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(54) USE OF WATER SOLUBLE AND AIR STABLE PHOSPHAADAMANTANES AS STABILIZER IN ELECTROLYTES FOR ELECTROLESS METAL DEPOSITION

(57) The present invention relates to the use of water soluble and air stable phosphaadamantanes 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. 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.

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Description

[0001] The present invention relates to the use of water soluble and air stable phosphaadamantanes 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 carbide layers are deposited by means of electroless deposition methods. In this respect, electroless deposited layers in many cases differ also in their chemical nature from the galvanically deposited layers.

[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 process the metal ions comprised in the electrolytes are reduced to the elemental metal by a reducing agent which is oxidized during this redox reaction.

[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.

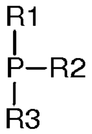
[0008] In known electroplating baths it is necessary to use a stabilizer to avoid the uncontrolled plate-out (wild deposition) of the electrolyte, which means the unregulated wild deposition of metal on the substrate surface and tank walls. Hitherto, in the state of the art, heavy metals like lead, bismuth, 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 aluminium 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] JP 2005-290415A discloses a stabilizing agent for electroless copper-plating electrolytes, which imparts adequate stability to an electroless copper-plating solution without lowering characteristics of an electroless copper-plated film, and is made of a highly safe material. The electroless copper-plating solution includes a phosphine compound expressed by the following general formula, as the stabilizing agent:



$$\begin{array}{l} R1 \\ | \\ P-R2 \\ | \\ R3 \end{array}$$

wherein R1, R2 and R3, are each the same or different, represent a monovalent aliphatic hydrocarbon group which may have a substituent group, an aryl group which may have a substituent group, or a heterocyclic group which may have a substituent group.

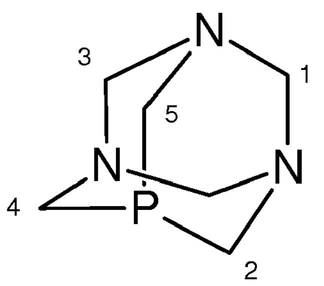
[0013] CN 101348927A discloses a cyanogen-free preplated copper solution. The solution adopts a nontoxic organic phosphine compound to replace cyanide as a complexing agent for the preplated copper, and is particularly suitable for preplated copper used to electroplate steel, aluminum, magnesium, zinc, 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 diphosphonic acid and 1-hydroxybutyleneidene 1.1 diphosphonic acid with the volume concentration of between 120 and 160 g/L; (c) one sort or two sorts of compounds selected from methylamino dimethylene diphosphonic 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, amine citrate or seignette salt with the volume concentration of between 6 and 12 g/L, and (e) polyethyleneimine alkyl slat 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.

[0014] 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" electroless nickel electrolytes the use of sulfur compounds is critical, since such compounds may negatively affect the corrosion resistance of the plated nickel layer.

[0015] It is therefore an object of the present invention to provide an improved formulation for electroless plating that is stabilized against uncontrolled plate-out of the metal to be deposited.

[0016] It is a more particular object of various preferred embodiments of the pending application to provide an electrolyte for the electroless deposition which is free of heavy metal stabilizers, cyanides, selenium compounds, and/or sulfur compounds comprising sulfur in an oxidation state between -2 and +5.

[0017] This object is solved by an aqueous electrolyte for the electroless deposition of a metal layer on a substrate, comprising a metal ion source for the metal to be deposited, a reducing agent, a complexing agent, an accelerator, and a stabilizer, characterized in that the electrolyte comprises as stabilizer a phosphaadamantane according to the general formula I



(Formula I)

wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom.

[0018] It is a further object of the present invention to provide an improved stabilizer for electroless plating processes, and a new electrolyte as well as a method for the electroless deposition of a metal layer having improved properties.

[0019] Surprisingly, it was found that phosphaadamantanes according to the general formula I are capable to replace heavy metal stabilizers, cyanides, selenium compounds as well as sulfur compounds comprising sulfur in an oxidation state between -2 and +5 in electrolytes for the electroless deposition of metal layers, totally.

[0020] While not being bound to this theory, the applicant believes that the phosphaadamantanes according to general formula I due to their indirectly tertiary amino groups as well as their tertiary phosphorus group are capable to at least temporarily jam the active centers on the substrate surface which are responsible for the uncontrolled deposition. So the wild deposition of the metals can be avoided. Additionally, also the foreign ions comprised in the electrolyte which are responsible for the wild deposition, too, are inactivated by the used such phosphaadamantanes.

[0021] A further benefit of the inventive electrolyte is that an effect known as edge weakness can be avoided. When using electrolytes for the electroless deposition of metal layers which comprise heavy metal ions as stabilizers at high convection of the electrolyte a decreased deposition of metal at the edges of the substrate occurs. This is deemed to be related to an increased assembly of the heavy metal ions used as stabilizers in these areas. This effect deteriorates the outline accuracy of the plating. Surprisingly, by the use of phosphaadamantanes according to general formula I as stabilizers in electroless plating methods this edge weakening effect can be avoided which significantly increases the overall outline accuracy of the plating especially when plating large substrates.

[0022] Furthermore, the use of a phosphaadamantane according to general formula I as stabilizer results in a more even deposition having less nodules.

[0023] Especially on alumina or zincate substrates the use of phosphaadamantanes according to general formula I as stabilizers result in an improved deposition and a significant reduction of discard.

[0024] 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.

[0025] An 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.

[0026] Further benefits of the stabilizer according to the present invention are, that it is metal free; provides a deposit having significantly better corrosion resistance including excellent resistance vs. nitric acid; is environmental friendly (non-toxic additive); has a higher phosphorus concentration at given pH level; and lower plating temperatures can be used to achieve the same plating speed and phosphorus content.

[0027] Surprisingly, it was found that by the use of phosphaadamantanes according to the general formula I 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 quit sensitive to foreign metals and therefore required intensive rinse steps after the activation, the inventive plating electrolytes does not show any significant deterioration even at Pd-concentrations >> 2mg/L.

[0028] In particular, phosphaadamantanes according to general formula I having no hydrogene substituted are found to be very effective as stabilizers in electroless plating electrolytes. Hence, 1,3,5-Triaza-7-phosphatricyclo[3.3.1.1]decane (PTA) is a preferred embodiment of the phosphaadamantanes according to general formula I. Beneficially, PTA has a sufficiently high solubility in aqueous systems and has a high oxidations stability.

[0029] The phosphaadamantanes according to general formula I can be comprised in the inventive electrolyte within a range of $\geq$0.05 mg/L and $\leq$ 100 mg/L, preferably between $\geq$0.1 mg/L and $\leq$ 25 mg/L, most preferably between $\geq$0.5 mg/L and $\leq$ 10 mg/L.

[0030] 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 hypophosphite, formaldehyde, dimethylaminoborane, aminoborane, 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 comprises e,g, sodium hypophosphite (mono hydrate) with a concentration of 10 to 40 g/l, and even more preferably with a concentration of 12 to 30 g/l.

[0031] 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 ascorbinate 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. 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 16hPa at 20 °C it will evaporate from the electrolyte under the plating conditions and can be recovered from the exhaust air system.

[0032] 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), EDTA, and amino acetic 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.

[0033] Preferably, the inventive electrolyte comprises an accelerator, which may preferably comprise a compound of the group consisting of saccharin, hydantoin, rhodanine, or carbamide and its derivates. The accelerator may be comprised in the electrolyte in a concentration of between 0.05 mmol/L and 0.1 mol/L, preferably 0.005 mol/L and 0.025mol/L.

[0034] 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 bathes is possible by the inventive electrolyte.

[0035] 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.

[0036] 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, hypophosphorus acid, sulfonic acids or combinations of these.

[0037] With respect to the bases, e.g. sodium carbonate, ammonium hydroxide, sodium hydroxide, potassium hydroxide, lithium hydroxide, or combination of these may be comprised in the electrolyte.

[0038] With respect to the buffer the electrolyte may comprise e.g. an acetic acid/ acetate buffer, or a citric acid / citrate buffer.

[0039] According to another embodiment of the invention the electrolyte may comprise as an additional stabilizer a ß-amino acid.

[0040] Preferably, ß-amino acids having a pK_a-value within a range of 4 to 8, preferably within a range of 5 to 7 seems to be suitable in this respect. In particular, 3-amino propionic acid (ß-alanin), 3-aminobutyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (Taurin) are usable as additional stabilizers.

[0041] The ß-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 preferred 200 mg/L to 1.5 g/L.

[0042] 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 ß.-amino acid and at least one carboxyl component which may be introduced into the aqueous medium as, e.g., the free carboxylic acid or a salt thereof.

[0043] The condensation product of the ß-amino acid (e.g. ß-alanine) and a carboxylic functional group as derived for the carboxylic acid or its salt, is a ß-amide. The condensation product is present in a monomeric, oligomeric and/or polymeric form, i.e., as the N-terminal amide of a ß-amino acid monomer, dimer, trimer, oligopeptide and polypeptide.

[0044] The condensation product of the ß-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 preferred 200 mg/L to 1.5 g/L.

[0045] The addition of a pre mixture of a ß-amino acid, like e.g. ß.-alanine, with a carboxylic acid, like e.g. lactic acid, glycine, or malic acid increases the stabilizing effect and can those beneficially be used as a second stabilizer in sense of the invention. It has been discovered that the carboxylic acid reacts with ß-amino acids to form amide structures which is deemed to be the reason for the enhanced stabilizing effect.

[0046] 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 .alpha.-hydroxy acids. It is also possible to use other organic compounds having a carboxylic functional group. In particular, the salts of carboxylic acids (carboxylate anion $-RCO_2^-$) can be used.

[0047] The electrolyte according to this invention may additionally comprise an inorganic stabilizer, preferably antimony. 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.

[0048] Yet in another embodiment of the invention the electrolyte may comprise three different stabilizers, one being a phosphine according to the general formula I, like e.g. PTA, a second one being a ß-amino acid, and a third one being an inorganic stabilizer, like e.g. antimony.

[0049] By the use of the inventive electrolyte a metal layer on a surface of a substrate is deposited, wherein the phosphorous content of the metal layer is 2-6%, 6-10% or >10.5%. The amount of phosphorous has a considerable effect on the properties of the metal layer. A high phosphorous content of the metal layer leads to improved properties, for example improved corrosion resistance and a lower phosphorous content for example improved hardness of the metal layer.

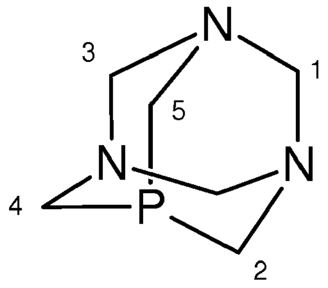
[0050] A further property of a metal layer according to the present invention is that it is very passive.

[0051] A further advantage of the metal layers according to the present invention is the good residual compressive stress.

[0052] Using a stabilizer according to the present invention, it is possible to yield metal layers having various phosphorus content: low phosphorus, 3-5% (crystalline); middle phosphorus, 5-7 (9) % (partially crystalline); high phosphorus, >10% (amorphous).

[0053] 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 iodite, potassium iodate, sodium iodite, sodium iodate, potassium chloride, potassium chlorate, sodium bromide, lithium chloride, lithium iodate or lithium chlorate.

[0054] 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 phosphaadamantane according to the general formula I



(Formula I)

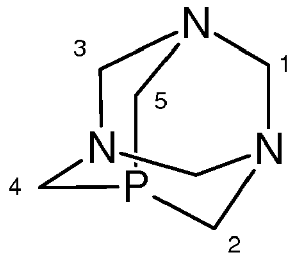
wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom.

[0055] 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.

[0056] According to another embodiment of the inventive method, the substrate is contacted with the electrolyte for a time between ≥ 1s and ≤ 480 min, preferably between ≥ 10s and ≤ 240 min.

[0057] 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.

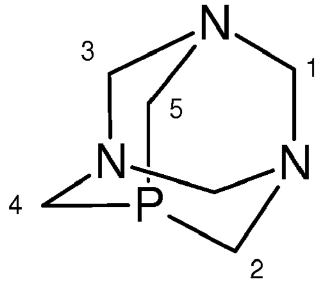
[0058] In preferred embodiments, the formulation of the invention contains ions of at least one metal of the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. As source for these metal ions salts of the metals are comprised in the electrolyte, e.g. metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbinate 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 0.4mol/L. As an accelerator 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 mmol/L and 0.1 mol/L, preferably, 5 mmol/L and 0.25 mol/L. As stabilizer the electrolyte comprises at least a phosphaadamantane according to the general formula I



(Formula I)

wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom. Said phosphadamantne is comprised within a range of ≥0.05 mg/L and ≤ 100 mg/L, preferably between ≥0.1 mg/L and ≤ 25 mg/L, most preferably between ≥0.5 mg/L and ≤ 10 mg/L. The use of a phosphaadamantane according to general formula I as stabilizer results in a more even deposition having less nodules.

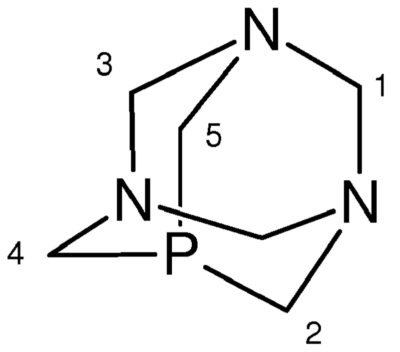
[0059] According to another embodiment of the invention, the formulation of the invention contains ions of at least one metal of the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. As source for these metal ions salts of the metals are comprised in the electrolyte, e.g. metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbinate 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 0.4mol/L. As an accelerator 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 mmol/L and 0.1 mol/L, preferably, 5 mmol/L and 0.25 mol/L. As stabilizer the electrolyte comprises at least a phosphaadamantane according to the general formula I



(Formula I)

wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom. Said phosphadamantne is comprised within a range of ≥0.05 mg/L and ≤ 100 mg/L, preferably between ≥0.1 mg/L and ≤ 25 mg/L, most preferably between ≥0.5 mg/L and ≤ 10 mg/L. As an additional stabilizer the electrolyte comprises at least one ß-amino acid having a pK_a-value within a range of 4 to 8, preferably within a range of 5 to 7. In particular, the electrolyte comprises at least one ß-amino acid of the group consisting of 3-amino propionic acid (ß-alanin), 3-aminobutyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (Taurin). The ß-amino acid is comprised in this 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 preferred 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.

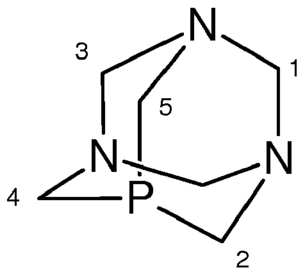
[0060] In another preferred embodiment of the invention the formulation of the invention contains ions of at least one metal of the group consisting of nickel, copper, cobalt, boron, silver, palladium and gold. As source for these metal ions salts of the metals are comprised in the electrolyte, e.g. metal chloride, metal sulfate, metal acetate, metal nitrate, metal propionate, metal formiate, metal oxalate, metal citrate, and metal ascorbinate 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 0.4mol/L. As an accelerator 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 mmol/L and 0.1 mol/L, preferably, 5 mmol/L and 0.25 mol/L. As stabilizer the electrolyte comprises at least a phosphaadamantane according to the general formula I



(Formula I)

wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom. Said phosphadamantne is comprised within a range of ≥0.05 mg/L and ≤ 100 mg/L, preferably between ≥0.1 mg/L and ≤ 25 mg/L, most preferably between ≥0.5 mg/L and ≤ 10 mg/L. As an additional stabilizer the electrolyte comprises antimony as an inorganic stabilizer. Antimony is 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. The antimony is added as water soluble salt, preferably as chloride, sulfate, acetate, nitrate, propionate, formiate, oxalate, citrate, ascorbinate, or a mixture of these.

[0061] 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 ascorbinate 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 0.4mol/L. As an accelerator 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 mmol/L and 0.1 mol/L, preferably, 5 mmol/L and 0.25 mol/L. As stabilizer the electrolyte comprises at least a phosphaadamantane according to the general formula I



(Formula I)

wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom. Said phosphadamantne is comprised within a range of ≥0.05 mg/L and ≤ 100 mg/L, preferably between ≥0.1 mg/L and ≤ 25 mg/L, most preferably between ≥0.5 mg/L and ≤ 10 mg/L. As an additional stabilizer the electrolyte comprises at least one ß-amino acid having a pK_a-value within a range of 4 to 8, preferably within a range of 5 to 7. In particular, the electrolyte comprises at least one ß-amino acid of the group consisting of 3-amino propionic acid (ß-alanin), 3-aminobutyric acid, 3-amino-4-methyl valeric acid and 2-aminoethane-sulfonic acid (Taurin). The ß-amino acid is comprised in this 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 preferred 200 mg/L to 400 mg/L. As a third stabilizer the electrolyte comprises antimony as an inorganic stabilizer. Antimony is 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. The antimony is added as water soluble salt, preferably as chloride, sulfate, acetate, nitrate, propionate, formiate, oxalate, citrate, ascorbinate, or a mixture of these.

[0062] In preferred embodiments, the formulation of the invention contains a carboxyl component. For example, the electrolyte formulation may contain a monocarboxylic, dicarboxylic, or tricarboxylic organic acid. This component can comprise an aryl carboxylic acid, an aliphatic carboxylic acid, or a heterocyclic carboxylic acid. Among the suitable aliphatic carboxylic acids are fatty acids, α-hydroxycarboxylic acids, including α-hydroxy dicarboxylic acids particularly C_1 to C_4, α-ß-unsaturated carboxylic acids, particularly C_1 to C_4 and especially acrylic.

EXAMPLE 1:

[0063] In a preferred embodiment of the invention the electrolyte according to the present invention comprises:

13.03 g/l nickel sulfate;
1.925 mg/L potassium iodide
17.27 g/l lactic acid;
5.94 g/l malic acid;
40.2 g/l sodium hypophosphite;
9.81 g/l sodium hydroxide; and
1.00 mg/L PTA
wherein the pH is in a range of pH 4 to pH 7.

Example 2:

[0064] 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 tertahydrat;
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
2.0 mg/l PTA
2

wherein the pH is in a range of pH 4 to pH 5 at a temperature between 80 and 94°C an aluminum panel was plated in an electrolyte with the above mentioned composition. The aluminum was treated according to the standard pre-treatment cycle before plating in the electroless 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:

[0065] In another preferred embodiment of the invention the electrolyte according to the present invention comprises:

8.8 g/L nickel acetate tertahydrat;
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
0.5 mg/L PTA
15 mg/L potassium antimony 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:

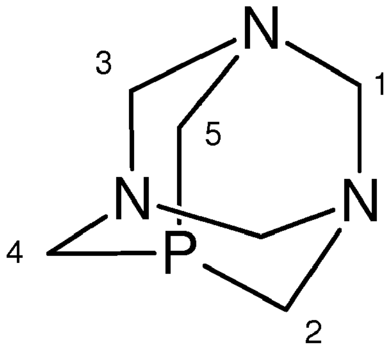
[0066] In another preferred embodiment of the invention the electrolyte according to the present invention comprises:

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 ß-alanin
15.5 g/l sodium hydroxide solution, 33 % by weight;
20 g/L sodium acetat
35 g/L sodium hypophosphite dihydrate
0.5 mg/l PTA
18 mg/L potassium antimony 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 phosphorous.

Claims

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 as stabilizer a phosphaadamantane according to the general formula I



(Formula I)

wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom.

2. The aqueous electrolyte composition according to claim 1, wherein the phosphaadamantane is comprised in a concentration between ≥0.05 mg/L and ≤ 100 mg/L, preferably between ≥0.1 mg/L and ≤ 25 mg/L, most preferably between ≥0.5 mg/L and ≤ 10 mg/L.

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

4. The aqueous electrolyte composition according to any of the preceding claims, wherein accelerator is at least one accelerator of the group consisting of saccharine, hydantoin, rhodanine, carbamide and carbamide derivates.

5. The aqueous electrolyte composition according to any of the preceding claims, wherein the electrolyte is essentially free of inorganic stabilizers, specifically free of lead, bismuth, zinc and/or tin.

6. The aqueous electrolyte composition according to any of the preceding claims, 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 any of the preceding claims, 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, aromatic 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.

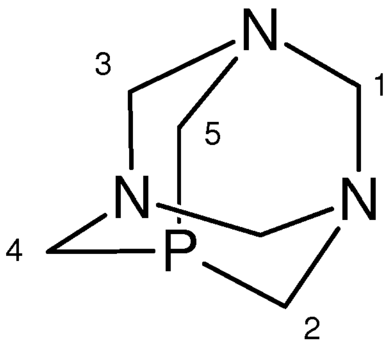
9. The aqueous electrolyte composition according to any of the preceding claims, wherein the pH-value of the composition is in the range of between pH 4 and pH 7.

10. The aqueous electrolyte composition according to any of the preceding claims, 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 any of the preceding claims, wherein the complexing agent is at least one compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic 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 phosphaadamantane according to the general formula I



(Formula I)

wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom.

13. The method according to claim 12, wherein the substrate is contacted with the electrolyte at a temperature within the range of between ≥20 °C and ≤ 85 °C, preferably between ≥25 °C and ≤ 70 °C.

14. The method according to any of the claims 11 and 12, wherein the substrate is contacted with the electrolyte for a time between ≥ 1s and ≤ 180 min, preferably between ≥ 10s and ≤ 60 min.

15. Use of 1,3,5-Triaza-7-phosphatricyclo[3.3.1.1]decane (PTA) as stabilizer in an electrolyte composition for the deposition of a metal layer on a substrate surface.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 18 9465

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 138 803 A2 (INFINEON TECHNOLOGIES AG [DE]) 4 October 2001 (2001-10-04) * examples 1, 5 * * paragraphs [0022] - [0025] * -----	1-3,5,6, 9,10, 12-15	INV. C23C18/36 C23C18/40 C23C18/44 ADD. C23C18/50
A,D	JP 2005 290415 A (OKUNO CHEM IND CO) 20 October 2005 (2005-10-20) * abstract * * example 1 * * compound 1 * -----	1,12	
A	US 6 183 545 B1 (OKUHAMA YOSHIAKI [JP] ET AL) 6 February 2001 (2001-02-06) * abstract * * compound 1 * -----	1,12	

TECHNICAL FIELDS SEARCHED (IPC)
C23C

~~The present search report has been drawn up for all claims~~

1

Place of search	Date of completion of the search	Examiner
The Hague	1 April 2016	Lange, Ronny

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

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Application Number
EP 15 18 9465

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

2, 3, 5, 6, 9, 10, 12-15(completely); 1(partially)

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 15 18 9465

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2, 3, 5, 6, 9, 10, 12-15(completely); 1(partially)

Inventive concept I regards 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 as stabilizer a phosphaadamantane according to the general formula I as defined in claim 1 of the present application, wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom, wherein the phosphaadamantane is comprised in a concentration between >0.05 mg/L and < 100 mg/L, preferably between >0.1 mg/L and < 25 mg/L, most preferably between >0.5 mg/L and < 10 mg/L.
Inventive concept also concerns a method for the electroless deposition of a metal layer on a substrate comprising the steps of contacting the substrate to be plated with said aqueous electrolyte composition.
Moreover inventive concept I also regards the use of 1,3,5-Triaza-7-phosphatricyclo[3.3.1.1]decane (PTA) as stabilizer in an electrolyte composition for the deposition of a metal layer on a substrate surface.

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2. claims: 4(completely); 1(partially)

Inventive concept II regards 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 as stabilizer a phosphaadamantane according to the general formula I, as defined in claim 1 of the present application, wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom, wherein the accelerator is at least one accelerator of the group consisting of saccharine, hydantoin, rhodanine, carbamide and carbamide derivates.

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3. claims: 7, 8(completely); 1(partially)

Inventive concept III regards an aqueous electrolyte composition for the electroless deposition of a metal layer

LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 15 18 9465

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

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 phosphaadamantane according to the general formula I, as defined in claim 1 of the present application, wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom, further comprising at least one additional carboxylic acid and/or at least one salt of a carboxylic acid
1.2 and wherein preferably 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, tricarboxylic acids, straight chained carboxylic acids, heterocyclic carboxylic acids, saturated carboxylic acids, unsaturated carboxylic acids, and ?-hydroxy acids.

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4. claims: 11(completely); 1(partially)

Inventive concept IV regards 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 as stabilizer a phosphaadamantane according to the general formula I, as defined in claim 1 of the present application, wherein the hydrogen atoms on carbon atom 1 to 6 may independently from each other substituted by a moiety of the group consisting of F, Cl, Br, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, and an alcohol group having 1 to 6 carbon atom, wherein the complexing agent is at least one compound of the group consisting of 2-hydroxy propionic acid, propanedioic acid (malonic acid), EDTA and amino acetic acid.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 15 18 9465

01-04-2016

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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- JP 2005290415 A **[0012]**
- CN 101348927 A **[0013]**