrolyte, a copper layer with a thickness of about 0.4 to 0.6 μm was plated on the substrate within 20 min at a temperature of 40°C. The plating result was fully comparable to the plating result achieved when depositing a copper layer under equal conditions on an ABS plastic substrate from an electrolyte commercially available as Enthone Enplate CU872, wherein Enthone Enplate CU872 comprises heavy metal ions.

Example 10

At a plating rate of about 9 μm/h a semi glossy nickel layer was deposited on the steel surface.
10 g/l sodium hydroxide  
10 ml/l formaldehyde (as 37% by weight solution in H2O)  
23 g/l quadrol (N, N, N', N'-Tetrakis(2-hydroxypropyl) ethylenediamine)  
200 - 400 mg/l β-alanine

**[0043]** Addition of copper:

The copper was added to this electrolyte prior to contacting the ABS samples via Donnan dialysis via alkaline stable cation selective ion exchange membrane to the electrolyte. As copper source a copper-sulfate solution is used. The plating solution and copper-sulfate solution counterflushed through the dialysis membrane system. Sodium ions in the plating solution were replaced by copper ions from copper sulfate solution without dragging in/out the counter (hydroxide & sulfate) ions. The flow velocity was 1 l/m² ion exchange membrane surface until the copper. The Donnan dialysis was performed until the copper concentration in the bath reaches 2.5 g/l. After then the dialysis was only switched on if the copper concentration was lower than 2.3 g/l.

**[0044]** Maintaining of the electroless copper electrolyte - replenishment of parts of hydroxide. In order to stop the increase of salt freight during plating an additional Donnan dialysis was performed. This dialysis system used for this additional dialysis consisted of an alkaline stable anion exchange membranes. Formiate and Cobalons (unwanted byproducts) were replaced selectively by hydroxide which is used for the electroless copper deposit reaction.

**[0045]** The plating solution and sodium hydroxide solution (20 g/l) were counterflown. The flow velocity was 1 - 2 l/(m²*h) for the plating solution and 0.5 - 1 l/(m²*h) for the NaOH solution. The exchange rate was 7-15 g (NaOH)/(h*m²) (related to the concentration of formiate and carbonate in the bath).

**[0046]** By help of the dialysis the drift to a higher salt freight was stopped.

**[0047]** As plating result a copper layer having a thickness of 0.4 μm was deposited within 25 min at a temperature of 40°C on the plastic substrates.

**Claims**

1. Electrolyte for the electroless deposition of a metal layer on a substrate, comprising a metal ion source for the metal to be deposited, a reducing agent, a complexing agent, an accelerator, as well as a stabilizer, characterized in that the electrolyte comprises a β-amino acid as stabilizer.

2. Electrolyte according to claim 1, characterized in that the β-amino acid has a pKα-value within 4 and 8, preferably within 5 and 7.

3. Electrolyte according to one of the preceding claims, wherein the β-amino acid is an acid of the group consisting of 3-aminopropanoic acid, 3-aminobutyric acid, 3-amino-4-methylvaleric acid, and 2-aminoethanesulfonic acid.

4. Electrolyte according to one of the preceding claims, wherein as a reducing agent a compound of the group consisting of sodium hypophosphite, formaldehyde, dimethyl aminoborane, amino borane, and other organic boranes is comprised.

5. Electrolyte according to one of the preceding claims, wherein the electrolyte as a metal ion source comprises a metal compound of the group consisting of metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbinate.

6. Electrolyte according to one of the preceding claims, wherein the electrolyte comprises as a complexing agent a compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA and amino acetic acid.

7. Electrolyte according to one of the preceding claims, wherein the electrolyte as an accelerator comprises a compound of the group consisting of saccharine, hydantoin, rhodanine, carbamide and carbamide derivates.

8. Electrolyte according to one of the preceding claims, wherein the electrolyte is free of inorganic stabilizers, specifically free of lead, bismuth, antimony, zinc and/or tin.

9. Electrolyte according to one of the preceding claim, wherein the metal to be deposited is a metal of the group consisting of nickel, copper, cobalt, boron, gold or an alloy comprising at least one of these metals.

10. Electrolyte according to one of the preceding claims, wherein the electrolyte is free of cyanides, selenium compounds and sulfur compounds comprising sulfur in an oxidation state between -2 and +5.

11. Method for the electroless deposition of a metal layer on a substrate, wherein the substrate to be plated is brought into contact with an electrolyte comprising a β-amino acid as stabilizer.

12. Use of a β-amino acid as stabilizer in an electrolyte for the electroless deposition of a metal layer on a
substrate surface.
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The present search report has been drawn up for all claims.

Place of search: The Hague
Date of completion of the search: 10 November 2009
Examiner: Gault, Nathalie
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