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(54) Plating bath composition for immersion plating of gold

(57) The present invention relates to a cyanide-free aqueous immersion-type plating bath for deposition of gold, comprising gold ions, at least one complexing agent, sulfite ions, thiosulfate ions, and at least one ureylene polymer additive. The gold layer deposited from the plating bath according to the present invention shows a lemon-yellow colour and a sufficient wettability for tin based solder materials.

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Description

Field of the Invention

[0001] The present invention relates to aqueous plating bath compositions for immersion plating of gold layers onto a substrate. The plating bath is particularly suitable in the manufacture of printed circuit boards, IC substrates, semiconducting devices, interposers made of glass and the like.

Background of the Invention

[0002] Immersion-type plating is an established method to deposit a layer of gold onto a metal substrate. Gold ions present in such plating bath compositions are reduced to metallic gold when in contact with a metal present on the substrate surface which is less noble than gold. Thereby, the metal from the substrate surface is oxidised and transferred to the gold plating bath. Such plating bath compositions do not contain a strong reducing agent such as hypophosphite ions or formaldehyde which is common in plating baths for electroless deposition of e.g., nickel alloys and copper.

[0003] Immersion plated gold layers are frequently used as solderable and/or wire bondable surfaces in the manufacture of printed circuit boards, IC substrates, semiconducting devices and the like. Gold layers are usually deposited by immersion-type plating onto a barrier layer such as a nickel phosphorous alloy or onto an intermediate layer such as a palladium or palladium alloy layer.

[0004] An important property of the deposited gold layer is a sufficient wettability of a molten solder material which is usually a tin based alloy on the surface of the gold or gold alloy layer. Furthermore, the gold layer should be applicable for wire bonding with e.g. aluminium, copper and gold wires.

[0005] Another desired property of the gold layer is the optical appearance: a discoloration of the gold layer is not acceptable.

[0006] Furthermore, toxic ingredients such as cyanide ions or heavy metal ions as stabilising agents commonly used in such immersion type plating baths need to be replaced by less or non toxic raw materials.

[0007] A cyanide-free immersion type plating bath comprising a source for gold ions, a sulfite salt, complexing agents, a heavy metal ion stabiliser (antimony or bismuth) and a quaternary ammonium salt type polymer is disclosed in JP 2004-250765 A.

[0008] A cyanide-free immersion type plating bath comprising gold ions, a pyrosulfurous acid compound, a thiosulfuric acid compound, a sulfurous acid compound and an aminocarboxylic acid is disclosed in US 2006/0269761 A1.

Objective of the Invention

[0009] It is the objective of the present invention to provide an aqueous immersion-type gold plating bath composition which is free of cyanide ions and from which gold layers can be deposited having an improved wettability for tin-based solder materials and showing no discoloration.

Summary of the Invention

[0010] This objective is solved by an aqueous immersion type plating bath composition which is free of cyanide ions, the plating bath composition comprising

(i) a source of gold ions,

(ii) at least one complexing agent,

(iii) sulfite ions,

(iv) thiosulfate ions, and

(v) at least one ureylene polymer additive represented by formulae (I) and (II):

$$A\left[L-A\right]_n L \qquad \text{(I)}$$

$$A\left[L-A\right]_n L-A \qquad \text{(II)}.$$

[0011] Gold layers having a sufficient wettability to tin based solder materials and the desired lemon-yellow colour are obtained by the aqueous immersion-type plating bath composition according to the present invention. Furthermore, in case the gold layer is deposited onto a nickel or nickel alloy layer, a reduced corrosive attack of the underlying nickel or nickel alloy layer is observed when plating a gold layer from the aqueous plating bath according to the present invention.

Detailed Description of the Invention

[0012] The aqueous immersion-type plating bath according to the present invention comprises gold ions in either Au^+, Au^{3+} or both oxidation states. The source of gold ions is a water soluble salt such as trisodium gold disulfite, tripotassium gold disulfite and triammonium gold disulfite, gold thiosulfate, gold thiocyanide, gold sulfate, gold chloride, and gold bromide. Preferably, the source of gold ions is added to the aqueous plating bath in the form of a gold sulfite solution. The concentration of gold ions in the aqueous plating bath preferably ranges from 0.1 to 10 g/l, more preferably from 0.3 to 6 g/l.

[0013] The at least one complexing agent present in the aqueous plating bath is preferably selected from the group comprising carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids or a salt of the aforementioned and serves as a complexing agent for gold ions as well as for metal ions dissolved from the substrate during plating, e.g., nickel ions. A preferred carboxylic acid is for example oxalic acid or a salt thereof. Preferred hydroxycarboxylic acids are for example tartaric acid, citric acid, lactic acid, malic acid, gluconic acid and salts of the aforementioned. Preferred aminocarboxylic acids are for example glycine, cysteine, methionine and salts of the aforementioned. In all cases also the sodium, potassium and ammonium salts of said compounds are also suitable. The concentration of the at least one complexing agent preferably ranges from 0.1 to 25 g/l, more preferably from 0.5 to 10 g/l.

[0014] More preferably, the aqueous plating bath comprises two different complexing agents and/or salts thereof, such as a hydroxycarboxylic acid or salt thereof and an aminocarboxylic acid or salt thereof.

[0015] Most preferably, the aqueous plating bath comprises three different complexing agents such as two different hydroxycarboxylic acids or salts thereof and one aminocarboxylic acid or salt thereof.

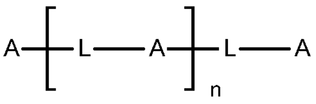
[0016] The aqueous plating bath according to the present invention further comprises sulfite ions which also serve as a complexing agent for gold ions. Sulfite ions are added to the aqueous plating bath in form of a water soluble sulfite salt such as sodium sulfite, potassium sulfite and ammonium sulfite or together with gold ions as trisodium gold sulfite, tripotassium gold sulfite and ammonium gold sulfite. The concentration of sulfite ions in the aqueous plating bath preferably ranges from 0.05 to 20 g/l, more preferably from 0.1 to 10 g/l.

[0017] The aqueous plating bath according to the present invention further comprises thiosulfate ions which also serve as a complexing agent for gold ions. Suitable sources for thiosulfate ions are water soluble salts of thiosulfate such as sodium thiosulfate, potassium thiosulfate and ammonium thiosulfate. The concentration of thiosulfate ions in the plating bath preferably ranges from 0.1 to 20 g/l, more preferably from 0.5 to 10 g/l.

[0018] The aqueous plating bath according to the present invention further comprises at least one ureylene polymer additive which enhances the wettability of the tin based solder materials on the gold layer.

[0019] The at least one ureylene polymer additive is represented by formulae (I) and (II):

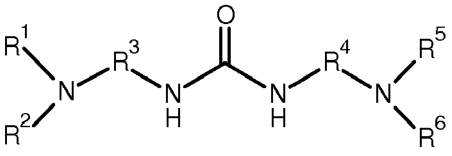
$$A\left[L-A\right]_n L \qquad \text{(I)}$$



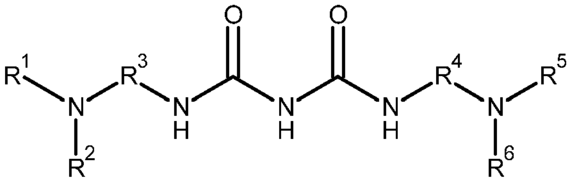
$$A\left[-L-A-\right]_n L-A$$

(II)

wherein n is an integer and preferably ranges from 1 to 40, more preferably from 3 to 30 and most preferably from 5 to 20. Monomer A is derived from a diamino compound represented by compounds according to formulae (III) to (V):



(III)



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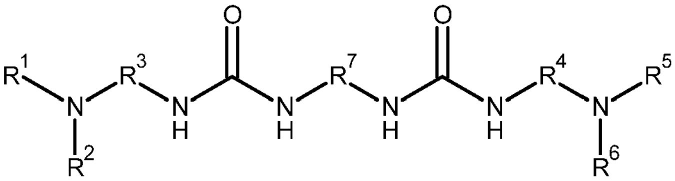


(V)

wherein R^1, R^2, R^5, and R^6 are independently selected from the group consisting of a substituted or unsubstituted hydrocarbon residue with 1 to 10 carbon atoms, preferably methyl, ethyl, hydroxyethyl or $-CH_2CH_2(OCH_2CH_2)_y-OH$, wherein y is between 0 and 4, and

R^3, R^4 and R^7 are independently selected from the group comprising $(CH_2)_p$, wherein p stands for an integer of 2 to 12, preferably for an ethylene or propylene group, or for a $-[CH_2CH_2O]_m-CH_2CH_2-$ group, wherein m is between 1 and 40, preferably for a $-(CH_2)_2-O-(CH_2)_2-$ or $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$ group.

[0020] Preferably, monomer A is selected from compounds according to formula (III).

[0021] Monomer L in the at least one ureylene polymer additive according to formulae (I) and (II) stands for a divalent residue, which is selected from the group consisting of

$-(CH_2)_p-$, wherein p is an integer between 1 and 12, preferably between 1 and 6, and most preferably between 2 and 4, $-CH_2-CH(OH)-CH_2-$, $-[CH_2O]_q-CH_2CH_2-$ and $-[CH_2CH_2O]_q-CH_2CH_2-$, wherein q is an integer between 1 and 40, preferably $-(CH_2)-O-(CH_2)_2-$,

$-(CH_2)_2-O-(CH_2)_2-$ or $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$,

and $-CH_2-CH(OH)-CH_2-$.

[0022] The concentration of the at least one ureylene polymer additive according to formulae (I) and (II) in the aqueous plating bath preferably ranges from 0.005 to 10 g/l, more preferably from 0.01 to 5 g/l.

[0023] The term "polymer" has to be understood in a broad sense in connection with the present invention. It comprises any compound which has been formed by reaction of at least two monomer molecules A and one divalent residue L. The term "polymer" does comprise, in particular, compounds which are typically designated as oligomers. The term "polymer" is, in connection with the present invention also applied to compounds, which are formed by a poly "condensation" reaction.

[0024] The ureylene polymer additive according to formulae (I) and (II) can be obtained by reacting one or more diamino compounds of formulae (III) to (V) with one or more compounds of the following formula (VI)

$$P-L-Q \qquad (VI)$$

wherein L has the same meaning as in formulae (I) and (II) and wherein P and Q may each be the same or different and represent halogens such as Cl, Br and I or pseudohalogens such as mesylate, triflate, nonaflate, methanesulfonate, or tosylate. The compounds of the formula (VI) are organic di(pseudo)halogen compounds.

[0025] In case of ureylene polymer additives according to formula (I), the molar ratio (n_A n_B) of the total amount of substance used of the compound(s) of formulae (III) to (V) (n_A) to the total amount of substance of the compound(s) of formula (VI) (n_B) is 1 : 1.

[0026] In case of ureylene polymer additives according to formula (II), the molar ratio ($n_A : n_B$) of the total amount of substance used of the compound(s) of formulae (III) to (V) (n_A) to the total amount of substance of the compound(s) of formula (VI) (n_B) is preferably at least 1.1 : 1, more preferably at least 1.3 : 1, and most preferably at least 1.5 : 1.

[0027] This means that in the preparation of ureylene polymer additives according to formula (II), the di(pseudo)halogen compound of the formula (VI) is used in a substoichiometric amount with respect to component(s) of the formulae (III) to (V). Thus, it is effected that the chain of the ureylene polymer additive according to formula (II) has units A having amino groups at both ends. These terminal amino groups are at first tertiary (as in the compounds of formulae (III) to (V)), but may be quaternized. In acidic solution, the amino groups exist in completely or partially protonated form.

[0028] The linkages between units A and residues L occur via quaternary ammonium groups, which are formed by substitution of groups P and Q in the compounds of formula (VI) by the tertiary amino groups of the compounds of the formulae (III) to (V).

[0029] These terminal tertiary amino groups may be quaternized in accordance with the desired properties by using an organic monohalide, such as benzyl chloride, allyl chloride, alkyl chloride, such as 1-chloro-hexane or their corresponding bromides, or by using an appropriate mineral acid, such as hydrochloric acid, hydrobromic acid, hydroiodic acid or sulfuric acid.

[0030] The ureylene polymer additives according to formulae (I) and (II) preferably have a weight average molecular mass M_W of 1000 to 25000 Da, more preferably of 2000 to 20000 Da.

[0031] The reaction of diamino compounds of the formulae (III) to (V) with the compounds of the formula (VI) may preferably be carried out in aqueous or aqueous-alcoholic solutions or solvent-free substances at temperatures of preferably 20 to 100 °C.

[0032] The ureylene polymer additives according to formula (II) do not contain any organically bound (pseudo-)halogen, such as a covalent C-Cl moiety.

[0033] In another embodiment of the present invention, halide ions serving as the counter ions of the positively charged ureylene polymer additives according to formulae (I) and (II) are replaced after preparation of the polymer by anions such as hydroxide, sulfate, hydrogensulfate, carbonate, hydrogencarbonate, alkylsulfonate such as methane sulfonate, alkarylsulfonate, arylsulfonate, alkylcarboxylate, alkarylcarboxylate, arylcarboxylate, phosphate, hydrogenphosphate, dihydrogenphosphate, and phosphonate. The halide ions can be for example replaced by ion exchange over a suitable ion exchange resin. The most suitable ion exchange resins are basic ion exchange resins such as Amberlyst® A21. Halide ions can then be replaced by adding an inorganic acid and/or an organic acid containing the desired anions to the ion exchange resin.

[0034] The aqueous plating bath according to the present invention may further comprise sulfate ions. Suitable sources for optional sulfate ions are water soluble salts of sulfate ions such as sodium sulfate, potassium sulfate, and ammonium sulfate. The concentration of the optional sulfate ions preferably ranges from 0.05 to 20 g/l, more preferably from 0.1 to 10 g/l.

[0035] The aqueous plating bath according to the present invention is prepared by adding the ingredients to water. In one embodiment of the present invention, concentrates of the aqueous plating bath are prepared and further diluted with water prior to use of the plating bath.

[0036] Preferably, the cyanide-free aqueous immersion-type bath according to the present invention is free of antimony or bismuth ions.

[0037] In one embodiment of the present invention, a kit comprising two different aqueous solutions is provided. The first solution contains at least one complexing agent, thiosulfate ions and the at least one ureylene polymer additive according to formulae (I) and/or (II). The second solution contains gold ions and sulfite ions. Prior to use of the immersion-type plating bath, the first solution and the second solution of the kit are mixed to obtain the immersion-type plating bath according to the present invention.

[0038] The pH of the aqueous plating bath according to the present invention preferably ranges from 5 to 8, more preferably from 5.5 to 7.5. The target pH value can be adjusted using for example sulfuric acid or sodium hydroxide.

[0039] The substrate to be plated with gold or a gold alloy has a surface area consisting of a metal or metal alloy less noble than gold and is contacted with the aqueous plating bath according to the present invention by either dipping the substrate into the plating bath or by spraying the plating bath onto the substrate.

[0040] Gold or a gold alloy is then deposited onto the surface area consisting of a metal or metal alloy less noble than gold, selected from the group comprising nickel, nickel alloys such as nickel phosphorous alloys, nickel boron alloys, cobalt, cobalt alloys such as cobalt phosphorous alloys, cobalt molybdenum phosphorous alloys, cobalt molybdenum boron alloys, cobalt molybdenum boron phosphorous alloys, cobalt tungsten phosphorous alloys, cobalt tungsten boron alloys, cobalt tungsten boron phosphorous alloys, palladium, palladium alloys such as palladium phosphorous alloys, palladium boron alloys, copper and copper alloys.

[0041] The temperature of the aqueous plating bath is preferably in the range of 30 to 70 °C, more preferably from 40 to 60 °C during plating. The plating time is preferably in the range of 40 to 60 min, more preferably in the range of 5 to 30 min.

[0042] The immersion-type plating bath according to the present invention may be used with horizontal, vertical and spray plating equipment.

[0043] The following non-limiting examples further illustrate the present invention.

Examples

General Procedures

[0044] The weight average molecular mass M_W of the ureylene polymer additives according to formulae (I) and (II) was determined by gel permeation chromatography (GPC) using a GPC apparatus from WGE-Dr. Bures equipped with a molecular weight analyzer BI-MwA from Brookhaven, a TSK Oligo +3000 column, and Pullulan and PEG standards with M_W = 400 to 22000 g/mol. The solvent used was Millipore water with 0.5 % acetic acid and 0.1 M Na_2SO_4.

[0045] Substrates (length: 27.5 mm, width: 12.5 mm) containing 40 plated through-holes (0.8 mm diameter, 1.5 mm land size, and a surface consisting of a plated nickel phosphorous alloy) were used throughout all examples. Gold was deposited onto the plated through-holes.

[0046] Test C1, a solder float test with lead-free solder according to IPC J-STD-003B (March 2007) was applied to all gold plated samples in order to asses the solder wettability of the gold layers. A SnAg3.0Cu0.5 solder bath was used. Next, three reflow cycles in air atmosphere were applied to each sample prior to inspection. The samples are evaluated after the test with an optical microscope (magnification: 10 x). A sufficient wetting of the gold layer with solder material is achieved when at least 95 % of the gold surfaces being tested exhibit good wetting.

[0047] An aqueous immersion type gold plating bath stock solution comprising

1.5 g/l	trisodium gold sulfite
3.72 g/l	$Na_2S_2O_3 \cdot 5H_2O$
1 g/l	oxalic acid
3.1 g/l	trisodium citrate dihydrate
5 g/l	methionine

was used throughout all examples. Further additives added to the stock solution are indicated in the respective example.

[0048] The plating bath pH was 6.

[0049] The plating bath temperature during plating was 50 °C and the plating time was 15 min. The thickness of the deposited gold layers ranged between 60 and 80 nm.

Comparative Example 1

[0050] No ureylene polymer additive according to formulae (I) or (II) was added to the aqueous immersion-type gold plating bath stock solution.

[0051] The gold layer obtained has a green colour which is not desired.

[0052] A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was only achieved for 5 % of the gold plated area. Accordingly, the gold layer failed the solder float test.

Example 1

[0053] 0.1 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L = $(CH)_2O(CH_2)_2$ was added to the aqueous immersion-type gold plating bath stock solution. The polymer additive according to formula (II) was obtained according to preparation example 12 in WO 2011/029781 A1 and comprises chloride ions as counter ions. The weight average molecular mass M_W of the ureylene polymer additive obtained was 5380 Da.

[0054] The gold layer obtained has the desired lemon-yellow colour.

[0055] A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 98 % of the gold plated area.

Example 2

[0056] 0.3 ml/l of a solution comprising 25 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L = $(CH_2)_2O(CH_2)_2$ was added to the aqueous immersion-type gold plating bath stock solution.

[0057] The ureylene polymer additive was prepared by reacting 20 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 22.77 g oxybis-(ethane-2,1-diyl)-methanesulfonate (monomer L) in a molar ratio of 4 : 3 for 12 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises methanesulfonate as counter ions and has a weight average molecular mass M_W of 5677 Da.

[0058] The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 96 % of the gold plated area.

Example 3

[0059] 0.3 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (I) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L = $(CH_2)_2O(CH_2)_2$ was added to the aqueous immersion-type gold plating bath stock solution.

[0060] The polymer additive according to formula (I) was prepared by reacting 20 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 22.7 g oxybis-(ethane-2,1-diyl)-methanesulfonate (monomer L) in a molar ratio of 1 : 1 for 20 h at a temperature of 80 °C. The ureylene polymer additive according to formula (I) comprises methanesulfonate as counter ions and has a weight average molecular mass M_W of 17260 Da.

[0061] The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 98 % of the gold plated area.

Example 4

[0062] 0.3 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L = $(CH_2)_2O(CH_2)_2O(CH_2)_2$ was added to the aqueous immersion-type gold plating bath stock solution.

[0063] The polymer additive according to formula (II) was prepared by reacting 25 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 24.94 g ethane-1,2-diyl-bis(oxy)-bis(ethane-3,1-diyl)-dimethanesulfonate (monomer L) in a molar ratio of 3 : 2 for 24 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises methanesulfonate as counter ions and has a weight average molecular mass M_W of 7299 Da.

[0064] The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 100 % of the gold plated area.

Example 5

[0065] 0.3 ml/l of a solution comprising 20 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L = $CH_2-CH(OH)-CH_2$ was added to the aqueous immersion-type gold plating bath stock solution.

[0066] The polymer additive according to formula (II) was prepared by reacting 15 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 6.43 g 1,3-dichloropropane-2-ol (monomer L) in a molar ratio of 4 : 3 for 12 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises chloride as counter ions and has a weight average molecular mass M_W of 5202 Da.

[0067] The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-003B (March 2007), test C1 was achieved for 97 % of the gold plated area.

Example 6

[0068] 0.3 ml/l of a solution comprising 50 wt.-% of a polymer additive according to formula (II) consisting of monomer A according to formula (III) with R1, R2, R5 and R6 = methyl, and R3 and R4 = propylene, and monomer L = $(CH_2)_3$ was added to the aqueous immersion-type gold plating bath stock solution.

[0069] The polymer additive according to formula (II) was prepared by reacting the 45 g 1,3-bis-(3-dimethylamino)-propyl-urea (monomer A) with 18.6 g 1-bromo-3-chloro-propane in a molar ratio of 3 : 2 for 12 h at a temperature of 80 °C. The ureylene polymer additive according to formula (II) comprises bromide and chloride as counter ions and has a weight average molecular mass M_W of 5016 Da.

[0070] The gold layer obtained has the desired lemon-yellow colour. A sufficient wettability according to IPC J-STD-

003B (March 2007), test C1 was achieved for 99 % of the gold plated area.

Claims

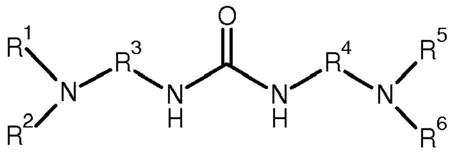
1. A cyanide-free aqueous immersion-type plating bath for deposition of gold, comprising

   (i) a source of gold ions,
   (ii) at least one complexing agent,
   (iii) sulfite ions,
   (iv) thiosulfate ions, and
   (v) at least one ureylene polymer additive selected from polymers according to formulae (I) and (II):

$$A-\left[L-A\right]_n-L \qquad \text{(I)}$$

$$A-\left[L-A\right]_n-L-A \qquad \text{(II)}$$

   wherein n is an integer between 1 and 40,
   wherein monomer A is selected from compounds according to formulae (III) to (V)



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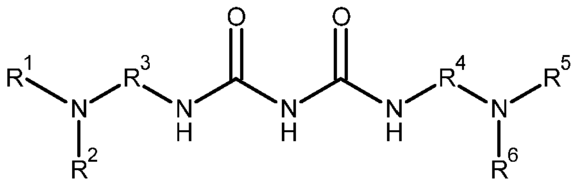

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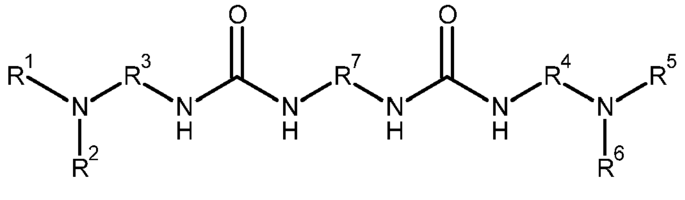

(V)

   wherein R^1, R^2, R^5, and R^6 are independently selected from the group consisting of a substituted or unsubstituted hydrocarbon residue with 1 to 10 carbon atoms,
   R^3, R^4 and R^7 are independently selected from the group comprising $(CH_2)_p$, wherein p stands for an integer of 2 to 12, $-[CH_2CH_2O]_m-CH_2CH_2-$ group, wherein m is between 1 and 40,
   and wherein

L stands for a divalent residue, which is selected from the group consisting of $-(CH_2)_p-$, wherein p is an integer between 1 and 12, $-CH_2-CH(OH)-CH_2-$, $-[CH_2O]_q-CH_2CH_2-$ and $-[CH_2CH_2O]_q-CH_2CH_2-$, wherein q is an integer between 1 and 40.

2. The cyanide-free aqueous immersion-type plating bath according to claim 1 wherein the concentration of gold ions ranges from 0.1 to 10 g/l.

3. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the at least one complexing agent is selected from the group comprising carboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids and salts of the aforementioned.

4. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the at least one complexing agent comprises a hydroxycarboxylic acid selected from the group comprising tartaric acid, citric acid, lactic acid, malic acid, gluconic acid or a salt of the aforementioned.

5. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the at least one complexing agent comprises an aminocarboxylic acid selected from the group comprising glycine, cysteine, methionine or a salt of the aforementioned.

6. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of the at least one complexing agent ranges from 0.1 to 25 g/l.

7. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of sulfite ions ranges from 0.05 to 10 g/l.

8. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of thiosulfate ions ranges from 0.1 to 20 g/l.

9. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein monomer A is selected from compounds according to formula (III).

10. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein R^1, R^2, R^5, and R^6 are independently selected from the group consisting of methyl, ethyl, hydroxyethyl and $-CH_2CH_2(OCH_2CH_2)_y-OH$, wherein y is between 0 and 4.

11. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein R^3, R^4 and R^7 are independently selected from the group consisting of $-(CH_2)_p-$, wherein p is 1 or 2, $-(CH_2)_2-O-(CH_2)_2-$ and $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$.

12. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the monomer L is selected from the group consisting of $-(CH_2)_p-$, wherein p is an integer between 1 and 6, $-(CH_2)-O-(CH_2)_2-$, $-(CH_2)_2-O-(CH_2)_2-$, $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$ and $-CH_2-CH(OH)-CH_2-$.

13. The cyanide-free aqueous immersion-type plating bath according to any of the foregoing claims wherein the concentration of the at least one ureylene polymer ranges from 0.005 to 10 g/l.

14. The cyanide-free aqueous immersion-type bath according to any of the foregoing claims which is free of antimony or bismuth ions.

15. A kit comprising a first solution which contains at least one complexing agent, thiosulfate ions and at least one ureylene polymer additive according to formulae (I) and/or (II) and a second solution which contains a source of gold ions and sulfite ions.

16. A method for depositing a gold layer onto a substrate, comprising, in this order, the steps

(i) providing a substrate having a surface area consisting of a metal or metal alloy less noble than gold
(ii) contacting the substrate with a cyanide-free aqueous immersion-type plating bath according to claims 1 to 14

and thereby depositing a gold layer onto the surface area consisting of a metal or metal alloy less noble than gold.

17. The method for depositing a gold or gold alloy layer onto a substrate according to claim 16 wherein the metal or metal alloy less noble than gold is selected from the group comprising nickel, nickel alloys, cobalt, cobalt alloys, palladium, palladium alloys, copper and copper alloys.

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EUROPEAN SEARCH REPORT

Application Number
EP 12 18 0227

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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