The present invention relates to aqueous plating bath compositions and methods for deposition of nickel and nickel alloys utilizing mixtures of stabilizing agents comprising ions of group IIIA metals and iodine containing, inorganic compounds in order to enhance bath stability.
PLATING BATH AND METHOD FOR ELECTROLESS DEPOSITION OF NICKEL LAYERS

FIELD OF THE INVENTION

[0001] The present invention relates to aqueous plating bath compositions for electroless deposition of nickel and nickel alloys. The present invention relates further to a method utilizing the aqueous plating bath compositions for electrolessly depositing nickel and nickel alloys. The aqueous plating bath compositions have high stability against undesired decomposition. The nickel and nickel alloy coatings obtained by the invention show high corrosion resistance and adhesion to the subjacent substrate.

[0002] Such coatings are suitable as a functional coating in aerospace, automotive, electronics and chemical industries. The metal layers deposited from such aqueous plating bath compositions are also useful as barrier and cap layers in semiconducting devices, printed circuit boards, IC substrates and the like. The metal layers deposited are also suitable as overcoat for hard disks or rigid memory disks (RMD).

BACKGROUND OF THE INVENTION

[0003] Barrier layers are used in electronic devices such as semiconducting devices, printed circuit boards, IC substrates and the like to separate layers of different composition, e.g., substrate layers and further layers, and thereby prevent undesired diffusion between such layers of different composition.

[0004] Another application of barrier layer materials in electronic devices is as a cap layer which is e.g. deposited onto copper to prevent corrosion of copper.

[0005] Rigid memory disks are used as magnetic data storage media in hard disk drives. The disks are basically composed of a substrate, made of aluminum, glass or ceramics. An overcoat is deposited onto the substrate by a vacuum deposition process or an electroless metal plating process. The overcoat may consist of various metallic, mostly non-magnetic, alloys one of which may be a nickel phosphorus alloy layer. The overcoat provides e.g. a smooth surface onto which the magnetic recording layers are deposited. Further protective layers are coated onto the recording layers.

[0006] Another application of nickel and nickel alloy deposits is corrosion protection for various substrates.


OBJECTIVE OF THE INVENTION

[0009] It is the objective of the present invention to provide an electroless plating bath for deposition of nickel and nickel alloys which has a high stability against undesired decomposition. It is a further objective of the present invention to provide electroless nickel and nickel alloy plating baths having high stability during use and during storage. Furthermore, it is an objective of the present invention to provide an electroless plating bath for deposition of nickel and nickel alloys which has a good plating performance and generates coatings of good quality.

SUMMARY OF THE INVENTION

[0010] This objective is solved by providing an aqueous plating bath composition for electroless deposition of nickel and nickel alloys, the composition comprising

[0011] (i) a source of nickel ions,

[0012] characterized in that the aqueous plating bath composition further comprises

[0013] (ii) a mixture of stabilizing agents comprising

[0014] a) at least one metal ion selected from indium ion and gallium ion, and

[0015] b) at least one selected from elementary iodine, iodide ion containing compounds, iodate ion containing compounds and periodate ion containing compounds.

[0016] The invention further relates to a method for deposition of nickel and nickel alloys by contacting the substrate to be plated with above described composition. The term “aqueous plating bath composition for electroless deposition of nickel and nickel alloys” is also abbreviated as “composition” herein. In addition, the invention relates to a method for stabilizing any electroless plating bath for deposition of nickel and nickel alloys by adding a mixture of stabilizing agents to the electroless plating bath.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Electroless nickel plating compositions for applying nickel coatings are well known in the art and plating processes and compositions are described in numerous publications such as U.S. Pat. Nos. 2,935,425; 3,338,726; 3,597,266; 3,915,716 and 4,780,342. Electroless plating generally describes methods without using external current sources for reduction of metal ions. Plating processes using external current sources are commonly described as electrolytic or galvanic plating methods. In the electroless plating solutions chemical reducing agents like hypophosphite, boranes or formaldehyde are used to reduce the metal ions to their metallic form and thereby forming a deposit on the substrate.

[0018] One commonly used nickel alloy deposit is nickel phosphorus (NiP) alloy. In general, NiP deposition solutions comprise at least three ingredients dissolved in a solvent, typically water. They are (1) a source of the nickel ions, (2) a reducing agent and (3) a complexing agent for metal ions sufficient to prevent their precipitation in solution. A large number of suitable complexing agents for NiP solutions are described in the above noted publications. If hypophosphate is used as the reducing agent, the deposit will contain nickel and phosphorus. Similarly, if an aminoborane is employed, the deposit will contain nickel and boron as shown in U.S. Pat. No. 3,953,054.
[0019] The aqueous plating bath composition for electrol ess deposition of nickel and nickel alloys of the present invention comprises a source of nickel ions. The source of nickel ions may be provided by the use of any soluble salt such as nickel sulfate, nickel chloride, nickel acetate, nickel methyl sulfonate, nickel sulfamate and mixtures thereof. The concentration of the nickel ions in the composition may vary widely and preferably ranges from 0.01 mol/l to 1 mol/l, more preferably from 0.03 mol/l to 0.8 mol/l, even more preferably from 0.06 mol/l to 0.3 mol/l.

[0020] The aqueous plating bath composition for electrol ess deposition of nickel and nickel alloys of the present invention further comprises at least one reducing agent. The at least one reducing agent is preferably a chemical reducing agent. Reducing agents provide the electrons needed to reduce metal ions to their metallic form and thereby form a metal deposit on a substrate. The at least one reducing agent is preferably a hypophosphite salt or hypophosphorous acid, more preferably a hypophosphite salt. The hypophosphite salt is supplied to the composition by any suitable source such as sodium, potassium, ammonium and nickel hypophosphite. Other reducing agents such as aminoboranes, borohydrides, hydrazine and derivatives thereof and form aldehyde may also suitably be employed. Two or more reducing agents may be employed as a mixture in the composition. The concentration of the at least one reducing agent is generally in molar excess of the amount sufficient to reduce the nickel ions in the composition. The concentration of the reducing agent preferably ranges from 0.01 mol/l to 3.0 mol/l, more preferably from 0.1 mol/l to 1 mol/l.

[0021] In case a hypophosphite compound is used as the reducing agent, a Ni—P alloy deposit is obtained. Such reducing agents provide the source of phosphorus in the deposited alloy. A borane-based compound as reducing agent leads to a Ni—B alloy deposit and a mixture of hypophosphite and borane-based compounds as the reducing agents leads to a ternary Ni—B—P alloy deposit. A nitrogen-based reducing agent such as hydrazine and derivatives thereof as well as formaldehyde as reducing agent lead to nickel deposits.

[0022] The aqueous plating bath composition for electrol ess deposition of nickel and nickel alloys of the present invention may be acidic, neutral or alkaline. An acidic or an alkaline pH adjustor may be selected from a wide range of materials such as ammonium hydroxide, sodium hydroxide, hydrochloric acid, sulfuric acid and the like. The pH of the composition may range from about 2 to 12. In one embodiment, the compositions are preferably acidic. More preferably, the pH of the acidic compositions ranges from 3.5 to 7, even more preferably from 3.5 to 6.5, most preferably from 3.5 to 5.5. In another embodiment, the compositions are preferably alkaline. More preferably the pH of the alkaline compositions ranges from 7.5 to 12, even more preferably from 8 to 10, most preferably from 8 to 9.

[0023] The aqueous plating bath composition for electrol ess deposition of nickel and nickel alloys of the present invention further comprises at least one complexing agent. A complexing agent (sometimes also referred to as chelating agent) or mixture of complexing agents is included in the composition for nickel and nickel alloy plating. A complexing agent keeps metal ions dissolved and prevents their undesired precipitation in solution. The at least one complexing agent is preferably selected from complexing agents for nickel ions and complexing agents for alloying metal ions, more preferably from complexing agents for nickel ions.

[0024] The at least one complexing agent is preferably selected from the group comprising alkyl amines, ammonia, carboxylic acids, hydroxyl carboxylic acids, amino carboxylic acids, salts of the aforementioned and mixtures thereof.

[0025] In one embodiment, carboxylic acids, hydroxy carboxylic acids, amino carboxylic acids and salts of the aforementioned or mixtures thereof may be employed as the at least one complexing agent. Useful carboxylic acids include the 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 composition as their sodium, potassium or ammonium salts. Some complexing agents such as acetic acid, for example, may also act as a pH buffering agent, and the appropriate concentration of such additive components can be optimised for any composition in consideration of their dual functionality.

[0026] Examples of such carboxylic acids which are useful as complexing or chelating agents in the composition of the present invention include: monocarboxylic acids such as acetic acid, hydroxyacetic acid (glycolic acid), amino acetic acid (glycine), propanoic acid, 2-amino propanoic acid (alanine); 2-hydroxy propanoic acid (lactic acid); dicar boxylic acids such as succinic acid, amino succinic acid (aspartic acid), hydroxy succinic acid (malic acid), propandioic acid (malonic acid), tartaric acid, hexane-1,6-dicarboxylic acid (adipic acid); tricarboxylic acids such as 2-hydroxy-1,2-propane tricarboxylic acid (citric acid); and tetracarboxylic acids such as ethylene diamine tetra acetic acid (EDTA). Preferred carboxylic acids are acetic acid, amino acetic acid, propanoic acid, 2-hydroxy propanoic acid, succinic acid, hydroxy succinic acid, adipic acid or 2-hydroxy-1,2-propane tricarboxylic acid. In one embodiment, mixtures of two or more of the above complexing/chelating agents are utilised in the composition according to the present invention.

[0027] Alkyl amines may also be used as the at least one complexing agent, for example mono-, di- and trialkylamines. C-3 alkyl amines, for example triethanol-amine are preferred. Ammonia may also be used as the at least one complexing agent.

[0028] The concentration of the at least one complexing agent or, in case more than one complexing agent is used, the concentration of all complexing agents in total preferably ranges from 0.01 mol/l to 3.0 mol/l, more preferably from 0.1 mol/l to 1.0 mol/l and even more preferably from 0.2 mol/l to 1.0 mol/l.

[0029] Furthermore, the aqueous plating bath composition for electrol ess deposition of nickel and nickel alloys comprises a mixture of stabilising agents according to (ii) comprising:

a) at least one metal ion selected from indium ion and gallium ion, and

b) at least one selected from elementary iodine (I₂), iodide ion containing compounds, iodate ion containing compounds (IO₃⁻) and periodate ion containing compounds.

[0030] Stabilising agents, also referred to as stabilizers, are compounds that stabilize an electrol ess metal plating solution against undesired plate out in the bulk solution and spontaneous decomposition. The term “plate out” means
undesired and/or uncontrolled deposition of the metal on surfaces other than substrate surfaces.

The indium ion may be selected from any indium ions, preferably from the group comprising indium(III) ions and indium(I) ions and mixtures thereof. More preferably, the indium ion is an indium(III) ion. The gallium ion may be selected from any gallium ions, preferably from the group comprising gallium(III) ions, gallium(I) ions and mixtures thereof. More preferably, the gallium ion is a gallium(III) ion. The iron ion or the gallium ion may be in the form of their salts. The salts of indium ions or gallium ions are preferably selected from the group comprising indium(III) sulfate (In₂(SO₄)₃), indium(III) hydroxide (In(OH)₃), indium(III) oxide (In₂O₃), indium(III) bromide (InBr₃), indium(III) chloride (InCl₃), indium(III) nitrate (In(NO₃)₃), indium(III) fluoride (InF₃), indium(III) acetate (In(CH₃COO)₃), indium(I) chloride (InCl), indium(I) bromide (InBr), gallium(III) sulfate (Ga₂(SO₄)₃), gallium(III) hydroxide (Ga(OH)₃), gallium(III) nitrate (Ga(NO₃)₃), gallium(III) chloride (GaCl₃), gallium(III) bromide (GaBr₃), gallium(III) iodide (GaI₃), gallium(III) acetate (Ga(CH₃COO)₃), gallium(III) fluoride (GaF₃), gallium(III) chloride (GaCl₃), gallium(III) bromide (GaBr₃), gallium(III) nitrate (Ga(NO₃)₃), and hydrates of the aforementioned; more preferably indium(III) sulfate (In₂(SO₄)₃), indium(III) hydroxide (In(OH)₃), indium(III) chloride (InCl₃), indium(III) bromide (InBr₃), gallium(III) nitrate (Ga(NO₃)₃), gallium(III) chloride (GaCl₃), gallium(III) bromide (GaBr₃), gallium(III) acetate (Ga(CH₃COO)₃), gallium(III) fluoride (GaF₃), gallium(III) chloride (GaCl₃), gallium(III) bromide (GaBr₃), gallium(III) nitrate (Ga(NO₃)₃), and hydrates of the aforementioned.

The concentration of the at least one metal ion according to (ii)a preferably ranges from 0.01 mmol/l to 0.5 mmol/l, more preferably from 0.01 mmol/l to 0.1 mmol/l, even more preferably from 0.02 mmol/l to 0.08 mmol/l. Higher concentrations of the at least one metal ion according to (ii)a result in deposition of nickel or nickel alloy layers of dull appearance and skin plating. Skin plating is a plating defect in which the coating undesirably does not cover all areas of the plated substrate. The mixture, i.e. the combination of metal ions according to (ii)a with stabilizing agents according to (ii)b allows to shift the lower concentration limit of metal ions according to (ii)a to the lower values as described above, without impairing stability of the composition. Thus, the concentration range of metal ions according to (ii)a suitable for stabilizing the composition and any electrolytic plating bath for deposition of nickel and nickel alloys, and suitable for depositing nickel or nickel alloy layers of good quality is widened. The wider process window improves process control for plating.

The at least one stabilizing agent according to (ii)b is preferably selected from the group comprising iodide ion containing compounds and iodate ion containing compounds; more preferably iodide ion containing compounds.

The iodide ion containing compounds are preferably selected from the group comprising potassium iodide, sodium iodide, ammonium iodide, calcium iodide, barium iodide, magnesium iodide, lithium iodide, zinc iodide, and hydrates of the aforementioned; more preferably potassium iodide, sodium iodide, ammonium iodide, and hydrates of the aforementioned; even more preferably potassium iodide and hydrates thereof.

The iodate ion containing compounds are preferably selected from water soluble iodate salts. The water soluble iodate salts are preferably iodate salts of alkali metals or earth alkali metals. The iodate salt is preferably selected from the group comprising potassium iodate, sodium iodate, ammonium iodate, calcium iodate, barium iodate, magnesium iodate, lithium iodate and hydrates of the aforementioned; more preferably potassium iodate, sodium iodate, ammonium iodate, lithium iodate and hydrates of the aforementioned; even more preferably potassium iodate and hydrates thereof.

The periodate ion containing compounds may be selected from the group comprising preferably metaperiodate ion containing compounds (IO₄⁻²), and orthoperiodate ion containing compounds (IO₃⁻²).

The periodate ion containing compounds are preferably selected from the group comprising potassium metaperiodate (KIO₄), sodium metaperiodate (NaIO₄) and sodium ortho periodate (Na₃H₂IO₆).

The concentration of the at least one stabilizing agent according to (ii)b preferably ranges from 0.05 to 50.0 mmol/l, more preferably from 0.1 to 30.0 mmol/l, even more preferably from 0.5 to 10.0 mmol/l, and even more preferred from 1.0 mmol/l to 5.0 mmol/l. Higher concentrations of the at least one stabilizing agent according to (ii)b result in lower deposition rates, in difficulties to initiate deposition on the substrate surface, in deposition of nickel or nickel alloy layers having low adhesion to the substrate, e.g. blistering, and less compressive stress. Lower concentrations of the at least one stabilizing agent according to (ii)b do not show the desired enhanced bath stability against undesired, spontaneous decomposition.

The stabilizing agents of the present invention, metal ions according to (ii)a and stabilizing agents according to (ii)b, are suitable to enhance the stability of the aqueous plating bath composition for electrolysis deposition of nickel and nickel alloys of the present invention against undesired, spontaneous decomposition. Undesired, spontaneous decomposition means undesired formation of a black precipitate, undesired plate out of nickel in the bulk solution or undesired and/or uncontrolled deposition of nickel, for example on the bottom of a plating tank or on other surfaces different from the substrate.

The stabilizing effect is particularly pronounced when the stabilizing agents are used as a mixture, i.e. in combination. The combination of metal ions according to (ii)a with stabilizing agents according to (ii)b provides in particular a long life to the composition of the present invention. The bath stability imparted by the combination of stabilizing agents is much higher than the stabilizing effect of one of the stabilizing agents alone. The combination of stabilizing agents of the present invention has a synergistic effect on the bath stability.

The combination of stabilizing agents of the present invention also imparts an improved resistance of the composition against contamination with catalytic metals. Contamination with catalytic metals may be caused by metal ions dissolving from the substrate material while in contact with the composition, or metal ions are dragged into the composition from pre-treatment or activation steps. Catalytic metals may be palladium, platinum, rhodium, ruthenium or mixtures thereof, preferably palladium.

For example, palladium is used for plating methods in which surface activation is needed. This causes subsequent contamination of the subsequent plating bath with palladium ions. An example is electrolysis plating on non-conductive substrates. Thus, the composition of the present
invention containing a combination of stabilizing agents, namely metal ions according to (ii)a and stabilizing agents according to (ii)b, are suitable for plating on electrically non-conductive substrates, on electrically conductive substrates, and on electrically semi-conductive substrates.

[0045] The combination of stabilizing agents according to the invention has a synergistic effect on the bath stability and the composition containing the combination of stabilizing agents is much less prone to contamination with catalytic metals.

[0046] Simultaneously, the combination of stabilizing agents according to the invention has only a low effect on the deposition rate, i.e. increasing the concentration of the stabilizing agents does not alter the deposition rate and the combination of stabilizing agents does not decrease the deposition rate of the composition of the present invention.

In addition, the deposited nickel or nickel alloy layers are of good quality, i.e. the quality of the nickel or nickel alloy layers are not influenced disadvantageously by the combination of stabilizing agents according to the invention. The deposited nickel or nickel alloy layers completely cover the substrate surface; no skip plating is obtained. The deposited nickel or nickel alloy layers are of uniform thickness, adhere well to the substrate surface and have a good appearance. Good appearance means herein, that the nickel or nickel alloy layers have no pitting, no blistering, no increased nodular structure and no unusual color. Thus, the combination of stabilizing agents according to the present invention has no negative effect on the plating bath performance and no negative effect on the coating quality.

[0047] The aqeous plating bath composition for electroless deposition of nickel and nickel alloys of the present invention further shows a high stability during idle periods. Idle periods are defined as time periods in which the operating parameters, like temperature or pH value, of a plating bath are adjusted to its desired value for plating operation, but no substrate is immersed in the plating bath. Thus, the combination of stabilizing agents according to the invention also keeps the composition stable against undesired, spontaneous decomposition during prolonged periods at high temperature while not plating. This effect is better than with stabilizing agents known in the art, e.g. tin ions, bismuth ions or antimony ions.

[0048] Other materials may be included in the composition according to the present invention such as pH buffers, wetting agents, accelerators, brighteners, additional stabilizing agents etc. The composition may contain further organic stabilizing agents and/or further inorganic stabilizing agents. These materials are known in the art.

[0049] The composition may contain further metal stabilizing agents such as Cu-, Se-, Sn-, Bi- or Sb-ions. The concentration of the metal ions can vary and e.g. range between 0.1-100 mg/l, preferably between 0.1-50 mg/l, more preferably between 0.1-10 mg/l. In one embodiment, the composition does not contain toxic heavy metals. In this embodiment, the composition does preferably not contain lead, cadmium, antimony, bismuth, arsenic or mercury.

[0050] The aqeous plating bath composition for electroless deposition of nickel and nickel alloys of the present invention may further comprise at least one alloying element. In this embodiment, nickel alloy layers containing the alloying element are deposited from the composition. The at least one alloying element may be selected from phosphorus, boron, and a metal which is not nickel.

[0051] The alloying elements phosphorus or boron may be comprised in the composition in the form of a hypophosphite salt, hypophosphorous acid or a borane-based compound, such as aminoboranes or borohydrides, as mentioned above as reducing agents.

[0052] The metal which is not nickel (abbreviated as M herein) may be comprised in the composition in the form of a water-soluble metal salt containing the ions of the alloying metal M. The optional alloying metal M is preferably selected from the group consisting of titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, copper, silver, gold, aluminium, iron, cobalt, palladium, ruthenium, rhodium, osmium, iridium, platinum, zinc, cadmium, gallium, indium, tin, antimony, thallium, lead, and bismuth. More preferably, the optional alloying metal M is selected from the group consisting of molybdenum, tungsten, copper, silver, gold, aluminium, zinc and tin.

[0053] The concentration of the optional alloying metal M preferably ranges from 10⁻⁵ to 0.2 mol/l, more preferably from 10⁻⁴ to 0.2 mol/l, even more preferably from 10⁻³ to 0.1 mol/l.

[0054] In case additional metal salts or metal ions are present in the composition the respective nickel alloy is obtained as deposit.

[0055] When adding an alloying metal M to the composition (depending on the kind of reducing agent present) ternary or quaternary alloys Ni-M-P, Ni-M-B, and Ni-M-B-P are deposited.

[0056] In another embodiment of the present invention, a water-soluble salt of an alloying metal M and a water-soluble salt of a second alloying metal M* are added to the composition. In this case, nickel alloy deposits comprising alloying metals M and M* are obtained.

[0057] A suitable composition may be formed by dissolving the ingredients in water and adjusting the pH to the desired range. The indium or gallium salts may be dissolved in an acid prior to adding them to the composition.

[0058] The present invention further relates to a method for electroless deposition of nickel and nickel alloys by contacting the substrate to be plated with the above described aqeous plating bath composition for electroless deposition of nickel and nickel alloys.

[0059] The deposition method comprises the steps of

[0060] (A) providing a substrate,

[0061] (B) contacting the substrate with the aqeous plating bath composition for electroless deposition of nickel and nickel alloys according to the invention as described above,

[0062] (C) and thereby depositing a nickel or nickel alloy onto the substrate.

[0063] The substrate to be nickel or nickel alloy plated may be plated to the desired thickness and deposit quantity by contacting the substrate with the composition. The inventive composition may be maintained over a temperature range of 20°C to 100°C, preferably 70°C to 95°C, more preferably 85°C to 95°C during deposition.

[0064] A deposit thickness of up to 100 μm, or higher may be employed. Preferably, the thickness of the nickel or nickel phosphorus (NiP) deposits varies between 1-60 μm. The thickness depends on the technical application and can be higher or lower for some applications. For example, if the nickel or NiP layer is deposited to provide a corrosion resistant coating, a thickness of between 30-60 μm is
The stabilizing agents of the inventive mixture may be added as a solid or a powder or may be dissolved in a solvent prior to adding to the electroless plating baths. Preferably, the indium or gallium salts may be dissolved in an acid prior to adding them to the electroless plating bath.

The aqueous plating bath composition for electroless deposition of nickel and nickel alloys and the methods of the present invention are suitable to provide nickel and nickel alloy coatings having an attractive bright or semi-bright appearance. Advantageously, the compressive stress of the deposited nickel or nickel alloy layers is maintained. In contrast to stabilizing agents known in the art, the mixture of stabilizing agents of the present invention does not shift the internal stress to neutral or tensile stress. The advantages of nickel or nickel alloy layers having compressive stress are high corrosion resistance and good adhesion to the substrate surface.

The above parameters of the aqueous plating bath composition for electroless deposition of nickel and nickel alloys and methods of the present invention are only provided to give general guidance for practicing the invention.

A high phosphorus NiP alloy is herein defined as a metallic coating containing less than 91 wt. % Ni and more than 9 wt. % P, e.g. 10.5 wt. %. Generally, high phosphorus alloys contain up to 15 wt. % P. A nickel-phosphorus (NiP) alloy containing more than about 10.5% phosphorus is known as a high phosphorus NiP coating and is paramagnetic (non-magnetic) as plated.

A mid phosphorus NiP alloy is herein defined as a metallic coating containing between 5-9 wt. % P. A low phosphorus NiP alloy is herein defined as a metallic coating containing between 1-5 wt. % P.

The aqueous plating bath composition for electroless deposition of nickel and nickel alloys and the methods of the present invention are suitable to provide nickel phosphorus alloy coatings with a wide range of P content of between 1-15 wt. % P. The composition and the methods of the present invention are particularly suitable for depositing nickel phosphorus alloys, e.g. high NiP alloys as defined above.

The combination of stabilizing agents according to the present invention does not change the phosphorus content of the deposited nickel alloy layers compared to electroless nickel-phosphorus baths containing no stabilizer or single stabilizing agents according to (iia) or (iib). Thus, the combination of stabilizing agents according to the present invention has no negative effect on the bath performance and no negative effect on the coating quality.

The phosphorus content of nickel alloy layers and the thickness of nickel or nickel alloy layers were measured by x-ray fluorescence (XRF) which is well known to persons skilled in the art. The XRF measurements make use of the characteristic fluorescence radiation emitted from a sample (substrate, deposit) being excited with x-rays. By evaluating the wavelength and intensities and assuming a layered structure of the sample, phosphorus content and layer thickness can be calculated.

High NiP alloys are obtained when the plating process is performed at a plating rate of preferably between 5-14 µm/hour, more preferred 6-12 µm/hour, even more preferred 6-10 µm/hour. Such plating rate can be obtained by adjusting the plating parameters, like pH or temperature.

High NiP alloys obtained by the composition according to the present invention contribute to generating alloys having high compressive stress. The stress values for example range between 0 to ~70 N/mm², preferably between...
Succinic acid (complexing agent/chelating agent) 6.1 g/l
Sodium hypophosphite monohydrate (reducing agent) 24.0 g/l

[0098] The composition of the stock solution corresponds to the composition of the electroless nickel bath disclosed in patent application WO 2010/045591 A1 (Example 4 therein) with the exception that the present stock solution does not contain lead nitrate as a stabilizer. Sodium orthophosphate was contained in the stock solution as a pre-aging salt. Orthophosphate salts are by-products of the chemical reduction process when hypophosphite is used as the reducing agent. The amount of this by-product in an electroless nickel plating bath depends on how long the bath has been used. This bath age is referred to in the plating industry as the number of metal turnovers or MTOs of the bath. When an electroless nickel plating bath is used, nickel salt and a reducing agent must be replenished as nickel is plated, so as to continue the effective use (or life) of the bath. When the amount of the replenished nickel salt is equal to the initial amount of nickel contained in the original plating bath, the bath is said to have plated one metal turnover (MTO). The amount of orthophosphate used herein corresponds to 2.5 MTO level. The stock solution did not contain any stabilizers.

[0099] Indium ions and iodide ions were added as stabilizers. Indium ions were added in the form of indium(III) hydroxide and iodide ions were added in the form of potassium iodide. Concentrations of the stabilizers in the electroless nickel plating bath were as outlined in Table 2. One batch of the electroless nickel plating bath was used without any stabilizer as comparison. The electroless nickel plating bath had a pH value of 4.4.

[0100] Stability of the electroless nickel plating baths containing the respective concentrations of stabilizers was measured by determining the stability number and by visual inspection.

Determination of the Stability Number:

[0101] 100 ml of the investigated plating bath were heated to 80±1° C. in a 200 ml glass beaker while stirring. Next, 0.2 ml of a palladium test solution (125 mg/l palladium chloride in deionized water) was added every 60 s to the plating bath. The test was finished when a gray precipitate associated with gas bubbles was formed in the plating bath which indicated the undesired decomposition and thus instability of the plating bath.

[0102] The stability number achieved for the investigated plating bath corresponds to the number of palladium test solution additions (each 0.2 ml) within a one minute interval to the plating bath until formation of a gray precipitate. The stability test was done twice for each plating bath sample. The average stability number is given in Table 2.

[0103] For example, the entry “5” for an electroless plating bath solely containing iodide ions as stabilizers (Table 2 in column “Stability Number”) corresponds to an addition of 5 times 0.2 ml of a palladium chloride solution to the plating bath. After 1 ml (5 times 0.2 ml added in one minute intervals) and 5 minutes, a gray precipitate occurs.

Determining Stability by Visual Inspection:

[0104] Stability was further evaluated visually in a separate plating experiment. The plating conditions were as
described in Example 2 below. In contrast to Example 2, the plating time was 90 minutes. The result of the test is the total number of substrates plated without stability issues. Excessive plating in the heating surface area of the beaker, i.e. the bottom of the beaker, was observed as a sign of instability. Prior to plating, the beaker and the magnetic stirrer were stripped in 50% (v/v) nitric acid for 30 minutes.

[0105] Results of stability determinations are summarized in Table 2. As becomes apparent from Table 2 the combination of stabilizing agents according to the present invention is suitable to provide high plating bath stability against undesired decomposition. The plating bath stability imparted by the combination of stabilizing agents is much higher than would be expected from the stabilizing effects of each single stabilizing agent. Thus, the combination of stabilizing agents has a synergistic effect on the stability of the electroless plating bath.

[0106] The test for determining the stability number does not only show improved stability of electroless nickel plating baths containing the combination of stabilizing agents, but also an improved resistance of such electroless nickel plating baths against contamination with catalytic metals, like Pd.

Example 2

[0107] Deposition from an Electroless Nickel Plating Bath

[0108] Aluminum plates were used as substrates for deposition of nickel-phosphorus alloy layers. The substrates were pre-treated as summarized in Table 1 in order to clean and double zincate the substrate surface prior to nickel deposition.

<table>
<thead>
<tr>
<th>Pre-treatment step</th>
<th>Atotech Product</th>
<th>Concentration</th>
<th>Temp. (°C)</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soak Cleaner</td>
<td>Uniclean 190</td>
<td>50 g/l</td>
<td>50</td>
<td>5 min</td>
</tr>
<tr>
<td>Rinse</td>
<td>Dip rinse</td>
<td></td>
<td></td>
<td>20 s</td>
</tr>
<tr>
<td>Etch</td>
<td>ALKLEAN AC-2</td>
<td>50 ml/l</td>
<td>RT</td>
<td>1 min</td>
</tr>
<tr>
<td>Rinse</td>
<td>Dip rinse</td>
<td></td>
<td></td>
<td>20 s</td>
</tr>
<tr>
<td>Decontam</td>
<td>HNO₃</td>
<td>35% (w/w)</td>
<td>RT</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>(350 ml/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rinse</td>
<td>Dip rinse</td>
<td></td>
<td></td>
<td>20 s</td>
</tr>
<tr>
<td>Zincate 1</td>
<td>Zincate M</td>
<td></td>
<td>RT</td>
<td>30 s</td>
</tr>
<tr>
<td>Rinse</td>
<td>Dip rinse</td>
<td></td>
<td></td>
<td>20 s</td>
</tr>
<tr>
<td>Zincate Strip</td>
<td>HNO₃</td>
<td>35% (w/w)</td>
<td>RT</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>(350 ml/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rinse</td>
<td>Dip rinse</td>
<td></td>
<td></td>
<td>20 s</td>
</tr>
<tr>
<td>Zincate 2</td>
<td>EDEN Zincate M</td>
<td></td>
<td>RT</td>
<td>15 s</td>
</tr>
<tr>
<td>Rinse</td>
<td>Dip rinse</td>
<td></td>
<td></td>
<td>20 sec</td>
</tr>
</tbody>
</table>

[0109] Afterwards, the substrates were immersed in electroless nickel plating baths of compositions as described in Example 1. Deposition was done in 2 L-beakers. Each beaker was placed on a heater and temperature was maintained at 89.5° C. Mechanical agitation with 175 RPM was supplied by a magnetic stirrer. Bath loading was 1.4 dm³/l corresponding to two substrates per bath volume. Deposition time was 60 minutes.

[0110] The phosphorus content and deposit thickness were measured at 5 points of each substrate by XRF using the XRF instrument Fischerscope XDV-SDD (Helmut Fischer GmbH, Germany).

[0111] The deposition rate was calculated by using the deposition time and the measured deposit thickness. Results are summarized in Table 2.

[0112] The deposited nickel-phosphorus alloy layers completely covered the substrate surface; no skip plating was obtained. The deposited nickel-phosphorus alloy layers were of uniform thickness, adhered well to the substrate surface and had a good appearance with technical brightness and a typical gray color.

[0113] As becomes apparent from Table 2 the combination of stabilizing agents according to the present invention did neither decrease the deposition rate nor changed the phosphorus content of the deposited nickel alloy layers compared to electroless nickel plating baths containing no stabilizer or a single stabilizing agent. Thus, the combination of stabilizing agents according to the present invention had no negative effect on the bath performance and no negative effect on the coating quality.

Example 3

Determination of Stress

[0114] Stress in the nickel-phosphorus coating was measured using a stress-strip finger. The test strips were made of copper and had spring like properties. After plating as described in Example 2, the test strip was mounted on the Testing Stand (Deposit stress analyzer Model No. 683 of Specialty Testing & Development Co., York, Pa., USA) which measured the distance which the test strip legs had spread after plating. The distance U is included in the following formula which allows for the deposit stress to be calculated.

\[
\text{Stress} = \frac{U}{A} \times T \times K
\]

[0115] U is the number of increments spread, T is the deposit thickness and K is the strip calibration constant.

[0116] The deposit thickness T was determined by XRF as described in Example 2.

[0117] Each lot of test strips manufactured will respond with slight differences when used for deposit stress test. This degree of difference was determined by the supplier when each lot of test strips was calibrated. The value for K was supplied with each lot of test strips provided by Specialty Testing & Development Co.

[0118] Stress was also determined to be of compressive or tensile nature. If the test strip legs were spread outward on the side that has been plated, the deposit stress was tensile in nature. If the test strip legs were spread inward on the side that has been plated, the deposit stress was compressive in nature.

[0119] The stress of the deposited nickel-phosphorus alloy layer was measured to be between -35 and -45 N/mm² and thus, was compressive. Results are summarized in Table 2.

[0120] Table 2 also shows that the combination of stabilizing agents according to the present invention did not change the stress of the deposited nickel-phosphorus layer compared to electroless nickel plating baths containing no stabilizer or only a single stabilizing agent. Thus, the combination of stabilizing agents according to the present invention had also no negative effect on the coating quality in terms of stress. In summary, the combination of stabilizing agents imparted a significantly higher stability to electroless plating baths for deposition of nickel and nickel alloys at comparable bath performance and coating quality.
TABLE 2
Results of Examples 1 to 3

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>In(III) [µmol/l]</th>
<th>Iodide [µmol/l]</th>
<th>Deposition rate [µm/h]</th>
<th>P content [wt.%]</th>
<th>Stability viscously</th>
<th>Stability number [minutes]</th>
<th>Stress [N/mm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No stabilizer (comparative)</td>
<td>0</td>
<td>0</td>
<td>6.6</td>
<td>11.8</td>
<td>0</td>
<td>0.5</td>
<td>-40.2</td>
</tr>
<tr>
<td>Only Iodide (comparative)</td>
<td>0</td>
<td>3.0</td>
<td>6.4</td>
<td>12.0</td>
<td>0</td>
<td>4.5</td>
<td>-45.3</td>
</tr>
<tr>
<td>Only Indium(III)</td>
<td>0</td>
<td>12.0</td>
<td>3.7</td>
<td>11.9</td>
<td>1</td>
<td>5.0</td>
<td>-33.5</td>
</tr>
<tr>
<td>Only Indium(III) + Iodide</td>
<td>0</td>
<td>24.1</td>
<td>3.7</td>
<td>12.1</td>
<td>2</td>
<td>5.0</td>
<td>-31.8</td>
</tr>
<tr>
<td>Indium(III)</td>
<td>60.3</td>
<td>0</td>
<td>6.3</td>
<td>12.0</td>
<td>1</td>
<td>3.5</td>
<td>-46.8</td>
</tr>
<tr>
<td>Indium(III) + Iodide (according to invention)</td>
<td>90.4</td>
<td>0</td>
<td>6.1</td>
<td>11.9</td>
<td>1.5</td>
<td>8.0</td>
<td>-36.1</td>
</tr>
</tbody>
</table>

Example 4
Stability of Electroless Nickel Plating Baths

[0123] Stability of electroless nickel plating baths containing In(III) ions and iodide ions as mixtures of stabilizing agents were measured by determining the stability number as described in Example 1. Concentrations of the stabilizers in the electroless nickel plating baths and resulting stability numbers are summarized in Table 3.

TABLE 3
Concentrations of stabilizing agents and stability numbers

<table>
<thead>
<tr>
<th>In(III) [µmol/l]</th>
<th>Iodide [µmol/l]</th>
<th>Stability number [minutes]</th>
</tr>
</thead>
<tbody>
<tr>
<td>comparative</td>
<td>0</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>48.2</td>
</tr>
<tr>
<td></td>
<td>60.3</td>
<td>0</td>
</tr>
<tr>
<td>according to invention</td>
<td>60.3</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>60.3</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>60.3</td>
<td>48.2</td>
</tr>
</tbody>
</table>

Example 5
Stability of Electroless Nickel Plating Baths

[0122] Stability of electroless nickel plating baths containing In(III) ions and iodate ions as mixtures of stabilizing agents were measured by determining the stability number as described in Example 1.

[0123] Indium ions were added in the form of indium(III) hydroxide to the stock solution of an electroless nickel plating bath. Iodate ions were added in the form of potassium iodate. Concentrations of the stabilizers in the electroless nickel plating bath and resulting stability numbers are summarized in Table 4.

TABLE 4
Concentrations of stabilizing agents and stability numbers

<table>
<thead>
<tr>
<th>In(III) [µmol/l]</th>
<th>Iodate [µmol/l]</th>
<th>Stability number [minutes]</th>
</tr>
</thead>
<tbody>
<tr>
<td>comparative</td>
<td>0</td>
<td>0.47</td>
</tr>
<tr>
<td>60.3</td>
<td>0</td>
<td>3.5</td>
</tr>
<tr>
<td>according to invention</td>
<td>60.3</td>
<td>0.47</td>
</tr>
</tbody>
</table>

[0124] As becomes apparent from Tables 3 and 4, the combination of stabilizing agents according to the present invention is suitable to provide high plating bath stability against undesired decomposition. The plating bath stability imparted by the combination of stabilizing agents is much higher than would be expected from the stabilizing effects of each single stabilizing agent. Thus, the combination of stabilizing agents has a synergistic effect on the stability of the electroless plating bath. The test for determining the stability number does also show an improved resistance of such electroless nickel plating baths against contamination with catalytic metals, like Pd.

Example 6
Determining Deposition Rate, Phosphorus Content and Internal Stress

[0125] Deposition rates of electroless nickel plating baths according to the invention and phosphorus contents of nickel layers deposited therefrom were measured as described in Example 2. Internal stress of the nickel layers deposited was measured as described in Example 3. Gallium ions were added in the form of gallium(III) sulfate to the stock solution of an electroless nickel plating bath. Iodate ions were added in the form of potassium iodate and iodide ions in the form of potassium iodide. Concentrations of stabilizing agents in the plating baths and results are summarized in Table 5.
The deposited nickel-phosphorus alloy layers completely covered the substrate surface; no skip plating was obtained. The deposited nickel-phosphorus alloy layers were of uniform thickness, adhered well to the substrate surface and had a good appearance with technical brightness and a typical gray color.

As becomes apparent from Table 5, the combination of stabilizing agents according to the present invention did neither decrease the deposition rate nor changed the phosphorus content of the deposited nickel alloy layers compared to electroless nickel plating baths containing no stabilizer (see Table 2). Thus, the combination of stabilizing agents according to the present invention had no negative effect on the bath performance and no negative effect on the coating quality.

Table 5 also shows that nickel-phosphorus alloy layers were deposited from the inventive nickel plating baths having compressive stress ranging from -45 to -49 N/mm². Thus, the combination of stabilizing agents according to the present invention did not change the stress of the deposited nickel-phosphorus layer or did advantageously increase the compressive stress. Thus, the combination of stabilizing agents according to the present invention had also no negative effect on the coating quality in terms of stress.

An aqueous plating bath composition for electroless deposition of nickel and nickel alloys, the composition comprising:

1. A source of nickel ions,
2. A mixture of stabilizing agents comprising
   a) at least one metal ion selected from indium ion and gallium ion, and
   b) at least one selected from elementary iodine, iodide ion containing compounds, iodate ion containing compounds and periodate ion containing compounds.

3. The aqueous plating bath composition according to claim 1 wherein the indium ion is an indium(III) ion.
4. The aqueous plating bath composition according to claim 1 wherein the gallium ion is a gallium(III) ion.
5. The aqueous plating bath composition according to claim 1 wherein the stabilizing agent according to (ii) is selected from iodide ion containing compounds and iodate ion containing compounds.
6. The aqueous plating bath composition according to claim 1 wherein the concentration of the at least one metal ion according to (ii) a) ranges from 0.01 to 0.5 mmol/l.
7. The aqueous plating bath composition according to claim 1 wherein the source of nickel ions is selected from nickel sulfate, nickel chloride, nickel acetate, nickel methyl sulfonate, nickel sulfamate and mixtures thereof.
8. The aqueous plating bath composition according to claim 1 wherein the concentration of nickel ions ranges from 0.01 to 1 mol/l.
9. The aqueous plating bath composition according to claim 1 wherein the aqueous plating bath composition further comprises at least one complexing agent.
10. The aqueous plating bath composition according to claim 9 wherein the concentration of the at least one complexing agent ranges from 0.01 to 3.0 mol/l.
11. The aqueous plating bath composition according to claim 1 wherein the aqueous plating bath composition further comprises at least one reducing agent.
12. The aqueous plating bath composition according to claim 11 wherein the concentration of the at least one reducing agent ranges from 0.01 to 3.0 mol/l.
13. The aqueous plating bath composition according to claim 1 wherein the aqueous plating bath composition further comprises at least one alloying element wherein the at least one alloying element is selected from phosphorus, boron, titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, copper, silver, gold, aluminum, iron, cobalt, palladium, ruthenium, rhodium, osmium, iridium, platinum, zinc, cadmium, gallium, indium, tin, antimony, thallium, lead, and bismuth.
14. A method for electroless deposition of nickel and nickel alloys comprising the steps of
   (A) providing a substrate,
   (B) contacting the substrate with the aqueous plating bath composition according to claim 1,
   (C) and thereby depositing a nickel or nickel alloy onto the substrate.
15. A method for stabilizing any electroless plating bath for deposition of nickel and nickel alloys, the method comprises the steps of
   (D) providing any electroless plating bath for deposition of nickel and nickel alloys, and
   (E) adding a mixture of stabilizing agents, wherein the mixture of stabilizing agents comprises
      (i) at least one metal ion selected from indium ion and gallium ion, and
      (ii) at least one selected from elementary iodine, iodide ion containing compounds, iodate ion containing compounds and periodate ion containing compounds.
16. The aqueous plating bath composition according to claim 9 wherein the aqueous plating bath composition further comprises at least one reducing agent.
17. The aqueous plating bath composition according to claim 16 wherein the concentration of the at least one reducing agent ranges from 0.01 to 3.0 mol/l.
18. The aqueous plating bath composition according to claim 9 wherein the aqueous plating bath composition further comprises at least one alloying element wherein the at least one alloying element is selected from phosphorus, boron, titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, copper, silver, gold, aluminum, iron, cobalt, palladium, ruthenium, rhodium, osmium, iridium, platinum, zinc, cadmium, gallium, indium, tin, antimony, thallium, lead, and bismuth.
19. The aqueous plating bath composition according to claim 16 wherein the aqueous plating bath composition further comprises at least one alloying element wherein the at least one alloying element is selected from phosphorus, boron, titanium, vanadium, chromium, manganese, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, copper, silver, gold, aluminum, iron, cobalt, palladium, ruthenium, rhodium, osmium, iridium, platinum, zinc, cadmium, gallium, indium, tin, antimony, thallium, lead, and bismuth.

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