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(71) Applicant: **Atotech Deutschland GmbH**
10553 Berlin (DE)

(72) Inventors:
- **Tuna, Kadir**
  10553 Berlin (DE)
- **Pugliesi Garcia, Thiago**
  10553 Berlin (DE)

(74) Representative: **Atotech Deutschland GmbH**
Intellectual Property
Erasmusstraße 20
10553 Berlin (DE)

(54) ELECTROLESS NICKEL OR COBALT PLATING SOLUTION

(57) An electroless nickel or cobalt plating solution, comprising
- nickel ions or cobalt ions,
- Ti^{3+} ions as reducing agent for reducing said nickel ions and cobalt ions,
- at least one accelerator selected from the group consisting of sulfites, dithionites, thiosulfates, tetrathionates, polythionates, disulfites, sulfides, disulfide, polysulfide, elemental sulfur and mixtures thereof; and
- one or more than one complexing agent,

wherein the pH value of the plating solution is from 5 to 10.5.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to an electroless nickel or cobalt plating solution, a method for electroless plating of a nickel or cobalt deposit, preferably a layer, on a substrate, and a respective electronic article comprising such a deposit and layer, respectively.

BACKGROUND OF THE INVENTION

[0002] Nickel and cobalt layers are widely used in electronic devices. Such layers and methods for producing them are known from the prior art. Nickel and cobalt layers are often used as barrier layers, to separate a copper layer from a tin layer or a gold layer. Migration of copper into the tin layer or gold layer is prevented by such a barrier layer which is located in between these layers.

[0003] Sviridov et al., J. Phys. Chem 1996, 100, 19632-19635 describe the use of Ti(III) complexes to reduce nickel and cobalt.

[0004] US 2015/0307993 A1 discloses a solution for electroless deposition of cobalt, comprising a reducing agent of Ti^{3+} ions and Co^{2+} ions. Pure cobalt layers are obtained and the solution is free of phosphorus-containing compounds.

[0005] Nakao et al., Surface and Coatings Technology, 169-170 (2003) 132-134 disclose a pure nickel film containing no phosphorus which was obtained from an electroless plating solution. The solution uses a titanium ion redox system. Two kinds of complexing agent were used, nitriloacetic acid and citric acid.

[0006] US 2012/0104331 A1 discloses a deposition solution to deposit metals and metal alloys such as for fabrication of electronic devices. According to one embodiment, the deposition solution comprises metal ions and a pH adjustor. The pH adjustor comprises a functional group having a general formula $(R_1R_2N)(R_3R_4N)C\text{-}N\text{-}R_5$ where: N is nitrogen; C is carbon; and R_1, R_2, R_3, R_4, and R_5 are the same or different and represent hydrogen, alkyl group, aryl group, or alkylaryl group. Possible metals to be deposited are nickel or cobalt.

[0007] Typically, conventional plating solutions show a plating behavior that starts with a very high plating rate which then decreases significantly over time of use. In some cases, the plating rates gives a sharp peak within the first minutes to then drop all the quicker. Such behavior is highly undesired as it makes it very difficult to control the plating outcome such as tin deposit homogeneity and thickness.

OBJECTIVE OF THE INVENTION

[0008] An objective of the present invention was to provide an electroless plating solution and a respective plating method which are suitable to produce highly pure nickel or cobalt layers. It was furthermore an objective to deposit cobalt and nickel, respectively, selectively on a metal without simultaneous metal plating on a non-conductive material, in particular selectively on copper without further activation of said copper. Furthermore, an increased/high deposition rate and increased stability of the electroless plating solution are desired.

[0009] It is a further objective of the present invention to overcome the shortcomings of the prior art. It is another objective to provide a plating solution having an improved plating rate compared to electroless plating solutions known from the prior art.

[0010] It is a further objective to provide a plating solution having a constant plating rate over time.

[0011] It is a further objective to provide a plating solution (sufficiently) stable against plate-out (e.g. for at least 4 h after make-up or during use).

[0012] It is a further objective to reduce the number of compounds and/or to reduce the number of compounds in the plating solution.

SUMMARY OF THE INVENTION

[0013] The present invention provides an electroless nickel or cobalt plating solution, a method for electroless plating, and an electronic article according to the independent claims and solves at least one, preferably all of above mentioned objectives. Further embodiments are disclosed in dependent claims and this description.

[0014] The present invention provides an electroless nickel or cobalt plating solution, comprising

- nickel ions or cobalt ions,
- Ti^{3+} ions as reducing agent for reducing said nickel ions and cobalt ions,
- at least one accelerator selected from the group consisting of sulfites, dithionites, thiosulfates, tetrathionates, polythionates, disulfites, sulfides, disulfide, polysulfide, elemental sulfur and mixtures thereof; and

- one or more than one complexing agent,

wherein the pH value of the plating solution is from 5 to 10.5.

[0015] The invention also provides a method for electroless plating of a nickel or a cobalt deposit on a substrate, the method comprising contacting the substrate with the electroless plating solution according to the present invention such that the nickel or cobalt deposit is electrolessly plated on the substrate.

[0016] The invention also provides an electronic article, comprising a nickel layer or a cobalt layer, wherein the nickel or the cobalt layer is obtainable or obtained from an electroless plating solution of the present invention, or obtained according to a method of the present invention, wherein the nickel layer or the cobalt layer comprises 99 wt% or more nickel or cobalt, based on the total weight of the nickel layer or the cobalt layer,
wherein the article comprises a copper layer, and wherein the nickel layer or the cobalt layer is disposed on the copper layer.

[0017] One or more of the following advantages are reached with the present invention in the general embodiment or in specific embodiments:

- highly pure cobalt or nickel deposits, preferably comprising 99 wt% or more, more preferably 99,9 wt% or more, cobalt or nickel can be produced with the electroless plating solution of the present invention.

- The plating solution of the invention allows a high deposition rate. As shown in the examples below it has surprisingly been found that with plating solutions according to the present invention significantly higher plating rates can be achieved.

- The plating solution of the invention allows selective deposition, particularly on copper.

- The plating solution of the invention shows high stability.

- The plating solution allows direct deposition of nickel or cobalt deposits on copper, without any previous activation step for activation of copper.

[0018] Further advantages are mentioned in the following description.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Where the term "comprising" is used in the present description and claims, it does not exclude other elements. For the purposes of the present invention, the term "consisting of" is considered to be a preferred embodiment of the term "comprising". If hereinafter a group is defined to comprise at least a certain number of embodiments or features, this is also to be understood to disclose a group which preferably consists only of these embodiments or features.

[0020] Where an indefinite or definite article is used when referring to a singular noun, e.g. "a", "an" or "the", this includes a plural of that noun unless something else is specifically stated. The terms "about" or "approximately" in the context of the present invention denotes an interval of accuracy that the person skilled in the art will understand to still ensure the technical effect of the feature in question.

[0021] If a layer is in this description named after a metal, like a gold layer, a tin layer, a nickel layer or a cobalt layer, this term also encompasses alloys comprising the respective metal as main component, if not otherwise mentioned.

[0022] The plating solution of the present invention is a nickel plating solution or a cobalt plating solution. Most preferably, if the plating solution of the present invention is a nickel plating solution, the plating solution does not comprise cobalt ions. If the plating solution of the present invention is a cobalt plating solution, the plating solution most preferably does not comprise nickel ions. This means that the present invention is in one aspect directed to a nickel plating solution only, and in another aspect directed to a cobalt plating solution only.

[0023] Preferred is a plating solution of the present invention, wherein the nickel ions comprise Ni^{2+} ions, preferably are (only) Ni^{2+} ions.

[0024] Preferred is a plating solution of the present invention, wherein the cobalt ions comprise Co^{2+} ions, preferably are (only) Co^{2+} ions.

Metal to be deposited from the plating solution:

[0025] In rare cases, further metals to be reduced and co-deposited are present in the nickel plating solution or the cobalt plating solution of the present invention, which is very less preferred. Preferably, nickel or cobalt is the main metal component in the solution, most preferably the only ones to be deposited. If one or more further metals to be reduced and co-deposited are present, nickel or cobalt, respectively, preferably constitute 95 mol% or more of all metals to be reduced and deposited in the plating solution. Titanium as reducing agent is excluded from this consideration.

[0026] In a preferred embodiment, no transition metals other than cobalt or nickel are present, except titanium as reducing agent, more preferably, no metals other than cobalt or nickel, except titanium as reducing agent, except lead, and except an alkaline and/or an alkaline earth metal are present.

[0027] The presence of lead is preferred if the plating solution is a nickel plating solution. Thus, if the plating solution is a cobalt plating solution, the solution preferably does not comprise lead.

[0028] Preferably, the plating solution of the present invention typically does not comprise tungsten, more preferably the plating solution of the present invention typically does not comprise antimony, arsenic, cadmium, chromium, copper, gold, indium, iridium, iron, manganese, molybdenum, osmium, palladium, platinum, rhodium, ruthenium, silver, tungsten, zinc, or mixtures thereof.

[0029] In particular, the plating solution of the present invention does not comprise tin.

[0030] As a result, in a main aspect of the present invention, the plating solution of the present invention is not an electroless nickel alloy plating solution or an electroless cobalt alloy plating solution.

[0031] However, in a rare number of applications, a plating solution of the present invention is preferred, wherein the plating solution comprises iron ions and/or molybdenum ions to be reduced and co-deposited with nickel and cobalt, respectively.

Reducing agent:

[0032] Ti^{3+} ions are used as a reducing agent for reducing the cobalt ions and nickel ions.

[0033] The plating solution of the present invention preferably additionally comprises Ti^{4+} ions, wherein the Ti^{4+} ions are present in a lower amount than the Ti^{3+} ions. Preferably, the Ti^{3+} ions are produced according to a method disclosed in WO 2013/182478 A2, which is incorporated by reference in its entirety in this disclosure. WO 2013/182478 A2 discloses a regeneration device which is preferably used to reduce Ti^{4+} ions to Ti^{3+} ions.

[0034] Preferred is a plating solution of the present invention, wherein titanium ions are present in a total concentration representing 95 mol% or more of all reducing agents for the nickel ions or cobalt ions in the plating solution, preferably 97 mol% or more, more preferably 98 mol% or more, most preferably 99 mol% or more.

[0035] The plating solution of the present invention preferably does not comprise any further reducing agent than titanium ions.

[0036] Preferably, the plating solution of the present invention does not comprise any reducing agent selected from the following group of compounds or classes of compounds:

- boranes, preferably alkyl, dialkyl and trialkyl amine boranes of the general formula: $R_nNH_{3-n}BH_3$, wherein in R_n, R denotes an identical or different alkyl group and n is the number of such alkyl groups attached to the nitrogen in the amine borane, wherein n is 0, 1, 2, or 3, more preferably including dimethylamine borane,
- hypophosphorous acid and hypophosphites, preferably including hypophosphite dimethylamine borane,
- borohydride,
- hydrazine,
- aldehydes,
- ascorbic acid and ascorbates,
- thiosulfites,
- manganese(II)-ions, and
- copper(I)-ions.

Accelerator:

[0037] The nickel or cobalt plating solution according to the present invention thus comprises at least one accelerator selected from the group consisting of sulfites, dithionites, thiosulfates, tetrathionates, polythionates, disulfites, sulfides, disulfide, polysulfide, elemental sulfur and mixtures thereof. Own research has shown that a) sulfite and/or b) a dithionite,

c) thiosulfate, d) tetrathionate, e) polythionate, f) disulfite, g) elemental sulfur and/or h) sulfide, disulfide, polysulfide serves as accelerators to improve the nickel or cobalt plating rate.

[0038] In one embodiment of the invention, the at least one accelerator is inorganic. If two or more accelerators are selected they preferably are all inorganic.

[0039] Preferable sources of sulfites, dithionites, thiosulfates, tetrathionates, polythionates, sulfide, disulfide, polysulfide and disulfites are the respective salts such as alkaline salts (e.g. sodium sulfite, potassium sulfite, sodium bisulfite), earth alkaline metal salts (e.g. magnesium sulfite, calcium sulfite), ammonium salts and mixtures of the aforementioned. Preferably the at least one accelerator is water soluble and the used counter ions as sodium or potassium will not co-deposited.

[0040] For the present invention, the term polythionates refers to oxoanions with the formula $S_n(SO_3)_2^{2-}$ with $n = 0, 1, 3, 4, 5, 6, 7$ or ≥ 8.

[0041] Dithionites, thiosulfates, tetrathionates, polythionates, disulfites, disulfide, polysulfide, and elemental sulfur are compounds containing at least one S-S moiety.

[0042] A nickel or cobalt plating solution according to the present invention is preferred, wherein the accelerator(s) is/are selected from the group consisting of alkaline metal sulfites, alkaline metal hydrogen sulfites, alkaline earth metal sulfites, alkaline earth metal hydrogen sulfites, ammonium sulfite, ammonium hydrogen sulfite, alkaline metal dithionites, alkaline metal hydrogen dithionites, alkaline earth met-al dithionites, alkaline earth metal hydrogen dithionites, alkaline metal thiosulfates, alkaline metal hydrogen thiosulfates, alkaline earth metal thiosulfates, alkaline earth metal hydrogen thiosulfates, ammonium thiosulfate, ammonium hydrogen thiosulfate, alkaline metal tetrathionates, alkaline metal hydrogen tetrathionates, alkaline earth metal tetrathionates, alkaline earth metal hydrogen tetrathionates, ammonium tetrathionates, ammonium hydrogen tetrathionate, alkaline metal polythionates, alkaline metal hydrogen polythionates, alkaline earth metal polythionates, alkaline earth metal hydrogen polythionates, ammonium polythionates, ammonium hydrogen polythionate, alkaline metal disulfites, alkaline metal hydrogen disulfites, alkaline earth metal disulfites, alkaline earth metal hydrogen disulfites, ammonium disulfites, ammonium hydrogen disulfite, alkaline metal sulfide, alkaline metal disulfide, alkaline metal polysulfide, ammonium sulfide and cyclo-octasulfur (S8).

[0043] A nickel or cobalt plating solution according to the present invention is further preferred, wherein the accelerator(s) is/are selected from the group consisting of sodium sulfite, potassium sulfite, sodium hydrogen sulfite (sodium bisulfite), potassium hydrogen sulfite (potassium bisulfite), calcium dihydrogen disulfit (calcium bisulfite), magnesium dihydrogen disulfit (magnesium bisulfite), ammonium sulfite, ammonium hydrogen sulfite, sodium dithionite, potassium dithionite, calcium dithionite, magnesium dithionite, sodium thiosulfate, sodium hydrogen thiosulfate, potassium thiosulfate, calcium thiosulfate, potassium thiosulfate, barium thiosulfate, ammonium thiosulfate, ammonium hydrogen thiosulfate, sodium tetrathionate, potassium tetrathionate, ammonium tetrathionate, ammonium hydrogen tetrathionate, barium tetrathionate, sodium polythionate, potassium polythionate, ammonium polythionate, ammonium hydrogen polythionate, sodium disulfite, potassium disulfite, ammonium disulfite, ammonium hydrogen disulfite, sodium or potassium sulfide, sodium or potassium disulfide, sodium or potassium polysulfide, ammonium sulfide and particulate cyclo-octasulfur (Ss).

[0044] In one embodiment, if the selected accelerators comprise inorganic sulfides as alkaline metal sulfide, the at least one pH adjuster is selected from the group consisting of ammonia or an inorganic ammonia derivate as ammonium hydroxide, ammonium chloride.

[0045] Sodium dithionite and/or sodium sulfite and/or sodium thiosulfate and/or sodium tetrathionate and/or sodium polythionate and/or sodium disulfite are used particularly preferably according to the invention. In case elemental sulfur is used in nickel or cobalt plating solutions according to the present invention, it is preferred that sulfur in its cyclo-Ss configuration is used. It is particularly preferred that the sulfur is present as sulfur particles, especially sulfur particles with an aerodynamic diameter determined via an aerodynamic particle sizer (APS) below 300 nm, preferably below 200 nm, more preferably below 100 nm. Although not wishing to be bound to any particular theory, it is believed sulfur converts to two different compounds, namely sulfite and sulfide.

[0046] In an alternative embodiment, the at least one accelerator is organic.

[0047] A preferred organic accelerator is thioacetamide.

[0048] Preferably, the molar ratio of all the accelerators used according to the present invention to the nickel ions or cobalt ions is at least 1 to 300. More preferably, the molar ratio of all accelerators used according to the present invention to the nickel ions or cobalt ions ranges from 1 : 200 to 1 : 5.000, even more preferably from 1 : 300 to 1 : 4.000, still even more preferably 1 : 500 to 1 : 1.500, most preferably from 1 : 550 to 1 : 1.000.

[0049] The total concentration of sulfites, dithionites, thiosulfates, tetrathionates, polythionates, disulfites, sulfides, disulfide, polysulfide and sulfur in the inventive electroless nickel or cobalt plating solution preferably ranges from 0.0008 to 0.80 mmol/L, more preferably from 0.008 to 0.40 mmol/L and even more preferably from 0.04 to 0.16 mmol/L.

[0050] Preferably, the total amount by weight of the accelerator(s) in the nickel or cobalt plating solution ranges from 0.01 to 300 ppm, preferably from 0.1 to 200 ppm, and more preferably from 0.5 to 175 ppm.

[0051] Preferably, the inventive nickel or cobalt plating solution is free of organic sulfites. The inventors have found that these compounds occasionally have a negative influence on the plating rate and increase the loss of plating rate over time and during use of a nickel or cobalt plating solution containing such organic sulfites.

[0052] An electroless nickel or cobalt plating solution according to the invention is preferred comprising nickel sulfate (hexahydrate) (or cobalt(II) chloride (hexahydrate), respectively), titanium (III) chloride and at least one accelerator selected from the group consisting of sodium sulfite, sodium dithionite, sodium thiosulfate, ammonium sulfide and mixtures thereof.

Complexing agent:

[0053] The plating solution of the present invention comprises one or more than one complexing agent independently selected from the group consisting of

- an organic phosphonic acid compound, its salts and esters,
- an organic polyphosphoric acid compound, its salts and esters,
- an inorganic polyphosphoric acid compound, its salts and esters, and
- an organic carboxylic acid compound, its salts and esters.

[0054] In a preferred embodiment, the plating solution of the present invention comprises one or more than one complexing agent independently selected from the group consisting of

- an organic phosphonic acid compound, its salts and esters,
- an organic polyphosphoric acid compound, its salts and esters, and
- an inorganic polyphosphoric acid compound, its salts and esters.

[0055] An organic phosphonic acid compound is a compound comprising at least one (preferably more than one, more preferably two or more) $\sim$C-PO(OH)$_2$ group. A salt or an ester thereof is also called a "phosphonate". For example, an ester in the context of the present invention comprises the structure $\sim$C-PO(OR)$_2$, wherein R is preferably an organic residue, more preferably independently alkyl or aryl.

[0056] Preferred is a plating solution of the present invention, with the proviso

- that the plating solution comprises at least one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters, preferably
- that the one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters is the only complexing agent in the plating solution.

[0057] Preferred is a plating solution of the present invention, wherein the organic phosphonic acid compound, its salts and esters, comprise 2, 3, 4, 5 or more phosphonate moieties, preferably 3, 4, 5 or more.

[0058] A phosphonate moiety in the context of the present invention includes above mentioned $\sim$C-PO(OH)$_2$ group, salts and esters thereof.

[0059] Preferred is a plating solution of the present invention, wherein the organic phosphonic acid compound, its salts and esters, comprise one two, three or more than three tertiary nitrogen atoms and/or one or more than one hydroxyl group not being connected to phosphorous. Such compounds are in particular beneficial in the plating solution of the present invention because they provide a strong complexation and stabilization, which prevents outplating and precipitation, even provided in comparatively low concentrations. These compounds are thermally stable, which is a great advantage over e.g. pyrophosphate, which decomposes under heat faster than said organic phosphonic acid compound, its salts and esters, most preferably than said organic phosphonic acid compound and its salts. Own experiments have shown that such a complexing agent has a very positive effect on a respective plating solution. Typically, the concentration of cobalt and nickel, respectively, is significantly reduced, as well as the concentration of complexing agent and Ti^{3+} ions, wherein simultaneously a very high deposition rate is maintained, e.g. compared to an inorganic polyphosphoric acid compound, its salts and esters, such as pyrophosphate. In the context of the present invention, above mentioned "hydroxyl group not being connected to phosphorous" preferably includes its deprotonated form (e.g. in a carboxylate group).

[0060] Preferred is a plating solution of the present invention, wherein the organic phosphonic acid compound, its salts and esters are selected from the group consisting of 1-Hydroxyethane 1,1-diphosphonic acid (HEDP, CAS No.

2809-21-4), its salts and esters, Aminotris(methylenephosphonic acid) (ATMP, CAS No. 6419-19-8), its salts and esters, Diethylenetriamine penta(methylene phosphonic acid) (DTPMP, CAS No. of sodium salt: 22042-96-2), its salts and esters, Ethylenediamine tetra(methylenephosphonic acid) (EDTMP, CAS No. of sodium salt: 15142-96-8), its salts and esters, Phosphonobutane tricarboxylic acid (PBTC, CAS No. 37971-36-1), its salts and esters, Hexanediamine tetra(methylenephosphonic acid) (HDTMP, CAS No. 23605-74-5), its salts and esters,
Hydroxyethylamino di(methylenephosphonic acid) (HEMPA, CAS No. 5995-42-6), its salts and esters, and
Bis(hexamethylene) triamine-pentakis(methylphosphonic acid) (BHMTMP, CAS No. 34690-00-1), its salts and esters.

[0061] In some cases, the plating solution of the present invention preferably comprises an organic polyphosphoric acid compound, its salts and/or esters, and/or an inorganic polyphosphoric acid compound, its salts and/or esters. A polyphosphoric acid compound is characterized by having a moiety comprising a phosphorous-oxygen-phosphorous arrangement, each phosphorous atom belonging to a phospho-building unit.

[0062] Preferred is a plating solution of the present invention, wherein the organic and/or inorganic polyphosphoric acid compound, its salts and esters, comprise 2 to 10 phospho-building units linked together, preferably 2 to 5, more preferably 2 to 3.

[0063] The inorganic polyphosphoric acid compound preferably comprises, more preferably is, a diphosphoric acid (also called pyrophosphoric acid), a tri- phosphoric acid, a tetra phosphoric acid, or even a higher phosphoric acid. A preferred salt of an inorganic polyphosphoric acid compound is di-phosphate (also called pyrophosphate), tri-phosphate, and tetra-phosphate, most preferred is pyrophosphate. In only rare cases, higher polyphosphates are employed in the plating solution of the present invention.

[0064] In some cases a plating solution of the present invention is preferred with the proviso that the plating solution does not comprise pyrophosphate (preferably pyrophosphate and pyrophosphonic acid), preferably does not comprise pyrophosphate (preferably pyrophosphate and pyrophosphonic acid) but one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters. This is in some cases preferred because pyrophosphate shows some instability over time under elevated temperatures. This is not observed with said organic phosphonic acid compound, its salts and esters, preferably not with said organic phosphonic acid compound and its salts.

[0065] An ester of an inorganic polyphosphoric acid compound is preferably selected from the group consisting of diphosphate ester and triphosphate ester. A non-limiting preferred example is a compound having the formula
$R\text{-}O\text{-}([(PO_2)\text{-}O\text{-}]_nPO_3)^{(2+n)-}$, wherein n is an integer and wherein R is an organic moiety, preferably alkyl or aryl. For example, if n is 1, the formula is $R\text{-}O\text{-}((PO_2)\text{-}O\text{-}PO_3)^{3-}$.

[0066] In some cases a plating solution of the present invention is preferred, wherein the plating solution only comprises phosphorous-containing complexing agents, including the complexing agents as defined above for the plating solution of the present invention, preferably comprises only phosphorous-containing complexing agents as defined for the plating solution of the present invention.

[0067] The plating solution of the present invention more preferably does not comprise any other complexing agent than mentioned before. Thus, preferred is a plating solution of the present invention, wherein the one or more than one complexing agent is independently only selected from the group consisting of

- an organic phosphonic acid compound, its salts and esters,
- an organic polyphosphoric acid compound, its salts and esters, and
- an inorganic polyphosphoric acid compound, its salts and esters,

preferably
from the group consisting of

- an organic phosphonic acid compound, its salts and esters, and
- an inorganic polyphosphoric acid compound, its salts and esters.

[0068] Preferred is a plating solution of the present invention, wherein the plating solution does not comprise a complexing agent selected from the following group of compounds or classes of compounds:

- carboxylic acids and salts thereof, most preferably tartaric acid, and tartrate,
- hydroxycarboxylic acids and salts thereof,
- ethylenediaminetetraacetic acid and salts thereof,
- amino acids, and salts thereof, preferably glycine and its salts,
- phosphonic acid (H_3PO_3) and salts thereof, and
- phytic acid and salts thereof.

[0069] Very preferred, the plating solution of the present invention does not comprise phosphonic acid (H_3PO_3), preferably does not comprise phosphonic acid (H_3PO_3) and pyrophosphonic acid.

Molar ratios of components in the plating solution:

[0070] In a preferred embodiment of the present invention, a molar ratio of the complexing agent to the Ti^{3+} ions is 1.5 : 1 or higher, preferably 1.7 : 1 or higher, most preferably is in a range from 1.9 : 1 to 3 : 1.

[0071] This in particular applies if the one or more than one complexing agent independently is only selected from the group consisting of

- an organic phosphonic acid compound, its salts and esters,
- an organic polyphosphoric acid compound, its salts and esters, and
- an inorganic polyphosphoric acid compound, its salts and esters.

[0072] Another preferred upper limit is 20 : 1, more preferably 16 : 1, most preferably 14 : 1, most preferably if the one or more than one complexing agent independently is only selected from the group consisting of an inorganic polyphosphoric acid compound, its salts and esters, even most preferably is pyrophosphate.

[0073] Most preferred is a plating solution of the present invention, wherein a molar ratio of the complexing agent to the Ti^{3+} ions is 1.5 : 1 or higher, preferably 1.7 : 1 or higher, most preferably is in a range from 1.9 : 1 to 3 : 1, and the one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters is the only complexing agent in the plating solution of the present invention. Such a molar ratio is in particular preferred because the Ti^{3+} ions are sufficiently stabilized against oxidation, e.g. by ambient air although the molar ratio is comparatively low. This furthermore stabilizes the entire plating solution of the present invention.

[0074] In contrast, a plating solution of the present invention is preferred, wherein the molar ratio of the complexing agent to the Ti^{3+} ions is 5 : 1 or higher, preferably 8 : 1 or higher, most preferably is in a range from 10 : 1 to 14 : 1, and the one or more than one complexing agent independently selected from the group consisting of an inorganic polyphosphoric acid compound, its salts and esters is the only complexing agent in the plating solution of the present invention.

[0075] Preferred is a plating solution of the present invention, wherein a molar ratio of the nickel ions or the cobalt ions to the Ti^{3+} ions is in a range from 1 : 3 - 5 : 1, preferably in a range from 1 : 2.5 - 4 : 1, more preferably in a range from 1 : 2 - 3 : 1, even more preferably in a range from 1 : 2 to 2 : 1.

[0076] Preferred is a plating solution of the present invention, wherein a molar ratio of complexing agent, a complexing agent preferably as described above as being preferred, to nickel ions or cobalt ions is 3 : 1 or higher, preferably is 4 : 1 or higher, more preferably is in a range from 4 : 1 - 7 : 1, more preferably is in a range from 4 : 1 - 6 : 1. In some cases a preferred upper limit is 10 : 1. The aforementioned molar ratios ensure that the nickel and cobalt ions, respectively, are sufficiently complexed to avoid outplating, most preferably at elevated temperatures as preferably used in the method of the present invention (see text below). Furthermore, these molar ranges provide a very good shelf-life of the plating solution of the present invention.

[0077] In some cases a plating solution of the present invention is preferred, wherein a molar ratio of the one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters to nickel ions or cobalt ions is in a range from 4 : 1 to 5 : 1, with the proviso that said complexing agent is the only complexing agent in the plating solution of the present invention.

Concentrations of components:

[0078] In an embodiment of the plating solution of the present invention, preferred is a concentration of the nickel ions or the cobalt ions in a range from 0.01 - 0.3 mol/L, preferably in a range from 0.015 - 0.2 mol/L, more preferably in a range from 0.02 - 0.1 mol/L, even more preferably in a range from 0.025 - 0.05 mol/L. If the concentration is in the range from 0.01 - 0.3 mol/L an outplating is typically fully avoided, even under elevated temperatures. An excellent stability of the plating solution is obtained if the concentration is in the above mentioned preferred ranges, even over a long plating time.

[0079] In an embodiment of the plating solution of the present invention, preferred is a concentration of the Ti^{3+} ions in a range from 0.03 - 0.2 mol/L, preferably in a range from 0.03 - 0.1 mol/L. If the concentration is significantly below 0.03 mol/L in a number of cases an insufficient/incomplete plating is observed. However, if the concentration is significantly above 0.2 mol/L in some cases an undesired instability of the plating solution is observed.

[0080] In an embodiment of the plating solution of the present invention, preferred is a concentration of the one or more than one complexing agent in a range from 0.03 - 2.0 mol/L, preferably in a range from 0.05 - 1.5 mol/L, more preferably in a range from 0.08 - 1.1 mol/L. The concentration is preferably the total concentration. An optimal stability of the plating solution of the present invention is achieved if the concentration is within the above mentioned concentration ranges, in particular within the preferred concentration ranges. By this a sufficient amount of complexing agent is provided for complexing the nickel or cobalt ions and for stabilizing the Ti^{3+} ions. This advantageously means that with the same complexing agent the metal to be plated and the reducing agent can be stabilized. This is a great advantage of the plating solution of the present invention. It furthermore reduces the number of different compounds in the plating solution and alleviated the replenishment of complexing agent. This also applies to the following preferred concentrations.

[0081] Even more preferred is in some cases a plating solution of the present invention, wherein a concentration of the complexing agent is in a range from 0.03 - 1.0 mol/L, preferably in a range from 0.05 - 0.8 mol/L, more preferably in a range from 0.08 - 0.5 mol/L, even more preferably in a range from 0.1 - 0.3 mol/L, most preferably in a range from 0.1 - 0.2 mol/L.

[0082] Most preferred is a plating solution of the present invention, wherein a concentration of all complexing agents independently selected from the group consisting of an organic phosphonic acid compound (preferably as described above as being preferred), its salts and esters, is in a range from 0.03 - 1.0 mol/L, preferably in a range from 0.05 - 0.8 mol/L, more preferably in a range from 0.08 - 0.5 mol/L, even more preferably in a range from 0.1 - 0.3 mol/L, most preferably in a range from 0.1 - 0.2 mol/L. Furthermore, most preferably no other complexing agents are present in the plating solution of the present invention.

Further components of the plating solution:

[0083] The plating solution of the present invention comprises a liquid solvent. The solution of the invention is preferably water based, i.e. an aqueous plating solution. This means that more than 50 vol% of the liquid solvent is water, preferably 70 vol% or more, more preferably 80 vol% or more, even more preferably 90 vol% or more. Most preferably, water is the only liquid solvent.

[0084] In some cases, the plating solution of the present invention preferably consist of

- nickel ions or cobalt ions,
- Ti^{3+} ions as reducing agent for reducing said nickel ions and cobalt ions,
- optionally Ti^{4+} ions,
- optionally a stabilizing agent, preferably an inorganic stabilizing agent, most preferably lead ions,
- at least one accelerator selected from the group consisting of sulfites, dithionites, thiosulfates, tetrathionates, polythionates, disulfites, sulfides, disulfide, polysulfide, elemental sulfur and mixtures thereof;
- one or more than one complexing agent as defined throughout the present text for the plating solution of the present invention, preferably those described as being preferred,
- a liquid solvent, preferably water,
- one or more than one pH adjustor, preferably
    - a base, more preferably a hydroxide, a carbonate, and/or ammonia; and/or
    - an acid, preferably phosphoric acid and/or sulfuric acid,
- one or more than one surfactant, and
- counter ions of the aforementioned compounds, preferably anions of the nickel or cobalt ions.

[0085] The compounds listed in the aforementioned list are preferably generally utilized in the plating solution of the present invention, irrespective of whether the plating solution of the present invention is defined by "comprising" or "consisting of".

[0086] Optionally, the plating solution of the present invention further comprises lead ions, most preferably if the plating solution comprises nickel ions, i.e. the plating solution is a nickel plating solution. Lead ions typically act as a stabilizer in a nickel plating solution. Preferred is a concentration of lead ions in a range from 0.5 - 10 μmol/L, preferably in a range from 0.1 to 8 μmol/L.

Further parameters of the plating solution

[0087] The plating solution of the present invention has a pH value of from 5 to 10.5. Preferred is a plating solution of the present invention, having a pH in a range from 4.0 - 9.5, preferably in a range from 5.0 - 9.0, more preferably in a range from 5.7 - 8.5, even more preferably in a range from 6.4 - 8.2.

Method of the present invention for electroless plating of a nickel or a cobalt layer

[0088] The aforementioned regarding the plating solution of the present invention preferably applies likewise to the method of the present invention (if applicable).

[0089] The method of the present invention is for electroless plating of a nickel or cobalt deposit on a substrate. In the method of the present invention, any plating solution of the invention, which is disclosed in this description, is preferably used. The nickel or cobalt deposit obtained by the method of the present invention is substantially free of phosphorous, preferably does not comprise phosphorous.

[0090] A preferred substrate, which is used in the method of the present invention, is an electronic article, a part, or a pre-product thereof or is a substrate finally resulting in an electronic article, a part, or a product thereof. A more preferred substrate is, without limitation: a wafer, a diced and/or further processed wafer, a printed circuit board, an integrated circuit package, parts, or pre-products thereof. In some cases, the substrate preferably comprises a resin, plastic, ceramic, glass, and/or a metal, preferably comprises at least a metal, more preferably comprises a combination of at least a metal and a non-conductive material. A preferred metal is coper, titanium, titanium alloys (preferably titanium nitride), cobalt, and cobalt alloys, preferably the metal is in a patterned condition, most preferably the metal is a patterned layer. In the context of the present invention "patterned" includes structured, i.e. the metal preferably has a three dimensional surface. Thus in some cases it is preferred that the metal is patterned, wherein in other cases the metal is a uniform layer; preferred is in some cases a patterned metal. A preferred non-conductive material is a resin, plastic, ceramic, glass, and/or a silicon-containing material.

[0091] In some particular cases, a method of the present invention is preferred, wherein the cobalt deposit and the nickel deposit, respectively, (preferably the cobalt deposit) is electrolessly plated on cobalt and alloys thereof, preferably on cobalt and alloys thereof in a recessed structure in order to partially or completely fill the recessed structure. In some cases it is preferred that the cobalt and alloys thereof prior to the method of the present invention is deposited by physical methods, preferably by sputtering. A very preferred metal is a stack of metals, comprising titanium or titanium alloys (preferably titanium nitride) followed by cobalt and alloys thereof (preferably cobalt), most preferably in a recessed structure. Plating on cobalt, preferably filling, by means of the method of the present invention is in particular beneficial if the recessed structures are small, preferably having an opening width of 20 nm or below, preferably of 10 nm or below.

[0092] Preferred is a method of the present invention, wherein the electroless plating solution has a temperature in a range from 30 - 80°C, preferably in a range from 50 - 75°C, more preferably in a range from 55 - 70°C. This temperature is the temperature of the plating solution of the present invention, which is significantly high. This comparatively high temperature allows a high deposition rate without compromising stability of the plating solution, e.g. by means of outplating and/or precipitation.

[0093] Preferred is a method of the present invention, wherein the cobalt deposit (preferably the cobalt layer) and the nickel deposit (preferably the nickel layer), respectively, is plated with a deposition rate in a range from 100 nm/h to 400 nm/h, preferably in a range from 150 nm/h to 380 nm/h, more preferably in a range from 200 nm/h to 360 nm/h, even more preferably in a range from 250 nm/h to 340 nm/h, most preferably in a range from 280 nm/h to 320 nm/h.

[0094] Preferably, the nickel or cobalt deposit is a nickel or cobalt layer. Thus, preferred is a method of the present invention for electroless plating of a nickel or a cobalt layer on a substrate, the method comprising contacting the substrate with the electroless plating solution according to the present invention such that the nickel or cobalt layer is electrolessly plated on the substrate. In this preferred case the nickel or cobalt deposit is a layer. However, in other cases the nickel or cobalt deposit is preferably used for filling structures.

[0095] In some cases, the method of the present invention is preferably used to deposit a cobalt or nickel barrier, preferably a layer thereof, on a metal, preferably on copper. So, in a specifically preferred embodiment of the method of the present invention, the substrate comprises a copper layer, preferably a patterned copper layer, wherein the nickel deposit, preferably the nickel layer, or the cobalt deposit, preferably the cobalt layer, is plated on the copper layer, preferably the nickel deposit, preferably the nickel layer, or the cobalt deposit, preferably the cobalt layer, is plated directly on the copper layer.

[0096] In the context of the present invention, "directly" denotes that no further activation of the copper layer is performed, i.e. prior to plating the cobalt or nickel deposit/layer on the copper layer, the copper layer is not contacted with a chemical compound facilitating the plating of cobalt or nickel.

[0097] Even more preferred is a method of the present invention, wherein the substrate comprises a metal, preferably copper, and during the method the nickel or cobalt deposit, preferably the nickel or cobalt layer, is selectively plated on the metal, preferably on the copper, without simultaneously being plated on substrate areas not exposing the metal, preferably on substrate areas not exposing the copper. This is in particular preferred, if the substrate comprises a copper and a resin.

[0098] As a result of the method of the present invention a plated substrate is obtained, which preferably comprises the following layers: Cu layer / Ni or Co layer, wherein the Ni or Co layer is preferably an outer layer, i.e. comprising a free, accessible surface. The sign "/" here means that the respective layers are in contact with each other, i.e. are neighboring layers.

[0099] A barrier layer typically prevents copper migration into a further metal layer. A nickel layer is preferably used to prevent migration into a tin layer. A cobalt layer is preferably used to prevent copper migration into a gold layer.

[0100] Thus, the method of the present invention preferably further comprises the step plating a gold layer or a tin layer on the nickel layer or on the cobalt layer, more preferably a gold layer on the cobalt layer, or alternatively a tin layer on the nickel layer. Thus the plated substrate preferably comprises the following layers, in this order: Cu layer / Ni or Co layer / Sn or Au layer, wherein the Sn and the Au layer is preferably an outer layer, i.e. comprising a free, accessible surface. Such a layer structure is also called a "stack" of layers, comprising the mentioned layers in the mentioned order. The Ni or Co layer separates the Cu layer from the respective Sn and Au layer.

[0101] The above mentioned layers preferably extend over a whole surface or preferably extend over a part of a surface.

[0102] In some cases it is preferred that the copper layer extends over only a part of a surface, i.e. is structured or patterned. In other cases it is preferred that the copper layer extends over a whole surface of the substrate.

[0103] In some cases it is preferred that the nickel or cobalt layer extends over only a part of the copper layer, i.e. is structured or patterned; preferably corresponding at least partly to the structured/patterned copper layer. In other cases it is preferred that the nickel or cobalt layer extends over the entire copper layer.

[0104] In some cases it is preferred that the Sn or Au layer preferably extends over a part of the nickel or cobalt layer. In other cases it is preferred that the nickel or cobalt layer extends over the entire nickel or cobalt layer.

[0105] The plating method of the present invention comprises the following redox reaction:

$$Ni^{2+} + 2Ti^{3+} \rightarrow Ni^0 + 2Ti^{4+}$$

and, respectively,

$$Co^{2+} + 2Ti^{3+} \rightarrow Co^0 + 2Ti^{4+}$$

[0106] As a result, during plating, the concentration of the Ti^{3+} ions decreases because of their oxidation to Ti^{4+} ions. Furthermore, the concentration of nickel ions and cobalt ions decreases because they are reduced and plated as a metallic deposit on the substrate.

[0107] Preferred is a method of the present invention, comprising the following additional step:

- regenerating the plating solution or at least a part of the plating solution, preferably by regenerating Ti^{4+} ions into Ti^{3+} ions, most preferably by regenerating Ti^{4+} ions into Ti^{3+} ions by means of an electrical current.

[0108] In such a regeneration, Ti^{3+} ions are regained and nickel and cobalt ions, respectively, are preferably replenished. Regeneration is preferably done according to a method as described in WO 2013/182478 A2, which is incorporated by reference in its entirety.

Electronic article of the invention

[0109] The present text furthermore refers to an electronic article (1), comprising a nickel layer or a cobalt layer (4), wherein the nickel layer or the cobalt layer (4) is obtainable or obtained from an electroless plating solution according to the present invention, or is obtained according to the method of the present invention, wherein the nickel layer (4) or the cobalt layer (4) comprises 99 wt% or more nickel or cobalt, based on the total weight of the nickel layer (4) or the cobalt layer (4),
wherein the article comprises a copper layer (3), and wherein the nickel layer or the cobalt layer (4) is disposed on the copper layer.

[0110] The present invention refers to an electronic article (1), comprising a nickel layer or a cobalt layer (4), wherein the nickel layer or the cobalt layer (4) is obtained according to the method of the present invention, wherein the nickel layer (4) or the cobalt layer (4) comprises 99 wt% or more nickel or cobalt, based on the total weight of the nickel layer (4) or the cobalt layer (4), wherein the article comprises a copper layer (3), and wherein the nickel layer (4) or the cobalt layer (4) is disposed on the copper layer, and further comprising a gold layer (5) or tin layer (5) on the nickel layer (4) or on the cobalt layer (4), respectively.

[0111] The aforementioned regarding the plating solution of the present invention and/or regarding the method of the present invention preferably applies likewise to the electronic article of the present invention (if applicable).

[0112] The electronic article of the present invention is also called an electronic device or electronic component or electronic part. The article of the present invention is preferably a product of the method of the present invention, for example the plated substrate. In this connection, it is referred to the whole disclosure above.

[0113] Preferably, the copper layer (4) is structured, more preferably forms a circuitry.

[0114] Without limitation, the electronic article is preferably selected from wafers, diced and/or further processed wafers, micro electro mechanical systems, integrated circuit packages, and printed circuit boards.

[0115] A preferred electronic article is a sensor, e.g. comprised in a micro electro mechanical systems.

[0116] According to the present invention, an electronic article is preferred, further comprising a gold layer or a tin layer, wherein the gold layer or the tin layer is disposed on the nickel layer or on the cobalt layer.

[0117] Preferably, in the electronic article of the present invention, the nickel or cobalt layer does not comprise phosphor (also called in this description "phosphorus").

[0118] Hereinafter, the invention is illustrated with regard to working examples. These examples are not to be construed to limit the scope of the invention.

BRIEF DESCRIPTION OF THE FIGURES

[0119] Fig. 1 shows an electronic article of the invention.

EXAMPLES

Example 1 - Plating of nickel

[0120] Autocatalytic (electroless) nickel plating with Ti^{3+} as reducing agent and pyrophosphate as complexing agent is carried out. Nickel sulfate (hexahydrate) is used as nickel salt. The reducing agent is synthesized in a regeneration cell as described in WO 2013/182478 A2.

Preparation of a solution comprising Ti^{4+}:

[0121] In a beaker, 1M or 330.34 g/L sodium pyrophosphate and 0.4 M or 39.17 g/L 85% orthophosphoric acid are dissolved in deionized water and the solution is heated to 85°C. Then, 0.1 M or 28.42 g/L Titanium(IV)iso-propoxide is slowly added. The pH is 7.8 - 7.9. The solution becomes turbid (including a white precipitate) and is heated until the white precipitate is dissolved and iso-propanol is completely evaporated. Subsequently, the solution is filtered and transferred into the regeneration cell.

Preparation of a reducing agent solution comprising Ti^{3+}:

[0122] In the regeneration cell a constant cathodic current is applied (current I = 20 A) and in the solution comprising Ti^{4+} ions the Ti^{4+} ions are reduced to Ti^{3+} ions. The finally obtained reducing agent solution comprises 0.8 M Ti^{3+} and 0.2 M Ti^{4+}.

Preparation of the electroless plating solution:

[0123] The electroless plating solution comprises among others the above-mentioned nickel salt and the reducing agent solution and has the following final composition:

Ni^{2+} = 0.05 M
Ti^{3+} = 0.060 M
Ti^{4+} = 0.011 M
pyrophosphate = 0.7 M
ammonium sulfide = see Table 1
pH = 8
T = 65°C
Pb^{2+} = 1 mg/L

Table 1: Dependence of deposition rate on ammonium sulfide

Solution		c (ammonium sulfide) [mg/L]	V [mL/L]	Dosing [mL/(h*L)	deposition rate [nm/h]
1a	Comparative	0	0	0	144
1b	Inventive	0,4	6	4	480

(continued)

Solution		c (ammonium sulfide) [mg/L]	V [mL/L]	Dosing [mL/(h*L)	deposition rate [nm/h]
1c	Inventive	0,6	9	4	600

[0124] As substrates, printed circuit boards comprising a non-conductive base material (FR4, a resin) and patterned copper are used. Plating was carried out for 60 minutes. Thereafter a nickel layer with a thickness of approximately 300 nm selectively on copper was obtained (FR4 was not affected).

[0125] The thickness of the nickel layer was measured with XRF throughout all examples.

[0126] Similar experiments with a plating solution having a significantly lower molar ratio of Ti^{3+} ions to pyrophosphate resulted in an undesired instability and precipitation (data not shown). This shows that a significant excess of pyrophosphate is necessary in order to stabilize the Ti^{3+} ions.

[0127] Furthermore, experiments with a significantly reduced concentration of nickel resulted in a very low deposition rate of far below 40 nm/h. In some cases no plating was observed at all (data not shown).

Example 2 - Plating of cobalt

[0128] Auto catalytic (electroless) cobalt plating with Ti^{3+} as reducing agent and pyrophosphate as complexing agent is carried out. Cobalt(II)chloride (hexahydrate) is used as cobalt salt. The reducing agent solution is prepared as defined in Example 1.

Preparation of the electroless plating solution:

[0129] The electroless plating solution comprises among others the above-mentioned cobalt salt and the reducing agent solution and has the following final composition:

Co^{2+} = 0.05 M
Ti^{3+} = 0.06 M
Ti^{4+} = 0.01 M
pyrophosphate = 0.7 M
ammonium sulfide = see Table 2
pH = 7.6
T = 70°C

Table 2: Dependence of deposition rate on ammonium sulfide

Solution		c (ammonium sulfide) [mg/L]	V [mL/L]	Dosing [mL/(h*L)	deposition rate [nm/h]
2a	Comparative	0	0	0	
2b	Inventive	0,4	6	4	
2c	Inventive	0,6	9	4	

[0130] Substrates as used in Example 1 are also utilized in Example 2. Plating is carried out for 30 minutes, wherein after 30 minutes a selectively plated cobalt layer with a thickness of approximately 160 nm to 180 nm is obtained, corresponding to a plating rate of approximately 320 nm/h.

[0131] Similar experiments with a plating solution having a significantly lower molar ratio of Ti^{3+} ions to pyrophosphate resulted again in an undesired instability and precipitation (data not shown).

[0132] Furthermore, experiments with a significantly reduced concentration of cobalt also resulted in a very low deposition rate of far below 50 nm/h. Again, in some cases no plating was observed at all (data not shown).

Example 3 - Electronic article:

[0133] Fig. 1 shows (not true to scale) an electronic article 1, for example a printed circuit board or a wafer, comprising a nickel layer 4 or a cobalt layer 4. The nickel layer 4 or the cobalt layer 4 was produced by contacting a substrate 2, 3 with a plating solution of the invention. The substrate 2, 3 comprises a carrier body 2, for example a wafer, and a copper layer 3 which is arranged on a surface of the carrier body 2.

[0134] When contacting the copper layer 3 of the substrate with the plating solution of the invention, a cobalt layer 4 or a nickel layer 4 is plated on the copper layer 3 without further activation of the copper layer 3. In a further method step, a gold layer 5 or a tin layer 5 is plated on the nickel layer 4 or the cobalt layer 4.

[0135] In the shown stack of layers, the cobalt layer 4 or nickel layer 4 serves as a barrier layer between the copper layer 3 and the gold layer 5 or tin layer 5.

Claims

1. An electroless nickel or cobalt plating solution, comprising

- nickel ions or cobalt ions,
- Ti^{3+} ions as reducing agent for reducing said nickel ions and cobalt ions,
- at least one accelerator selected from the group consisting of sulfites, dithionites, thiosulfates, tetrathionates, polythionates, disulfites, sulfides, disulfide, polysulfide, elemental sulfur and mixtures thereof; and
- one or more than one complexing agent,

wherein the pH value of the plating solution is from 5 to 10.5.

2. The plating solution according to claim 1, wherein the accelerator(s) is/are selected from the group consisting of alkaline metal sulfites, alkaline metal hydrogen sulfites, alkaline earth metal sulfites, alkaline earth metal hydrogen sulfites, ammonium sulfite, ammonium hydrogen sulfite, alkaline metal dithionites, alkaline metal hydrogen dithionites, alkaline earth metal dithionites, alkaline earth metal hydrogen dithionites, alkaline metal thiosulfates, alkaline metal hydrogen thiosulfates, alkaline earth metal thiosulfates, alkaline earth metal hydrogen thiosulfates, ammonium thiosulfate, ammonium hydrogen thiosulfate, alkaline metal tetrathionates, alkaline metal hydrogen tetrathionates, alkaline earth metal tetrathionates, alkaline earth metal hydrogen tetrathionates, ammonium tetrathionates, ammonium hydrogen tetrathionate, alkaline metal polythionates, alkaline metal hydrogen polythionates, alkaline earth metal polythionates, alkaline earth metal hydrogen polythionates, ammonium polythionates, ammonium hydrogen polythionate, alkaline metal disulfites, alkaline metal hydrogen disulfites, alkaline earth metal disulfites, alkaline earth metal hydrogen disulfites, ammonium disulfites, ammonium hydrogen disulfite, alkaline metal sulfide, alkaline metal disulfide, alkaline metal polysulfide, ammonium sulfide, and cyclo-octasulfur (Ss).

3. The plating solution according to claim 1 or 2, wherein the total amount by weight of the accelerator(s) in the plating solution ranges from 0.01 to 300 ppm, preferably from 0.1 to 200 ppm, and more preferably from 0.5 to 175 ppm.

4. The plating solution of one or more of the preceding claims, wherein the one or more than one complexing agent is/are independently selected from the group consisting of

- an organic phosphonic acid compound, its salts and esters,
- an organic polyphosphoric acid compound, its salts and esters,
- an inorganic polyphosphoric acid compound, its salts and esters, and
- an organic carboxylic acid compound, its salts and esters.

5. The plating solution of one or more of the preceding claims, with the proviso

- that the plating solution comprises at least one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters, preferably
- that the one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters is the only complexing agent in the plating solution.

6. The plating solution of one or more of the preceding claims, wherein the organic and/or inorganic polyphosphoric acid compound, its salts and esters, comprise 2 to 10 phospho-building units linked together, preferably 2 to 5, more preferably 2 to 3.

7. The plating solution of one or more of the preceding claims, with the proviso that the plating solution does not comprise pyrophosphate, preferably does not comprise pyrophosphate but one or more than one complexing agent independently selected from the group consisting of an organic phosphonic acid compound, its salts and esters.

8. The plating solution of one or more of the preceding claims, wherein a molar ratio of the complexing agent to the Ti^{3+} ions is 1.5 : 1 or higher, preferably 1.7 : 1 or higher, most preferably is in a range from 1.9 : 1 to 3 : 1.

9. The plating solution of one or more of the preceding claims, wherein a concentration of the Ti^{3+} ions is in a range from 0.03 - 0.2 mol/L, preferably in a range from 0.03 - 0.1 mol/L.

10. The plating solution of one or more of the preceding claims, wherein a concentration of the one or more than one complexing agent is in a range from 0.03 - 2.0 mol/L, preferably in a range from 0.05 - 1.5 mol/L, more preferably in a range from 0.08 - 1.1 mol/L.

11. The plating solution of one or more of the preceding claims, having a pH in a range from 4.0 - 9.5, preferably in a range from 5.0 - 9.0, more preferably in a range from 5.7 - 8.5, even more preferably in a range from 6.4 - 8.2.

12. A method for electroless plating of a nickel or a cobalt deposit (4) on a substrate (2, 3), the method comprising contacting the substrate with the electroless plating solution according to one or more of the preceding claims such that the nickel or cobalt deposit (4) is electrolessly plated on the substrate (2, 3).

13. The method of claim 12, wherein the electroless plating solution has a temperature in a range from 30 - 80°C, preferably in a range from 50 - 75°C, more preferably in a range from 55 - 70°C.

14. The method of claim 12 or 13, wherein the substrate (2, 3) comprises a copper layer (3), wherein the nickel or cobalt deposit (4) is plated on the copper layer (3), preferably the nickel or cobalt deposit (4) is plated directly on the copper layer (3).

15. An electronic article (1), comprising a nickel layer or a cobalt layer (4), wherein the nickel layer or the cobalt layer (4) is obtained according to a method of one or more of claims 12 - 14, wherein the nickel layer (4) or the cobalt layer (4) comprises 99 wt% or more nickel or cobalt, based on the total weight of the nickel layer (4) or the cobalt layer (4), wherein the article comprises a copper layer (3), and wherein the nickel layer or the cobalt layer (4) is disposed on the copper layer, and further comprising a gold layer (5) or tin layer (5) on the nickel layer (4) or on the cobalt layer (4), respectively.

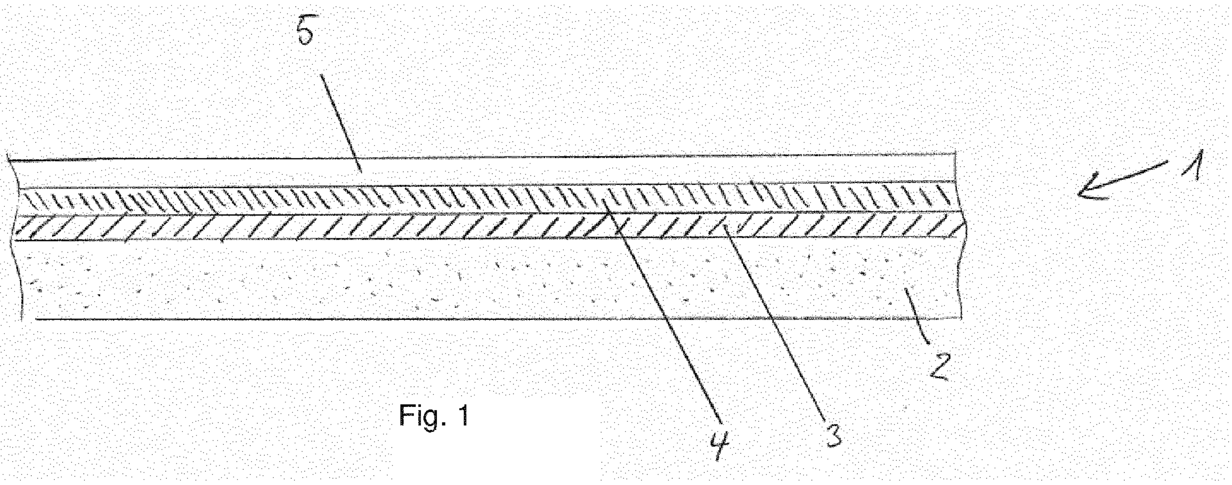

Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 20 17 9312

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 Y	US 2013/309404 A1 (KILIAN ARND [DE] ET AL) 21 November 2013 (2013-11-21) * paragraph [0002] - paragraph [0003]; claims 5, 6; examples 3, 4 * * paragraph [0012] * * paragraph [0031] * * paragraph [0044] * * paragraph [0048] * * paragraph [0055] - paragraph [0056] * -----	1-4,6,9,12-14 5	INV. C23C18/34
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	19 November 2020	Telias, Gabriela

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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page 1 of 2

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EUROPEAN SEARCH REPORT

Application Number
EP 20 17 9312

DOCUMENTS CONSIDERED TO BE RELEVANT

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TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	19 November 2020	Telias, Gabriela

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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

EP 20 17 9312

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