USE OF WATER SOLUBLE LANTHANIDE COMPOUNDS AS STABILIZER IN ELECTROLYTES FOR ELECTROLESS METAL DEPOSITION

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ABSTRACT

The present invention relates to the use of water soluble lanthanide compounds as stabilizer in electrolytes for electroleess metal deposition, an electrolyte as well as a method for the electroleess deposition of metals, particularly layers of nickel, copper, cobalt, boron, silver, palladium or gold, as well as layers of alloys comprising at least one of the aforementioned metals as alloying metal.
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[0001] The present invention relates to the use of water soluble lanthanide compounds as stabilizer in electrolytes for electroless metal deposition, an electrolyte as well as a method for the electroless deposition of metals, particularly layers of nickel, copper, cobalt, boron, silver, palladium or gold, as well as layers of alloys comprising at least one of the aforementioned metals as alloying metal.

[0002] The present invention further relates to an organic stabilizer for electroless plating processes, and 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, a stabilizer and preferably an accelerator, as well as a method for the electroless deposition of a metal layer on a surface from an electrolyte according to the invention.

[0003] Among electrolytic methods for the plating of substrates with metal layers, electroless plating methods have long been known from the state of the art. By electroless plating, also known 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 differ 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, nickel/boron or boron carbuide layers are deposited by means of electroless deposion methods. In this respect, electroless deposited layers in many cases differ also in their chemical nature from the galvanically deposited layers.

[0004] 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.

[0005] 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, e.g. for gas and/or oil industry applications.

[0006] Electroless plating methods are based on an autocatalytic process, in which the process metal ions comprised in the electrolytes are reduced to the elemental metal by a reducing agent which is oxidized during this redox reaction.

[0007] 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.

[0008] In known electroplating baths it is necessary to use a stabilizer to avoid the uncontrolled plate-out (wild deposition) of the electrolyte, which means the unregulated wild deposition of metal on the substrate surface and tank walls. 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. In addition, some heavy metal stabilizers are difficult to analyze. Since analyzing of concentration of said heavy metal stabilizers is mandatory but difficult, bath control can be difficult, too.

[0009] U.S. Pat. No. 6,146,702 discloses an electroless nickel cobalt phosphorus composition and plating process. The process is provided for enhancing the wear resistance of aluminum and other materials by depositing on the substrate a nickel, cobalt, phosphorus alloy coating using an electroless plating bath to provide a plated alloy having a cobalt content of at least about 20% by weight and a % Co%/P weight ratio of at least about 5.

[0010] 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.

[0011] JP 2009-149965A discloses a silver-plating method, which does not need to form an unnecessary layer of a nickel layer in between a substrate which is difficult to be plated and a silver-plated film, and can form the silver-plated film having sufficient adhesiveness directly on the substrate which is difficult to be plated with the use of a halide-free plating bath under a satisfactory working environment. The silver-plating method disclosed is used for forming the silver-plated film on the substrate on which an oxide film is easily formed and the oxide film hinders the adhesiveness of a plated film, and comprises at least the steps of: (A) degreasing the substrate; (B) removing the oxide film with a strongly acidic solution; and subsequently to the step (B), (C) plating the substrate with silver by using a phosphine-containing acidic silver-plating bath which essentially does not contain a halide ion and a cyanide ion while skipping a step of nickel strike plating or nickel-alloy strike plating.

[0012] CN 101348927A discloses a cyanogen-free pre-plated copper solution. The solution adopts a nontoxic organic phosphine compound to replace cyanide as a complexing agent for the preplated copper, and is particularly suitable for preplated copper used to electroplate steel, aluminum, magnesium, zinc, titanium and titanium alloy. The cyanogen-free preplated copper solution has the following main technical characteristic that the solution consists of (a) one sort of copper sulphate, basic cupric carbonate or copper nitrate with the volume concentration of between 30 and 60 g/L; (b) one sort or two sorts of compounds selected from methylene diphosphonic acid,
1-hydroxyethylidene 1,1 diposphonic acid and 1-hydroxybutyleneidene 1,1 diposphonic acid with the volume concentration of between 120 and 160 g/L; (c) one sort or two sorts of compounds selected from methylamin dimethylene diposphonic acid, hexamethylene diamine tetramethylene phosphonic acid and ethylenediamine tetramethylene phosphonic acid with the volume concentration of between 2 and 5 g/L; (d) one sort of potassium citrate, ammine citrate or seignette salt with the volume concentration of between 6 and 12 g/L; and (e) polyethylenimine alkyl salt or aliphatic amine ethoxy sulfonated substance (AESs) with the volume concentration of between 0.02 and 0.05 g/L. The cyanogen-free preplated copper solution has the characteristics of stable service performance, simple solution compositions, convenient maintenance, high safety, environmental protection, reliable plating coat binding and the like.

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. Especially for so-called “high phos” electroleless nickel electrolytes the use of sulfur compounds is critical, since such compounds may negatively affect the corrosion resistance of the plated nickel layer.

It is therefore an object of the present invention to provide an improved formulation for electroleless plating nickel, copper, cobalt, boron, silver, palladium or gold, as well as layers comprising at least one of the aforementioned metals as alloying metal, which formulation is stabilized against uncontrolled plate-out of the metal to be deposited.

It is a more particular object of various preferred embodiments of the pending application to provide an electrolyte for the electroleless deposition of the aforementioned metals 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 aqueous electrolyte for the electroleless 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 water-soluble lanthanide compound.

It is a further object of the present invention to provide an improved stabilizer for electroleless plating processes, and a new electrolyte as well as a method for the electroleless deposition of a metal layer having improved properties.

Surprisingly, it was found that water-soluble lanthanide compounds 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 electroleless deposition of metal layers, totally.

Lanthanide compounds in the meaning of this invention shall refer to compounds of the elements of the lanthanide group of the periodic system, i.e. lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. In the following it is referred to this group of elements as Ln.

Compounds in the meaning of this invention shall refer to salts, organic compounds, metal organic compounds or complexes. Examples for salts are, e.g. halides like fluorides, chlorides, bromides, or iodides, sulfates, phosphates, or nitrates. With respect to the halides, preferably such salts are of the general formula LnX₆, wherein X represents a halide and n=1 to 8. Examples for organic compounds are alkyl or aryl compounds of Ln, like LnR₄ with R=CH₃, C₂H₅, or Ar (aryl), and n=1 to 6, or Ln(C₂H₅)₂(n-1)Ar with n=1 to 8, preferably 2 to 4. Examples for metal organic compounds may be compounds of the general formula [Ln(C₂H₅)₃], [Ln(C₂H₅)₂X], or [Ln(C₂H₅)X₂] with X=F, Cl, Br, or I. [Ln(C₂H₅)₂Me], [Ln(C₂H₅)₃X] with X=F, Cl, Br, or I. [Ln(C₂H₅)₂]₃, or [Ln(C₂H₅)₃]. Examples for complexes may be (NH₄)₂[Ln(NO₃)₃], (NH₄)₃[Ln(SO₄)₃] or [Ln(NO₃)₃(OPP₃)₂].

Water soluble in the meaning of the invention shall mean that the Ln compound is soluble in an aqueous system to an extent of at least 0.007 mmol/L or 1 mg/L of Ln.

While not being bound to this theory, the applicant believes that water-soluble lanthanide compounds 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.

A further benefit of the inventive electrolyte is that an effect known as edge weakness can be avoided. When using electrolytes for the electroleless 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 water-soluble lanthanide compounds as stabilizers in electroleless plating methods this edge weakening effect can be avoided which significantly increases the overall outline accuracy of the plating especially when plating large substrates.

Furthermore, the use of a water-soluble lanthanide compounds as stabilizer results in a more even deposition having less nodules.

Especially on alumina or zinicate substrates the use of water-soluble lanthanide compounds as stabilizers result in an improved deposition and a significant reduction of discard.

A further benefit of the inventive electrolyte is that a significant reduction of deposition on components of the plating equipment, especially on the heating systems used in the plating equipment, occurs. By this, the need for maintenance is significantly reduced which in turn results in a notable economic benefit to the plating shops due to less down time.

Surprisingly, a electrolytic bath, with a single class of metal, containing the stabilizer of the present invention leads to deposited metal layers, having properties like an amorphous metal. These properties are, for example, that these layers have no edge weakness effect; they are very passive; have a good resistance against corrosion; wear-resistance; and good compressive stress properties.

Further benefits of a stabilizer according to the present invention are that it provides a deposit having significantly better corrosion resistance including excellent resistance vs. nitric acid; is more environmental friendly
(less toxic additive); and lower plating temperatures can be used to achieve the same plating speed.

[0029] Surprisingly, it was found that by the use of water-soluble lanthanide compounds plating electrolytes for the electroless deposition become less sensitive to foreign metal carry-over, like e.g. palladium ions resulting from the activation pretreatment of the substrate to be plated. This is especially relevant when non-conductive substrates, like e.g. plastics, are intended to be plated by direct plating processes using noble metal colloids for seeding the surfaces. While the known plating electrolytes turned out to be quite sensitive to foreign metals and therefore required intensive rinse steps after the activation, the inventive plating electrolytes do not show any significant deterioration even at Pd-concentrations>>2 mg/L.

[0030] In particular, water-soluble lanthanide compounds according to the general formula Ln(C₆H₄O₂)ₙ with n=1 to 8, preferably 2 to 4, like e.g. (Nd(C₆H₄O₂)₃), are found to be very effective as stabilizers in electroless plating electrolytes. Hence, neodymium(III)acetate is a preferred embodiment of a water-soluble lanthanide compound.

[0031] The water-soluble lanthanide compounds can be comprised in the inventive electrolyte within a range of ±0.05 mg/L and ±100 mg/L, preferably between ±0.1 mg/L and ±80 mg/L, most preferably between ±1 mg/L and ±50 mg/L calculated on the lanthanide.

[0032] Surprisingly, it was found that in case of oversedating the water-soluble lanthanide compounds the excess amount of the lanthanide compound can be reduced by use of ion exchange resins which are sensitive to cations in oxidation state +3. By use of such ion exchange resins the excess amount of the water-soluble lanthanide compounds can be reduced without significantly interfering with the concentration of the metals to be deposited as far as these metals are comprised in the electrolyte as metal ions in an oxidation state different to +3, like e.g. +1, +2, +4, or +5. An example for a cation exchange resin sensitive to cations in oxidation state +3 is Lewatit VP OC 1026 ( purchasable from LANXESS Deutschland GmbH).

[0033] According to an embodiment of the invention as reducing agent in the inventive electrolyte at least one reducing agent of the group consisting of sodium hypophosphate, formaldehyde, dimethylaminoborane, aminoaborane, or other organic boranes can be comprised. The reducing agent may be comprised in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably, 0.1 mol/L and 0.3 mol/L. Preferably, the electrolyte may comprise e.g. sodium hypophosphate (mono hydrate) with a concentration of 10 to 40 g/L, and even more preferably with a concentration of 12 to 30 g/L.

[0034] 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, i.e., the source of cations of the metal to be deposited may comprise the counter anion of any of such salts. Here, especially, 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. Hence, the word volatile anion should be understood as anions of volatile compounds, i.e. compounds having an initial boiling point in the range of 50° C. to 250° C. at a standard atmospheric pressure of 101.3 kPa. 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. Volatile ions in the sense of this invention are ions which form together with according counter ion moieties which are volatile at the temperature the electrolyte is commonly used at. An example for such volatile ions is acetate which forms under the plating conditions acetic acid. Since acetic acid has a vapor pressure of 16 hPa at 20° C. it will evaporate from the electrolyte under the plating conditions and can be recovered from the exhaust air system.

[0035] According to an embodiment of the invention as a complexing agent the inventive electrolyte comprises a compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), E DTA, and amino acid. The complexing agent may be comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably 0.2 mol/L and 0.4 mol/L.

[0036] Preferably, the inventive electrolyte comprises an accelerator, which may preferably comprise a compound of the group consisting of saccharin, hydantoin, rhodamine, or carbamide and its derivates. The accelerator may be comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.1 mol/L, preferably 0.005 mol/L and 0.025 mol/L.

[0037] As metal to be deposited the inventive electrolyte may comprise a metal of the group consisting of nickel, copper, cobalt, boron, silver, palladium 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 nickel/boron or the like can be deposited. Also, the deposition of nickel/PTFE-layers or nickel/boron carbide/graphite-layers from dispersion baths is possible by the inventive electrolyte.

[0038] The inventive electrolyte can have a pH-value within a range of between pH 4 and pH 7, preferably within pH 4 and pH 6. Hence, it is preferred that the inventive electrolyte is slightly acidic. To control the pH-value of the electrolyte it may comprise pH adjusting compounds, like e.g. acids, bases, and/or buffers.

[0039] With respect to the acids organic and inorganic acids may be comprised in the electrolyte, e.g. sulfuric acid, acetic acid, lactic acid, citric acid, hypohosphorous acid, sulfonic acids, methane sulfonic acid, methane disulfonic acid or combinations of these.

[0040] With respect to the bases, e.g. sodium carbonate, potassium carbonate, ammonium hydroxide, sodium hydroxide, potassium hydroxide, lithium hydroxide, or combination of these may be comprised in the electrolyte.

[0041] With respect to the buffer the electrolyte may comprise e.g. an acetic acid/acetate buffer, or a citric acid / citrate buffer.

[0042] According to another embodiment of the invention the electrolyte may comprise as an additional stabilizer a β-amino acid.

[0043] Preferably, β-amino acids having a pKₐ-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 propionate acid (β-alanin), 3-amino butyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (Taurin) are usable as additional stabilizers.
The β-amino acid may be comprised in the inventive electrolyte within a range of 1 mg/L to 5 g/L, preferably 100 mg/L to 2 g/L, and even more preferably 200 mg/L to 1.5 g/L.

The formulation of the invention may comprises an organic stabilizer for electroless plating processes comprising an organic molecule which is the condensation product (adduct) of at least one β-amino acid and at least one carboxylic component which may be introduced into the aqueous medium as, e.g., the free carboxylic acid or a salt thereof.

The condensation product of the β-amino acid (e.g. β-alanine) and a carboxylic functional group as derived for the carboxylic acid or its salt, is a β-amide. The condensation product is present in a monomeric, oligomeric and/or polymeric form, i.e., as the N-terminal amide of a B-amino acid monomer, dimer, trimer, oligopeptide and polypeptide.

The condensation product of the β-amino acid may be comprised in the inventive electrolyte within a range of 1 mg/L to 5 g/L, preferably 100 mg/L to 2 g/L, and even more preferably 200 mg/L to 1.5 g/L.

The addition of a pre mixture of a β-amino acid, like e.g. β-alanine, with a carboxylic acid, like e.g. lactic acid, glycine, or malic acid increases the stabilizing effect and can be beneficially be used as a second stabilizer in sense of the invention. It has been discovered that the carboxylic acid reacts with β-amino acids to form amide strucures which is deemed to be the reason for the enhanced stabilizing effect.

In this concern, in preferred embodiments of the invention the carboxylic acid may be a compound of the group consisting of acrylic acids, aromatic carboxylic acids, fatty acids, aliphatic carboxylic acids, keto acids, dicarboxylic acids, tricarboxylic acids, straight chain carboxylic acids, heterocyclic carboxylic acids, saturated carboxylic acids, unsaturated carboxylic acids, and α-hydroxy acids. It is also possible to use other organic compounds having a carboxylic functional group. In particular, the salts of carboxylic acids (carboxylic anion —RCO2⁻) can be used.

The electrolyte according to this invention may additionally comprise an inorganic stabilizer, preferably ammonium. Such an inorganic stabilizer may be comprised in a concentration of between 0.05 mg/L and 0.5 g/L, preferably 0.5 mg/L and 0.1 g/L.

Yet in another embodiment of the invention the electrolyte may comprise three different stabilizers, one being a lanthanide compound, i.e. at least one compound of a metal selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, a second one being a β-amino acid, and a third one being an inorganic stabilizer, like e.g. ammonium.

A further property of a metal layer deposited for an electrolyte according to the present invention is that it is very passive.

A further advantage of the metal layers deposited for an electrolyte according to the present invention is that it is good residual compressive stress. Furthermore, the metal layers exhibit an enhanced corrosion resistance.

According to another embodiment of the invention the electrolyte may comprise an alkali metal halogenide and/or an alkali metal halogenate, i.e. a salt of an alkali metal with a halogen or a conjugated base of a halogen acid wherein the halogen has an oxidation state of +5. Such halogen and/or halogen oxygen compounds may be comprised in the inventive electrolyte in a concentration of between 0.05 g/L and 5 g/L, preferably between 0.1 g/L and 2 g/L. While not being bound to this theory it is assumed that these compounds act as thermal stabilizers by which addition deposition of nickel on the heating elements or areas of local overheating is avoid. Example for alkali metal halogenides and/or an alkali metal halogenates are, e.g. potassium iodide, potassium iodate, sodium iodide, sodium iodate, potassium chloride, potassium chlorate, sodium bromide, lithium chloride, lithium iodate or lithium chloride.

With respect to the method the object of the invention is solved by a method for the electroless deposition of a metal layer on a substrate comprising the steps of contacting the substrate to be plated with an electrolyte 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 water-soluble lanthanide compound.

According to an embodiment of the inventive method, the substrate is contacted with the electrolyte at a temperature within the range of between 20°C and ±100°C, preferably between 25°C and ±95°C, e.g. between ±70°C and ±91°C.

According to another embodiment of the inventive method, the substrate is contacted with the electrolyte for a time between 1 s and ±480 min, preferably between ±10 s and ±240 min.

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.

In preferred embodiments, the formulation of the invention contains ion of at least one metal of the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. As source for these metal ions salts of the metals are comprised in the electrolyte, e.g. metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbinate of the respective metals. The metal ions are comprised in the electrolyte in a concentration between 0.01 mol/L to 0.5 mol/L, preferably between 0.02 mol/L to 0.2 mol/L. As reducing agent the electrolyte comprises at least one reducing agent of the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, or other organic boranes. The reducing agent may be comprised in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably 0.1 mol/L and 0.3 mol/L. As a complexing agent the electrolyte comprises a compound of the group consisting of 2-hydroxy propionic acid, propandioic acid (malonic acid), EDTA, and amino acetic acid. The complexing agent is comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably 0.2 mol/L and 0.4 mol/L. As an accelerator the electrolyte comprises a compound of the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivatives. The accelerator is comprised in the electrolyte in a concentration of between 0.05 mmol/L and 0.1 mol/L, preferably 5 mmol/L and 0.25 mol/L. As stabilizer the electrolyte comprises at least a water-soluble lanthanide compound. Said lanthanide compound may be at least one compound selected
from the group consisting of fluorides, chlorides, bromides, iodides, sulfates, phosphates, or nitrates, of at least one metal selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Said stabilizer may be comprised in the electrolyte in a concentration within a range of ±0.05 mg/L and ±100 mg/L, preferably between ±0.1 mg/L and ±80 mg/L, most preferably between ±1 mg/L and ±50 mg/L, calculated on the lanthanide metal.

[0060] According to another embodiment of the invention, the formulation of the invention contains ions of at least one metal of the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. As source for these metal ions salts of the metals are comprised in the electrolyte, e.g. metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbate of the respective metals. The metal ions are comprised in the electrolyte in a concentration between 0.01 mol/L and 0.5 mol/L, preferably between 0.02 mol/L and 0.2 mol/L. As reducing agent the electrolyte comprises at least one reducing agent of the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, or other organic boranes. The reducing agent may be comprised in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably 0.1 mol/L and 0.3 mol/L. As a complexing agent the electrolyte comprises a compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, and amino acetic acid. The complexing agent is comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably 0.2 mol/L and 0.4 mol/L. As an accelerator the electrolyte comprises a compound of the group consisting of saccharin, hydantoïn, rhodanine, or carbamid and its derivates. The accelerator is comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.1 mol/L, preferably 0.5 mol/L and 0.25 mol/L. As a complexing agent the electrolyte comprises at least a water-soluble lanthanide compound. Said lanthanide compound may be a least one compound selected from the group consisting of fluorides, chlorides, bromides, iodides, sulfates, phosphates, or nitrates, of at least one metal selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Said stabilizer may be comprised in the electrolyte in a concentration within a range of ±0.05 mg/L and ±100 mg/L, preferably between ±0.1 mg/L and ±80 mg/L, most preferably between ±1 mg/L and ±50 mg/L, calculated on the lanthanide metal. As an additional stabilizer the electrolyte comprises at least one β-amino acid having a pKₐ-value within a range of 4 to 8, preferably within a range of 5 to 7. In particular, the electrolyte comprises at least one β-amino acid of the group consisting of 3-amino propionic acid (β-alanine), 3-amino butyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (taurine). The β-amino acid is comprised in the embodiment of 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 preferably 200 mg/L to 400 mg/L. The use of a combination of two stabilizers beneficially results in a further improvement of the deposition by reduction of nodules.

[0061] In another preferred embodiment of the invention the formulation of the invention contains ions of at least one metal of the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. As source for these metal ions salts of the metals are comprised in the electrolyte, e.g. metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbate of the respective metals. The metal ions are comprised in the electrolyte in a concentration between 0.01 mol/L and 0.5 mol/L, preferably between 0.02 mol/L and 0.2 mol/L. As reducing agent the electrolyte comprises at least one reducing agent of the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, or other organic boranes. The reducing agent may be comprised in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably 0.1 mol/L and 0.3 mol/L. As a complexing agent the electrolyte comprises a compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, and amino acetic acid. The complexing agent is comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably 0.2 mol/L and 0.4 mol/L. As an accelerating the electrolyte comprises a compound of the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivatives. The accelerator is comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.1 mol/L, preferably 0.5 mol/L and 0.25 mol/L. As stabilizer the electrolyte comprises at least a water-soluble lanthanide compound. Said lanthanide compound may be a least one compound selected from the group consisting of fluorides, chlorides, bromides, iodides, sulfates, phosphates, or nitrates, of at least one metal selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Said stabilizer may be comprised in the electrolyte in a concentration within a range of ±0.05 mg/L and ±100 mg/L, preferably between ±0.1 mg/L and ±80 mg/L, most preferably between ±1 mg/L and ±50 mg/L, calculated on the lanthanide metal. As an additional stabilizer the electrolyte comprises stabilizer as an inorganic stabilizer. Antimony is comprised in a concentration of between 0.05 mol/L and 0.5 g/L, preferably 0.5 g/L and 1 g/L. The antimony is added as water soluble salt, preferably as chloride, sulfate, acetate, nitrate, propionate, formiate, oxalate, citrate, ascorbate, or a mixture of these.

[0062] In a preferred embodiment of the invention, the formulation of the invention contains ions of at least one metal of the group consisting of nickel, copper, cobalt, boron, silver, and gold. As source for these metal ions salts of the metals are comprised in the electrolyte, e.g. metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbate of the respective metals. The metal ions are comprised in the electrolyte in a concentration between 0.01 mol/L and 2 mol/L, preferably between 0.02 mol/L and 0.5 mol/L. As reducing agent the electrolyte comprises at least one reducing agent of the group consisting of sodium hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, or other organic boranes. The reducing agent may be comprised in the electrolyte in a concentration of between 0.08 mol/L and 0.5 mol/L, preferably 0.1 mol/L and 0.3 mol/L. As a complexing agent the electrolyte comprises a compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA, and amino acetic acid. The complexing agent is comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.5 mol/L, preferably 0.2 mol/L and 0.4 mol/L. As an accelerating the electrolyte comprises a compound of the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates. The accelerator is comprised in the electrolyte in a concentration of between 0.05 mol/L and 0.1 mol/L, preferably 0.5 mol/L and 0.25 mol/L. As stabilizer the electrolyte comprises at least a water-soluble lanthanide compound. Said lanthanide compound may be a least one compound selected from the group consisting of fluorides, chlorides, bromides, iodides, sulfates, phosphates, or nitrates, of at least one metal selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Said stabilizer may be comprised in the electrolyte in a concentration within a range of ±0.05 mg/L and ±100 mg/L, preferably between ±0.1 mg/L and ±80 mg/L, most preferably between ±1 mg/L and ±50 mg/L, calculated on the lanthanide metal. As an additional stabilizer the electrolyte comprises stabilizer as an inorganic stabilizer. Antimony is comprised in a concentration of between 0.05 mol/L and 0.5 g/L, preferably 0.5 g/L and 1 g/L. The antimony is added as water soluble salt, preferably as chloride, sulfate, acetate, nitrate, propionate, formiate, oxalate, citrate, ascorbate, or a mixture of these.
EXAMPLE 2

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

- 8.8 g/L nickel acetate tetrahydrat;
- 0.2 g/L potassium iodide;
- 30 g/L lactic acid;
- 2.5 g/L saccharine, sodium salt;
- 16 g/L sodium hydroxide solution, 33% by weight;
- 30 g/L sodium acetat;
- 35 g/L sodium hypophosphite dihydrate;
- 20.0 mg/L samarium (M) sulfate

wherein the pH is in a range of pH 4 to pH 5 at a temperature between 80° C. and 94° C. An electrolyte with the above mentioned composition. The electrolyte was treated according to the standard pre-treatment cycle before plating in the electrolec nickel bath. A glossy nickel deposit without nodules could be plated from this electrolyte with a plating speed of 6-8 μm/h with a composition of 88-89% by weight nickel and 11-12% by weight of phosphorous.

EXAMPLE 3

In another preferred embodiment of the invention the electrolyte according to the present invention comprises:

- 8.8 g/L nickel acetate tetrahydrat;
- 0.2 g/L potassium iodide;
- 30 g/L lactic acid;
- 2.5 g/L saccharine, sodium salt;
- 16 g/L sodium hydroxide solution, 33% by weight;
- 35 g/L sodium hypophosphite dihydrate;
- 5 mg/L neodymium acetate;
- 15 mg/L potassium antimonite tartrate

wherein the pH is in a range of pH 4.0 to pH 5 at a temperature between 80° C. and 94° C. A steel panel was plated in an electrolyte with the above mentioned composition. A glossy nickel deposit could be plated from this electrolyte with a plating speed of 8-10 μm/h with a composition of 88-89% by weight nickel and 10-11.5% by weight of phosphorous.

EXAMPLE 4

In another preferred embodiment of the invention the electrolyte according to the present invention comprises:

- 8.8 g/L nickel sulfate;
- 0.1 mg/L potassium iodate;
- 25 g/L lactic acid;
- 1.0 g/L saccharine;
- 2 g/L β-alanin;
- 15.5 g/L sodium hydroxide solution, 33% by weight;
- 20 g/L sodium acetat;
- 35 g/L sodium hypophosphite dihydrate;
- 40.00 mg/L cerium (III) iodide;
- 18 mg/L potassium antimonite tartrate

wherein the pH is in a range of pH 4.0 to pH 5 at a temperature between 80° C. and 94° C. An ABS plaque was plated in an electrolyte with the above mentioned composition. The ABS plaque was pre-treated in a standard POP (plating-on-plastic) pretreatment cycle before plating. A glossy nickel deposit could be plated from this electrolyte.
with a plating speed of 8-10 μm/h with a composition of 90-91% by weight nickel and 9-10% by weight of phosphorus.

1. An aqueous electrolyte composition 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 a water-soluble lanthanide compound.

2. The aqueous electrolyte composition according to claim 1, wherein the water-soluble lanthanide compound is comprised in a concentration between ±0.05 mg/L and ±100 mg/L.

3. The aqueous electrolyte composition according to claim 1, wherein the metal to be deposited comprises at least one metal selected from the group consisting of nickel, copper, cobalt, boron, silver, and gold.

4. The aqueous electrolyte composition according to claim 3, wherein the accelerator is at least one accelerator of selected from the group consisting of saccharine, hydantoin, rhodamine, carbamide and carbamide derivatives.

5. The aqueous electrolyte composition according to claim 3, wherein the electrolyte is essentially free of inorganic stabilizers.

6. The aqueous electrolyte composition according to claim 3, wherein the composition is essentially free of cyanides, selenium compounds and sulfur compounds comprising sulfur in an oxidation state between −2 and +5.

7. The aqueous electrolyte composition according to claim 3, further comprising at least one additional carboxylic acid and/or at least one salt of a carboxylic acid.

8. The aqueous electrolyte composition according to claim 7, wherein the carboxylic acid is a compound of the group consisting of acrylic acids, carboxylic acids, fatty acids, aliphatic carboxylic acids, keto acids, dicarboxylic acids, tricarboxylic acids, straight chained carboxylic acids, heterocyclic carboxylic acids, saturated carboxylic acids, unsaturated carboxylic acids, and α-hydroxy acids.

9. The aqueous electrolyte composition according to claim 3, wherein the pH-value of the composition is in the range of between pH 4 and pH 7.

10. The aqueous electrolyte composition according to claim 3, wherein the reducing agent is at least one compound of the group consisting of sodium hypophosphite, formaldehyde, dimethyl aminoborane, amino borane, and other organic boranes.

11. The aqueous electrolyte composition according to claim 3, wherein the complexing agent is at least one compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid, EDTA and amino acetic acid.

12. A method for the electroless deposition of a metal layer on a substrate comprising the steps of contacting the substrate to be plated with an electrolyte 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 water-soluble lanthanide compound.

13. The method according to claim 12, wherein the substrate is contacted with the electrolyte at a temperature within the range of between ±50°C and ±80°C.

14. The method according to claim 12, wherein the substrate is contacted with the electrolyte for a time between ±1 s and ±180 min.

15. (canceled)

16. The method according to claim 12, wherein the water-soluble lanthanide compound is comprised in a concentration between ±0.05 mg/L and ±100 mg/L.

17. The method according to claim 12, wherein the metal to be deposited comprises at least one metal selected from the group consisting of nickel, copper, cobalt, boron, silver, and gold.

18. The method according to claim 17, wherein the accelerator is at least one accelerator of the group consisting of saccharine, hydantoin, rhodamine, carbamide and carbamide derivatives.

19. The method according to claim 17, wherein the electrolyte is essentially free of inorganic stabilizers.

20. The method according to claim 17, wherein the composition is essentially free of cyanides, selenium compounds and sulfur compounds comprising sulfur in an oxidation state between −2 and +5.

21. The method according to claim 17, further comprising at least one additional carboxylic acid and/or at least one salt of a carboxylic acid.

22. The method according to claim 21, wherein the carboxylic acid is a compound of the group consisting of acrylic acids, aromatic carboxylic acids, fatty acids, aliphatic carboxylic acids, keto acids, dicarboxylic acids, tri-carboxylic acids, straight chained carboxylic acids, heterocyclic carboxylic acids, saturated carboxylic acids, unsaturated carboxylic acids, and α-hydroxy acids.

23. The aqueous electrolyte composition according to claim 2, wherein the water-soluble lanthanide compound is comprised in a concentration between ±0.1 mg/L and ±25 mg/L.

24. The aqueous electrolyte composition according to claim 2, wherein the water-soluble lanthanide compound is comprised in a concentration between ±0.5 mg/L and 10 mg/L.

25. The aqueous electrolyte composition according to claim 1, wherein the electrolyte is essentially free of lead, bismuth, zinc and/or tin.

26. The method according to claim 13, wherein the substrate is contacted with the electrolyte at a temperature within the range of between ±25°C and ±70°C.

27. The method according to claim 14, wherein the substrate is contacted with the electrolyte for a time between ±10 s and ±60 min.

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